

Review



Recent Advances in Graphene-Based Single-Atom Photocatalysts for CO₂ Reduction and H₂ Production

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Abstract: The extensive use of single-atom catalysts (SACs) has appeared as a significant area of investigation in contemporary study. The single-atom catalyst, characterized by its maximum atomic proficiency and great discernment of the transition-metal center, has a unique combination of benefits from both heterogeneous and homogeneous catalysts. Consequently, it effectively bridges the gap between these two types of catalysts, leveraging their distinctive features. The utilization of SACs immobilized on graphene substrates has garnered considerable interest, primarily because of their capacity to facilitate selective and efficient photocatalytic processes. This review aims to comprehensively summarize the progress and potential uses of SACs made from graphene in photocatalytic carbon dioxide (CO₂) reduction and hydrogen (H₂) generation. The focus is on their contribution to converting solar energy into chemical energy. The present study represents the various preparation methods and characterization approaches of graphene-based single-atom photocatalyst This review investigates the detailed mechanisms underlying these photocatalytic processes and discusses recent studies that have demonstrated remarkable H2 production rates through various graphene-based single-atom photocatalysts. Additionally, the pivotal roleof theoretical simulations, likedensity functional theory (DFT), to understand the structural functional relationships of these SACs are discussed. The potential of graphene-based SACs to revolutionize solar-to-chemical energy conversion through photocatalytic CO₂ reduction and H₂ production is underscored, along with addressing challenges and outlining future directions for this developing area of study. By shedding light on the progress and potential of these catalysts, this review contributes to the collective pursuit of sustainable and efficient energy conversion strategies to mitigate the global climate crisis.

Keywords: single atom; graphene; graphene oxide; N-doped graphene; photocatalysis

1. Introduction

There is a critical need for the improvement and utilization of photochemical technology to tackle the problem of global climate change and reach a point of carbon neutrality. Renewable energy transformation and storage technologies rely heavily on a broad class of photocatalytic processes [1–3]. In order to address the adverse environmental impacts connected to using fossil fuels, researchers must overcome the scientific challenges of developing a technologically favorable chemical process for the long-term generation of clean and renewable energy [4]. Solar energy has appeared as a very effective competitor among other energy sources because of its natural abundance, environmental purity, and sustainable nature. Developing effective ways for converting solar energy into chemical energy and then conserving this chemical energy inside molecule bonds for reuse later



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). is one of the primary goals of scientists working in this area of study. Creating fuels and chemicals is a primary objective in the field of chemistry, and it is now feasible to do so due to this energy storage [5,6]. For instance, CO₂ photoreduction and hydrogen production is a powerful strategy for restoring equilibrium to the carbon cycle. It has the twin benefit of creating valuable chemical compounds and a clean, sustainable, and competitive energy source [7,8].

Heterogeneous single-atom catalysts (SACs) are catalysts that have a precise atomic structure and include stable and reactive active centers made up of individual metal atoms, such as iron (Fe), cobalt (Co), or platinum (Pt), which are anchored to the substrate [9]. The active sites of single-atom catalysts (SACs) are typically individual metal atoms or clusters, which are different from metal-nitrogen-carbon (M-N-C) catalysts or molecular catalysts that depend on metal clusters or complexes [10,11]. Metal–nitrogen–carbon (M-N-C) catalysts form complex active sites by coordinating metal atoms with nitrogen and carbon atoms inside a support structure. Molecular catalysts are composed of individual molecules that include catalytically active metal cores. Nevertheless, their stability level may not be equivalent to that of SACs and metal-nitrogen-carbon (M-N-C) catalysts [12,13]. These SACs are capable of selectively converting chemical compounds via catalytic processes [14,15]. The domain of heterogeneous catalysis has seen a rapid growth in the subject of singleatom catalysis, establishing itself as a prominent area of research [15]. Furthermore, it has gathered the interest of researchers involved in both homogeneous and biological catalysis. This phenomenon may be recognized by the presence of single active sites of atoms in heterogeneous catalysis, which serve as intrinsic connections linking the domains of heterogeneous, homogeneous, and biological catalysis [16,17]. SACs use main-group or transition-metal atoms that are integrated into support materials, hence using active sites composed of discrete and isolated reactive metal atoms [14]. Because of their unusual structure, SACs can use metal atoms to their greatest potential and display remarkable selectivity [18]. The theoretical investigation of atoms active on a substrate sheds light on their inherent stability. The robust association between SAs and the supporting material may be attributed to the collective effects of ionic bonding and covalent bonding. This phenomenon is designated by the acronym CMSI, which stands for covalent metal-support contact [19,20]. The extraordinary constancy and long-lasting catalytic capabilities of SACs have been supported by several empirical and theoretical studies [21]. These isolated metal atoms may be firmly attached to any number of substrates, including metallic oxides [22], nonmetal oxides [23], pure metals [24], carbon materials [25], graphene [26], metal–organic frameworks [27], zeolites [28], etc.

Graphene, a carbonaceous substance, has attracted much attention as a potential catalyst [29]. Graphene, a two-dimensional form of carbon, is a very adaptable substance that finds uses in nanotechnology, electronics, and biomedicine. This is because it has exceptional qualities such as excellent electrical and thermal conductivity, flexibility, and chemical stability [30]. Its mechanical strength, characterized by a Young's modulus of 1.1 TPa, makes it suitable for structural applications [31]. The electrical qualities of graphene are influenced by its unique band structure, resulting in both high charge-carrier mobility and the ability to adjust these features by gate voltage. The optical behavior is controlled by the band structure, and interband transitions are triggered by 2EF photons [32]. The remarkable thermal conductivity of graphene is ascribed to phonon transport and may reach up to 5×10^3 W/mK. Graphene's unique shape and electrical properties make it an exceptional instrument for conducting quantum chemical theoretical investigations and experiments on the physical chemistry of single-atom catalysts (SACs) at the molecular level [33]. Graphene's distinct electrical and structural characteristics make it a reliable substrate for attaching single catalytic atoms, allowing for the fine-tuned regulation of reaction sites [34]. The photocatalytic performance is improved as a result of the atomiclevel control over light absorption, charge separation, and reaction kinetics [35]. In practical applications, the process of heteroatom doping in graphene often entails the exchange of carbon atoms with nitrogen, boron, sulfur, or phosphorus atoms [36,37]. The nitrogen

atoms in N-doped graphene serve as good conductors for electron mobility, avoiding random migration and instead guiding electrons in a deliberate manner [38]. Furthermore, GO has attracted a lot of attention in the study of single-atom photocatalysis because of its unique characteristics and broad range of potential uses [39,40]. The many benefits that GO, a two-dimensional, carbon-based material, offers make it an outstanding option for boosting the performance of single-atom photocatalysts [41,42].

Prior to the actual production and synthesis of graphene-based SACs, theoretical analyses had already been carried out [43]. In 2013, Sun et al. effectively fabricated the first metal SAC including graphene by the use of the atomic layer deposition (ALD) method [44]. The study serves as the foundation for investigating the use of metal-/nonmetal-doped graphene-based single-atom catalysts [45]. Therefore, both experiments and theoretical calculations have shown that graphene-derived carbon compounds offer excellent promise as substrates for SACs. Graphene may be converted from a passive catalyst into one with excellent catalytic efficiency and selectivity by the insertion of metal single atoms (SAs) for CO₂ reduction [46,47], activation of the C–H bond, selective hydrogenation [48], conversion of N₂ (including electrochemical nitrogen reduction reaction (NRR)) [49], CO₂ photocatalytic reduction reaction [50], and photocatalytic hydrogen evolution [51].

Recently, various types of reviews have been published on SACs for different applications. For instance, Gawande et al. [52] reported a review of single-atom photocatalysts based on carbon material for different catalytic applications. Ma et al. [53] reported a review on MOF-based single-atom catalysts for electro- and photocatalytic applications. Zeng et al. [54] gave an overview of a single-atom-based N-doped carbon for advanced oxidation reactions. However, compact data on graphene-based single-atom photocatalysts for photocatalytic CO_2 transformation and hydrogen H_2 production are not reported yet. As a result, we mean to present the advancement of graphene-based SACs for effective CO_2 reduction and H_2 production. The most recent developments in the area of singleatom photocatalysts based on graphene are reviewed in this work. This study aims to explore how these photocatalysts' efficiency may be increased by means of metal-support interactions. Additionally, this review explores a detailed analysis of different single-atom catalytic materials, employing key spectroscopic characterization approaches to explain their classification as single-atom catalysts. Furthermore, this study aims to explain the significant contributions of graphene-based SACs in the field of photocatalysis. Specifically, it will focus on their ability to modulate light absorption, facilitate charge transfer processes, and influence surface reactions. Through this investigation, a thorough comprehension of the intricate connections between the structural properties and performance of graphenebased SACs in the context of photocatalysis will be established. Furthermore, this study investigates the examination of theoretical simulations using density functional theories (DFTs) in relation to single-atom catalysts based on graphene.

Furthermore, this study emphasizes the usage of diverse single-atom photocatalysts to convert solar energy into practical energy, specifically for the purpose of reducing carbon dioxide (CO_2) and generating hydrogen (H_2) via photocatalysis. Furthermore, this research examines the challenges and possible remedies associated with the creation and use of photocatalysts consisting of individual atoms.

2. Graphene-Based Single-Atom Photocatalysts

Graphene-based single-atom photocatalysts represent a cutting-edge advancement in the realm of photocatalytic applications. These innovative materials harness the remarkable properties of graphene, a single layer of carbon atoms organized in a hexagonal lattice, with the combined efficiency of single-atom catalytic sites [26,33]. This convergence creates a powerful platform for driving photocatalytic processes with unparalleled precision and efficacy. The integration of single atoms, such as metals or nonmetals, onto graphene sheets could not only enhanced the utilization of catalytic active sites but also enhance light absorption due to graphene's exceptional electronic properties [55,56]. This synergy enables the photocatalyst to initiate and accelerate complex chemical reactions, like water

splitting and pollutant degradation, under mild light conditions. The ultrathin nature of graphene offers high surface area-to-volume ratios, ensuring an abundance of active sites within a minimal space. This results in improved reaction kinetics and selectivity, contributing to higher yields and reduced energy consumption [57].

Additionally, the stability and durability of graphene provide a long-lasting foundation for sustained photocatalytic activity. Graphene-based single-atom photocatalysts hold great promise for addressing critical global challenges, including clean energy generation and environmental remediation [58]. Their exceptional efficiency, selectivity, and sustainability make them a pivotal player in the advancement of green technologies and a brighter, more sustainable future [59].

2.1. Synthesis of Graphene-Based Single-Atom Photocatalysts

The first SACs were synthesized for the first time in 1995 [60]. The benefits of homogeneous and heterogeneous catalysis may be combined in SACs, making them a viable catalyst. Therefore, they are used as models for studying how the catalyst structure affects catalytic performance. There have been a lot of studies dedicated to synthesizing and designing single-atom catalysts (SACs) on diverse substrates. A wide range of substrates has been created for use in the field of photocatalysis. Semiconducting nanoparticles like titanium dioxide (TiO₂) [61], carbon nitride (C_3N_4) [62], graphene [63], zeolites [64], and metal–organic frameworks (MOFs) [65] are examples of such types of materials. Despite the rapid progress made in the area of graphene-supported single-atom catalysts (G-SACs), major difficulties remain in maintaining the metal sites that are dispersed at the atomic level inside the graphene matrix [66]. Graphene's binding energy for metals is slightly lower than the cohesive energy of atomistically dispersed metal sites, which may explain why single metal atoms prefer to form clusters and nanoparticles. Because of this, pure graphene has to be altered so that uniform metal sites may be present. To do this, vacancies or heteroatoms might be introduced into the graphene framework [67]. Significant efforts have been made to advance the synthetic approaches necessary for the efficient use of G-SACs in real-world settings [26]. This section offers a detailed summary and analysis of numerous synthetic methods for creating graphene-based single-atom photocatalyst (G-SACs).

2.1.1. Pyrolysis

The primary technique used in the fabrication of graphene-supported atomically spread metal catalysts (known as G-SACs) typically includes submitting the materials to a process of high-temperature treatment. This approach is preferred because of its simple technique that avoids the need for complex equipment [68]. The procedure involves the deliberate selection of metal and carbon precursors, followed by controlled thermal treatment at ideal temperatures. As a consequence, the immobilization of metal sites on the graphene substrate gives rise to discrete coordination environments and electronic configurations for each individual metal site. This ultimately leads to a substantial development in the catalytic activity of the system [69].

For single-atom catalysts (SACs), temperature is the most important factor in determining their structure and characteristics. An important property for anchoring individual atoms and avoiding clustering is powerful metal–support interactions, which are enhanced at high temperatures. Yet, metal atom migration and sintering may be induced by very high temperatures, which can also destroy the support material. On the other hand, at low temperatures, the metal remains in its isolated condition, but precursor activation and strong metal–support interactions are hindered. Controlled growth and consistent dispersion are achieved with moderate ramping during heating and cooling, but cluster formation and uneven distribution are dangers with rapid ramping. In addition to solvents and gas atmospheres, which can be either inert or reactive precursor behavior, support chemistry and the morphology of the SAC are all affected [70].

For instance, Fei et al. [71] created a N-doped graphene-based Co catalyst consisting of a SAC, as illustrated in Figure 1a. Initially, a solution containing cobalt chloride hexahydrate

and graphene oxide (GO) was prepared, by carefully mixing all of the components. In order to inhibit the restacking of graphene oxide (GO) sheets, the precursor solution underwent the process of lyophilization. The ultimate catalyst was acquired by pyrolysis at a temperature of 750 $^{\circ}$ C in the presence of an Ar/NH₃ environment. The morphology of Co-NG was described by SEM and TEM, which revealed sheetlike structures similar to graphene, shown in Figure 1b, and surface ripples, shown in Figure 1c. Co atoms on the nanosheets were too tiny to be seen with the naked eye. This structure, known as a Co-NG paper, functions as a self-supporting electrode for the production of hydrogen (H_2) . Figure 1d shows a scanning electron microscopy (SEM) picture of a material that is all 15 μ m thick. The exact steps used to obtain this layer were filtering a solution that contained graphene oxide (GO) and then heating the material in ammonia (NH_3). This method works well to make cobalt-doped nitrogenated graphene (Co-NG) into a material that looks like paper. The managed manufacturing method makes sure that the shape stays the same, which is important for the material to work well in energy-related uses. Co-NG, with paperlike morphology, has good qualities, like a lot of surface area and better conductivity, which makes it a good choice for many energy-transfer technologies.



Figure 1. (a) Representation of the synthesis of graphene-based Co single atom (b) SEM image of GO. (c) SEM image of GO with Co metal. (d) SEM image of N-doped graphene-based Co single atom, scale bar, 50 nm. Reprint from reference [71]. (e) Synthesis of graphene-based single atom by pyrolysis method. Reprint from reference [72].

Furthermore, it was essential to accurately regulate the quantity of metal precursor used, as an excessive amount of metal might result in the aggregation and subsequent creation of nanoparticles, thereby reducing the catalytic efficacy.

Additionally, Liu et al. [72] used a thermal pyrolysis methodology to produce a hybrid material consisting of a single metal atom with high doping levels. This synthesis process included the utilization of glucose, dicyandiamide, and inorganic metal salts, with

temperatures above 750 °C, as seen in Figure 1e. The use of this methodology facilitated the attainment of a uniform distribution of metallic atoms inside the nitrogen-doped graphene structure by promoting a strong chemical interface with metal species and carbon precursors. The incorporation of heteroatomic carbon precursors facilitated the application of thermal treatment on the material, resulting in the generation of functionalized graphene nanosheets that had embedded trapping sites. Similarly, by using SiO₂ as a template to control the synthesis of Mo atoms, Liu et al. [68] were able to successfully build single-atom Mo catalysts on nitrogen-doped carbon. In order to achieve the desired temperature of 750 °C, the pyrolysis procedure was carried for three hours at a temperature of 750 °C in the presence of an argon atmosphere.

2.1.2. Atomic Layer Deposition (ALD)

Noble metal-containing single-atom catalysts (SACs) may be efficiently synthesized by the use of the ALD process [73]. The effectiveness of this phenomenon arises from its exceptional accuracy at the atomic level and its strong stability [74,75]. ALD is a technique that allows for the controlled and exact deposition of individual metal sites onto a substrate surface. This is achieved by a series of self-limiting chemical processes [76]. For instance, Sun et al. [77] successfully prepared durable dimeric Pt2/graphene catalysts using the ALD method. In this process, individual Pt1 atoms were placed onto a graphene substrate to serve as nucleation sites. The nucleation of single Pt atoms was facilitated by the graphene substrate owing to its distinctive characteristics and extensive specific area. The catalysts composed of dimeric Pt2/graphene had a notably elevated catalytic activity of 2800 mol_{H2} molPt⁻¹min⁻¹ at ambient temperature, 45 times superior to the efficiency of Pt/graphene catalysts.

Similarly, Yan et al. [78] successfully synthesized single-atom Pd1/graphene by employing the ALD technique, shown in Figure 2a. The process involved several steps. Initially, the graphene support was attained by subjecting graphene oxide to high-temperature (1050 °C) thermal deoxygenation. This procedure enabled meticulous regulation of the specific kind and amount of surface functions that are present on the substrate. After the annealing process, the graphene support still included phenolic oxygen groups. These oxygen groups acted as anchor sites for the Pd precursor (Pd-(hfac)₂), leading to the creation of surface species known as -O-Pd-hfac. The ALD process involved alternating exposure of Pd(hfac)₂ and formalin to the reduced graphene support at 150 °C. It was reported that a Pd loading of 0.25 wt% was achieved after a single ALD cycle, which is confirmed by SEM images, as demonstrated in Figure 2b.

In another study, Sun et al. [79] used the atomic layer deposition (ALD) approach to develop single platinum (Pt) atoms that were securely bonded to graphene nanosheets, as seen in Figure 2c. ALD has the benefit of specific control over the size distribution of catalysts, including a wide range from individual atoms and subnanometer clusters to larger nanoparticles.

2.1.3. Ball-Milling Approach

Ball milling is a conventional solid-state technique employed for the production of diverse complexes. This method harnesses significant mechanical energy, which is transmitted to the precursor materials, inducing the reformation of chemical bonds and the generation of supplementary surface regions [80].

For instance, Deng et al. [81] for the first time utilized this approach for the synthesis of G-SACs. In their study, graphite was exposed to ball milling under an argon-purged environment at a rotational speed of 450 revolutions per minute (rpm) for a duration of 20 h. After that, the graphene nanosheets were combined with iron phthalocyanine (FePc) in suitable amounts, followed by further ball milling using the same conditions. The ball-milling process facilitated the breakdown of the molecular structure of FePc, allowing for the reconstruction of atomically dispersed FeN₄ moieties. These moieties were subsequently confined within the defects present in the graphene structure. Consequently,

ball milling offers a cost-effective and straightforward strategy for synthesizing G-SACs. The dimensions of the resultant catalysts may be manipulated by adjusting the rotating velocity of the milling balls.



Figure 2. (a) Synthesis of single-atom Pd1/graphene from ALD technique. (b) SEM image graphenebased Pd1 single atom. Reprint from reference [78]. (c) Synthesis of graphene-based Pt single atom. Reprint from reference [79].

2.1.4. Chemical Vapor Deposition

CVD is used to enable the production of SACs with graphene as the substrate. The methodology entails the deposition of a precursor gas onto a substrate composed of graphene, subsequent to the formation of discrete metal atoms on the graphene surface. The reported SACs demonstrated the levels of catalytic activity and selectivity, hence demonstrating considerable potential for a diverse array of potential applications [82,83].

Tavakkoli et al. [84] successfully devised a one-step catalytic chemical vapor deposition (CVD) technique to create a composite material comprising graphene nanoflakes that are doped with nitrogen (N), cobalt (Co), and molybdenum (Mo) atoms simultaneously. The N–Co–Mo–GF/CNT material exhibits a notable degree of graphitization, as seen in Figure 3a, which illustrates its structural arrangement. The high-resolution transmission electron microscopy (HR-TEM) pictures in Figure 3b,c clearly show the existence of graphene flakes measuring 50–70 nm in size. The imaging technique STEM is used, specifically employing a 60 keV electron probe. This allowed for the acquisition of high-resolution pictures using HAADF (high-angle annular dark-field) and MAADF (medium-angle annular dark-field) detectors. EELS gave spectroscopic data in a simultaneous manner. Z-contrast imaging facilitated the discrimination of dense atoms and nanoparticles from the carbon substrate. Carbon nanotubes (CNTs) connecting graphene flakes significantly improved the conductivity of the material, as seen in Figure 3d,e. The presence of metallic Co and Mo was not seen in the monolayer graphene, as shown in Figure 3f,g. However, nitrogen was directly detected in the STEM picture. The acquired



material exhibits a mesoporous structure, which augments its surface area and facilitates the passage of oxygen inside the catalyst film, hence enhancing its effectiveness.

Figure 3. (a) Synthesis of graphene-based single-atom catalyst (N–Co–Mo–GF/CNT). HR-TEM pictures of N–Co–Mo–GF/CNT were obtained for (b,c), whereas STEM images were obtained for (c-h). (b) Transmission electron microscopy (TEM) image of graphene flakes (GFs) measuring 30–50 nm in size, and (c) TEM image of a few-layer graphene flake. Additionally, (d,e) show STEM images of the interconnected GFs with carbon nanotubes (CNTs), where (f) specifically shows the CNTs bridging the GFs. Furthermore, (g,h) show high-resolution STEM images captured from a single layer of graphene, revealing its characteristic honeycomb structure. Lastly, (i) show STEM images of double- or few-layer graphene flakes. Reprint from reference [84].

Similarly, Wang et al. [85] used a chemical vapor deposition (CVD) method to fabricate catalysts consisting of Si/graphene. This included the deposition of individual silicon (Si) atoms onto a graphene substrate. The Si atoms gradually replaced the lattice of carbon atoms (graphene), forming a stable structure. Through experimental observations, it was determined that these Si/graphene catalysts offered dynamic behavior, stability, and high selectivity, thus presenting opportunities for the development of stable molecular devices at the atomic scale.

2.1.5. Freeze-Drying Method

The production of single-atom catalysts supported by graphene material was conducted using a freeze-drying-assisted approach. The methodology used in the study included subjecting a catalyst precursor solution to freezing, followed by sublimation to eliminate the solvent. This process led to the creation of individual platinum (Pt) atoms that were evenly distributed over a graphene substrate [86].

Yi et al. [87] effectively synthesized a catalyst devoid of noble metals. This was achieved by using nitrogen-doped graphene in conjunction with a solitary cobalt atom (Co-NG) as a support material for the TiO_2 nanobelts, as seen in Figure 4a. The Co-NG material was manufactured using a sequential procedure including pyrolysis, followed by calcination in NH₃ to introduce nitrogen into graphene oxide (GO). As a result of the exfoliation of Co-NG in deionized water, the loading quantity of Co-NG in Co-NG/TiO₂ nanobelt

composites could be precisely controlled, as shown by the XRD analysis (Figure 4b). Enhanced synergy between Co-NG and TiO₂ nanobelts was achieved using a calcination process at a temperature of 500 °C for a period of 10 min under an argon atmosphere. TEM and HRTEM were used to analyze the morphology and microstructure of Co-NG/TiO₂ nanobelt composites, providing valuable insights. Figure 4c,d display the presence of TiO₂ nanobelts on Co-NG sheets, showcasing their well-dispersed nature. These nanobelts have widths ranging from 20 to 50 nm and lengths of several micrometers. These nanobelts of TiO₂ seem almost translucent and thin. The HRTEM images in Figure 4e, along with the inset, show a crystallized nanobelt with clear lattice fringes measuring 0.39 nm, which correspond to the (100) facet of anatase TiO₂.



Figure 4. (a) Synthesis of Co-NG/TiO₂ nanobelts from freeze-drying method. (b) XRD spectra of Co-NG/TiO₂ photocatalyst. (c,d) TEM and (e) HRTEM images of a composite with 3.5 weight percent Co-NG-TiO₂ nanobelts. Reprint from reference [87].

Zhou et al. [88] provide an efficient method for fabricating N-doped graphene-based Pd single atom (referred to as Pd1/N-graphene) via a freeze-drying process. The use of this method had a crucial impact on the effective distribution of palladium (Pd) atoms over the nitrogen-doped carbon substrate during the final pyrolysis phase. The experimental protocol included the initial creation of an aqueous solution, followed by the process of freezing and subsequent freeze-drying in order to eliminate the water content. The powder was then exposed to a thermal treatment at a temperature of 800 °C in an argon atmosphere, leading to the formation of Pd1/N-graphene.

2.1.6. Arc-Discharge Method

The arc-discharge approach was utilized to successfully synthesize single-atom catalysts using graphene material. The procedure involves the application of an arc discharge produced between two graphite electrodes inside a gas environment devoid of reactivity. Metal clusters are formed with the introduction of metal precursors over the course of the process [89]. Single-atom catalysts are generated by the use of annealing and etching techniques, which distribute individual metal atoms over a graphene substrate [90].

For example, Jung et al. [91] developed a bottom-up arc-discharge technique to create single-atom catalysts (SACs) by using nanocarbon materials, as seen in Figure 5. This unique technique enables the integration of different metal atoms, including Co, Ni, Mn, Fe, and Pt, into the crystalline carbon structure. Table 1 represents some advantages and limitations of these synthesis methods for the synthesis of graphene-based single-atom catalysts.



Figure 5. Synthesis of N-doped graphene-based single atom from bottom-up arc-discharge approach. Reprint from reference [91].

Table 1. Represent the advantages and limitations of various synthesis methods used in graphenebased single-atom catalysts.

Synthesis Method	Advantages	Disadvantages				
Pyrolysis	High temperature can facilitate single-atom dispersionScalable and relatively simple process	 Limited control over single-atom dispersion Potential for graphene damage during synthesis 				
Atomic layer deposition	 Precise control over single-atom deposition and uniformity Can coat complex structures with high conformity 	 Requires specialized equipment and expertise Slow deposition rate 				
Ball milling	 Effective for mass production Mechanical energy promotes atom dispersion on graphene surface 	 Limited control over single-atom dispersion Requires post-treatment to achieve desired properties 				
CVD	 Scalable and controllable deposition process Can achieve high quality graphene films Can tune catalyst deposition temperature for desired properties 	 Single-atom dispersion can be challenging 				
Freeze-drying method	 Simple and cost-effective method Can preserve single-atom dispersion on graphene surface 	 Limited control over single-atom dispersion Potential for agglomeration during drying process 				
Arc-discharge method	 High yield of single-atom dispersion Can produce graphene with excellent electronic properties 	 Limited scalability High energy consumption 				

3. Characterization of Graphene-Based SACs

The identification of intrinsic structural characteristics of SACs, and their distinction from nanoscale metal catalysts, is of great importance after their production. The measurement of atomic dispersion and the particular arrangement of individual atom sites inside SACs is a key aspect of this undertaking [92]. In response to this issue, innovative approaches for characterization have been developed. Some examples of analytical

techniques often used in scientific research are Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), high-angle Annular dark-field scanning transmission electron microscopy (HAADF-STEM) with spherical aberration correction, and X-ray absorption spectroscopy (XAS). Various methodologies have been used to clarify the unique characteristics of SACs [93]. The information obtained by these characterization approaches and their advantages and limitations are represented in Table 1.

3.1. Fourier Transform Infrared Spectroscopy

The FTIR method is often used in the investigation of molecular structures by measuring the infrared absorption. In this experimental technique, a sample is subjected to a range of infrared light frequencies, resulting in the selective absorption of certain frequencies that correspond to molecular vibrations. As a result, the shift of molecules from their lowest energy level (ground state) to a higher-energy state (excited state) occurs as a consequence of the absorption of infrared light. The process of absorption leads to the reduction of transmitted infrared light at certain wavelengths. An infrared spectrum is formed by the recording of the connection between the wavelength of transmitted infrared light and its corresponding percentage. FTIR is a very valuable method for the characterization of catalyst molecules [93,94].

In work conducted by Lyu et al. [95], a new material known as Mn-NGO was synthesized. Doping N in graphene oxide (GO) serves two purposes: it offers a stable location for Mn atoms to settle, and it modifies the electronic structure of GO to improve its adsorption-photocatalytic capabilities. A solitary Mn atom serves as a mediator between the valence band and conduction band during the electron trapping and electron transfer processe FTIR spectroscopy was used to retrieve a functional group in both graphene oxide (GO) and Mn-NGO. Distinctive peaks were observed in the acquired spectra, as represented in Figure 6a. The observed vibrational modes included stretching vibrations occurring at wavenumbers of 3450 cm^{-1} , 1529 cm^{-1} , and within the spectral range of $1000-1250 \text{ cm}^{-1}$. The observed peaks in question are indicative of distinct molecular attributes, namely, the presence of O-H, C=C/C-O, and C-O bonds within the structure of GO. Significantly, a noteworthy finding was discovered with regard to the Mn-NGO substance. Within the spectral region of 1000–1250 cm⁻¹, the changed material had a discernibly different stretching pattern in comparison to graphene oxide (GO). The observed change was ascribed to the impact of C-N bonding, suggesting the effective integration of nitrogen atoms into the structure of graphene oxide (GO). Furthermore, a noticeable decrease in the distinctive vibrational behavior of C=C bonds within the graphene structure was detected subsequent to the alteration procedure.

3.2. High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy

The HAADF-STEM approach has the capacity to attain sub-angstrom resolution, successfully addressing the spherical phase aberration that is often seen in conventional transmission systems. This methodology facilitates the observation of discrete light spots, allowing for the observing of individual atoms or clusters. Consequently, it permits the collection of chemical composition data at the atomic level. Within the range of θ 3, the prevailing signals consist of electron beams that are transmitted and electrons that are scattered. The signals obtained inside the θ 2 range mostly include electrons that have undergone Bragg scattering [96,97]. The HAADF picture is formed when the received signals within the θ 1 range are mostly influenced by high-angle incoherent scattering electrons. It is worth noting that the area of high intensity in the resultant picture regularly aligns with the atomic column under investigation. HAADF-STEM plays a crucial role in a wide range of fields, such as materials science, chemistry, and physics, hence resulting in significant implications [98].



Figure 6. (a) FTIR spectra of Mn-NGO. Reprint from reference [95]. (b,c) HAADF-STEM images of Pd1/graphene at low magnifications. (d) Atomically dispersed Pd atoms in image are highlighted by the white circles. Reprint from reference [78]. (e,f) Typical HAADF-STEM images of Co-NG, where individual Co atoms are highlighted with white circles. (g) Enlarged HAADF-STEM image of Co-NG in correspondence with the area selected in yellow square in (f). Reprint from reference [87].

Yan et al. [78] presented a noteworthy discovery in the realm of catalysis. They used a catalyst consisting of discrete palladium (Pd) atoms supported on a graphene substrate. The catalyst exhibited remarkable attributes, including a significant degree of catalytic activity, exceptional selectivity towards butene, and enduring stability across continuous chemical reactions. The scientists used HAADF-STEM to provide the proof, which showcases the random dispersion of individual Pd atoms on the graphene substrate, as illustrated in Figure 6b–d. The unique steric effects exhibited by individual palladium (Pd) atoms were seen when subjecting them to an annealing temperature of 1050 °C. The particular characteristic of this feature was essential in enhancing the catalytic efficacy of the Pd1/graphene catalysts.

Yi et al. [87] fabricated a novel composite photocatalyst composed of TiO₂ nanobelts, nitrogen-doped graphene, and single Co atoms (Co-NG), thereby eliminating the need for noble metals. Using aberration-corrected HAADF-STEM imaging, the spatial arrangement of Co atoms within a matrix of nitrogen-doped graphene was investigated. The HAADF-STEM image at low resolution lacked discernible Co clusters or particles, indicating the potential presence of finely dispersed infinitesimal Co clusters or isolated atoms that are undetectable by conventional STEM techniques. The high-resolution analysis depicted in Figure 6e,f, illustrates the uniform dispersion of highly concentrated Co single atoms inside N-doped graphene. The bright dots in Figure 4b, which are isolated and circled in white, are undeniably carbon atoms because of the Z-contrast difference between the bigger Co atoms and the other atoms. Enlarged HAADF-STEM image of (Co-NG) is represented in Figure 6f. It was evident that the nitrogen-doped graphene contained a uniform distribution of densely populated Co atoms.

3.3. X-ray Absorption Spectroscopy (XAS)

XAS is a technique used to ascertain the specific chemical arrangements inside singleatom catalysts (SACs) by observing alterations in the energy levels of metal atoms [99]. The X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) are the two primary parts of the X-ray absorption fine structure (XAFS) spectrometer [100]. Single-scattering effects from the interactions of excited inner-shell photoelectrons with X-rays are captured by the EXAFS at energies between 50 and 100 eV. However, XANES extends to energies below 10 eV and over 50 eV, principally due to the complex scattering interactions of X-ray-excited inner-shell photoelectrons [101].

Liu et al. [102] used X-ray absorption spectroscopy techniques (XANES and EXAFS analyses) to confirm the presence of nickel (Ni) atoms dispersed over a graphene substrate. The authors' findings provided significant insights into the oxidation state and environment of the nickel atoms in this system, in comparison to the conventional complex NiII-Pc (nickel(II) phthalocyanine). In Figure 7a, the XANES and EXAFS spectra of graphene-supported single-atom nickel (Ni SA-NG) are shown. The spectra indicate that the valence state of nickel in the Ni SA-NG closely resembles that of NiII-Pc. This similarity suggests that the nickel atoms in the Ni SA-NG are in a moderately oxidized state. Figure 7b also displays Fourier-transformed EXAFS (FT-EXAFS) spectra, which exhibit a sharp peak at 1.4 Å, indicative of a coordination environment similar to NieN coordination and in NiII-Pc. Significantly, the Ni K-edge EXAFS spectra further suggested that adjacent atoms around the Ni atom on the graphene substrate displayed a significantly deformed shape. These results highlighted the value of accurate quantitative XAFS analysis in describing the atomic-level nickel deposition on graphene.

In another study, Deng et al. [81] used X-ray absorption fine structure (XAFS) spectroscopy to elucidate the coordination arrangement and valence state properties of individual iron (Fe) atoms inside the FeN4/GN catalysts, as seen in Figure 7c,d. X-ray absorption near-edge structure (XANES) measurements of the FeN4/GN catalysts revealed spectrum characteristics around the Fe K-edge that were very similar to those reported in the parent FePc (iron phthalocyanine) compound. The C=N bond count decreased significantly, suggesting that the FeN4 coordination structure is rather stable. Ni K-edae

(a)1.8

1.6

1.4

1.2

0.8 0.6

0.4 0.2

0.0

8320

Fe K-edge

8330

8340

XANES 1.0

(c)







3.4. XPS

XPS is an instrumental method that has significant value in the investigation of SACs by providing insights into their elemental composition and enabling the characterization of the valence states of certain elements present in these structures. Although the atomic ratios of individual metal atoms in SACs are intrinsically low, XPS may provide accurate information on the chemical configurations of nitrogen inside metal–Nx active sites [92,103].

Zhou et al. [88] used a freeze-drying technique to effectively produce atomically distributed Pd catalysts on nitrogen-doped graphene (termed Pd1/N-graphene). Pd²⁺ ions were shown to be encapsulated in the Pd1/N-graphene structure using XPS study. Figure 8a shows two distinct peaks with a relative area ratio of 3:2 in the XPS spectra of the Pd 3d region for Pd1/N-graphene. With the Pd 3d_{5/2} feature centered at 337.7 eV, which is typical binding energy for Pd²⁺ ions, these peaks were unambiguously ascribed to the Pd_{5/2} and Pd_{3/2} signals of Pd²⁺ species. Pd nanoparticles (Pd NPs) reinforced on nitrogen-doped graphene (Pd NPs/N-graphene) showed two separate sets of Pd signals in their XPS spectra. Both 335.8 and 338.1 eV was found to be the binding energies for Pd $3d_{5/2}$. The binding energies were determined to be due to Pd0 (57% of the area) and Pd²⁺ (43% of the area). This suggests that Pd²⁺ was partially reduced to Pd0 during the synthesis of Pd NPs/N-graphene, with the latter state being linked to the production of Pd nanoparticles. In addition, as demonstrated in Figure 8b, the nitrogen concentration and its different forms within Pd1/N-graphene and Pd NPs/N-graphene were comparable.



Figure 8. (a) X-ray photoelectron spectra of Pd 3d region for Pd1/N-graphene. (b) X-ray photoelectron spectra of N 1S region for Pd1/N-graphene. Reprint from reference [88]. (c) X-ray photoelectron spectra of Co-N-Gr. (d) Two-dimensional structure of Co-N-Gr. Reprint from reference [104]. (e) XPS spectra of Ni-NG/CdS photocatalyst. Reprint from reference [105].

Likewise, Meng et al. [104] provide a scalable approach to the synthesis of a group of metal atoms with high content, which are incorporated into nitrogen-doped graphene frameworks. The atomic concentration of cobalt (Co) in Co-N-Gr was determined using X-ray photoelectron spectroscopy (XPS), yielding a value of 1.16 atom% (Figure 8c). The acquired measurement exhibited a little deviation from the result obtained by the analysis conducted using inductively coupled plasma atomic emission spectroscopy (ICP-AES), which reported a Co atomic concentration of 1.2 atom% and a weight percentage of 5.85 wt%. XPS testing revealed a maximum nitrogen concentration of 14.3 atom%, which is good for heavy metal loading. The 2D structure of Co-N-Gr is illustrated in Figure 8d. Furthermore, deconvolution of the N 1s spectrum can provide important information about the presence of various types of doped nitrogen whose peaks cannot be identified directly by the main N 1s spectrum peak or nitrogen-containing substance. The N 1s XPS spectrum (Figure 3e) reveals four distinct nitrogen species, corresponding to pyrrole (399.3 eV), pyridine (398.0 eV), graphite (400.7 eV), and nitrogen oxide (401.9 eV). Single Ni atom stability and dispersion on the graphene matrix are improved by pyridinic and pyrrolic nitrogen, which usually provide lone pairs that may firmly coordinate with metal atoms. Contributing to the electrical structure, graphitic nitrogen may enhance conductivity and charge transfer characteristics. Nitrogen oxide suggests more complicated interactions in the electrical environment. These nitrogen species working together provide a strong and very active catalytic site that is essential to maximizing the photocatalytic efficiency for uses like hydrogen synthesis and CO_2 reduction [105].

3.5. Scanning Tunneling Microscopy (STM)

The use of STM is a very advantageous analytical technique that enables the direct investigation of the electronic characteristics of SACs [106]. Additionally, it provides a more indirect way of identifying components that possess comparable atomic numbers. In a comprehensive and rapid STM investigation, Patera et al. [107] examined the development of epitaxial graphene on a Ni (111) substrate. The analysis revealed the occurrence of individual Ni atoms at distinct kink locations situated throughout the periphery of the graphene, especially under increasing temperatures. The temporal resolution of their measurements achieved a level of precision in the millisecond range. The edge termination of the epitaxial graphene was recognized by the researchers as consisting of zigzag (zz) and Klein (k) edges. In each of these boundary configurations, the researchers observed kink sites, which are distinguished by discontinuities in the last two rows of carbon atoms. These spots were found to be occupied by individual nickel (Ni) atoms. The identified kink points were seen to serve as nucleation sites for the formation of graphene. The growth process entails the systematic completion of the carbon rows that were previously stopped while simultaneously progressing the kink site. The empirical findings indicated that mobile nickel (Ni) adatoms exhibited diffusion behavior along the borders of graphene, and that these individual Ni atoms located at the kink points directly influenced the development process. Furthermore, the study team performed molecular dynamics (MD) simulations, whereby Ni adatoms exhibited stochastic motion on the uncoated metal surface until they contacted a graphene edge, under a temperature of 710 K. Upon reaching a boundary of graphene, the nickel (Ni) atoms dispersed in a direction parallel to the boundary and demonstrated notably extended periods of residence when meeting a location with a kink. In the series of experimental scanning tunneling microscopy (STM) images, it was often seen that the existence of adatoms coincided with the proximity of attached C dimers, which provides compelling evidence for the catalytic function of the individual Ni atom. Figure 9 depicts a sequence that corresponds to K-edge. Within this sequence, two shortlived configurations of Ni adatoms were seen at the kink locations (namely, panels B, C, F, and G). The generated pictures at a constant height (panels D and H) are aligned with the relevant scanning tunneling microscopy (STM) data. Both the stable configurations seen using scanning tunneling microscopy (STM) and theoretical considerations indicate the significant involvement of individual nickel (Ni) atoms in accelerating the insertion of



carbon atoms at kink sites. This catalytic activity promotes the formation of graphene on a metal surface.

Figure 9. (**A**) Single nickel atom shows diffusion on a surface inside an area bounded by graphene edges. (**B**,**F**) High-speed scanning tunneling microscopy (STM) images. (**C**,**G**) Laplace images obtained from (**B**,**F**). The simulated figures in (**D**,**H**) obtained using scanning tunneling microscopy (STM) are at a constant height and are generated using the estimated geometries of (**E**,**I**). Reprint from reference [107].

3.6. Electron Energy-Loss Spectroscopy (EELS)

X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning tunneling microscopy/spectroscopy (STM/STS) are some characterization methods that can be used to describe the atomic structure of a material. The latter three technologies clearly have an advantage in directly imaging the structure of local disorder such as atomic-scale flaws, whereas XRD has its limitations in the spatial resolution [108]. Nowadays, sub-/atomic-resolution imaging is readily available using TEM or scanning TEM. Therefore, the preferred methods for seeing the atomic structure of the defects in conjunction with local chemical and electrical data include energy-dispersive X-ray spectroscopy (EDX), electron energy-loss spectroscopy (EELS), and Z-contrast imaging. However, sub-/atomicresolution transmission electron microscopy (TEM) imaging of graphene and BN remains challenging because of the weak electron scattering power of the light components. To lessen the impact of beam irradiation and enhance electron scattering, a voltage 20–80 kV lower than the knock-on threshold is used. In transmission electron microscopy (TEM), energy-loss spectroscopy may be used to investigate the sample's valence electron excitation loss (VEELS) in order to provide details about its local electronic structure via inelastic scattering of high-energy electrons [109]. We have successfully demonstrated band-gap determination or plasmon excitation using VEELS. For chemical identification and mapping, high-loss spectroscopy or core-loss EELS may be used. These techniques allow for the investigation of the sample's atomic excitations in addition to the low-loss zone, where valence electron excitation is predominant. Besides valence state mapping and chemical shift measurement, core-loss EELS is a versatile tool that is separate from EDX.

Using low-energy ion implantation, Bangert et al. [110] paternally doped monolayer graphene with B and N atoms. Graphene has a high substitution-to-vacancy ratio, which means that ions with different energies can move B or N atoms into the lattice. This creates vacancies that are filled by dopants. As seen in Figure 10b, the monolayer structure mostly consists of hexagonal graphene lattices, with the exception of dopant impurities. Using electron energy-loss spectroscopy (EELS) and annular dark-field (ADF) imaging, they can check the chemical and structural features of dopants in graphene, such as the elements they are made of and the types of bonds they form. Figure 10a,c show that the B and N atoms have different ADF intensities, with the B dopant being darker and the N atom being brighter; the yellow dashed rectangles indicate this difference. By using STEM-EELS to look at the rectangular areas in more detail, they confirmed the chemical species of both dopants (Figure 10b,d). The ADF image and the clear K-edges of the B and N atoms in an sp² hybridization show that they have been substituted into the graphene lattice. As previously stated, this finding is also an image of a graphitic N dopant atom at the atomic scale.



Figure 10. (a) Double Gaussian filtered atomic-resolution pattern of a substitutional B atom in graphene. (b) Core-loss K-edges of B dopants. (c) Double Gaussian filtered atomic-resolution pattern of a substitutional N atom in graphene. (d) Core-loss K-edges of N dopants. Reprint from reference [110].

In addition, Ramasse et al. [111] identified both kinds of silicon dopants in graphene using annular dark-field imaging and EELSELNES. Their demonstration showed that the estimated ELNES (electron energy loss near-edge structure) of planar fourfold-coordinated

19 of 48

silicon matches the experimental results and verified its sp^2 d hybridization. The deformed geometry of Si-C3 provides a more precise simulation compared to the planar structure when compared to the experimental spectrum. This suggests that Si-C₃ is sp^3 hybridized.

3.7. Energy-Dispersive X-ray Spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) is a method of analysis that is used to determine the elemental composition or chemical properties of a material. The process entails the interaction between an electron beam and the sample, resulting in the emission of distinct X-rays from the constituent constituents of the material [112]. EDS can determine the elemental composition of a sample by measuring the energy and intensity of the X-rays emitted. For instance, Han et al. [113] describe the use of single Mo atoms attached to nitrogen-doped porous carbon as an economically efficient form of catalysis. The energy-dispersive X-ray spectroscopy (EDS) analysis reveals that the Mo, C, and N elements are evenly distributed throughout the structure, as shown in Figure 11a–c. This catalyst has a high level of catalytic activity due to its ideally high density of active sites and hierarchically porous carbon frameworks.

3.8. Raman Spectroscopy

Raman spectroscopy is a crucial method for examining and characterizing graphenebased photocatalysts composed of individual atoms. This paper provides a thorough examination of the structural, electrical, and vibrational properties of graphene. It enables the identification of flaws, quantification of doping levels, and investigation of the interaction between graphene and individual atoms. These observations are essential for improving the effectiveness of photocatalytic processes [114]. For instance, Zhu et al. [115] reported a method to pyrolyze EDTA-Pt complex to N-doped graphene with isolated Pt single atomic sites (Pt-ISA/NG) using Na₂CO₃ salts, with a Pt loading of up to 5.3% wt%. The Pt-N₄ structure supported by nitrogen shows atomic dispersion of single Pt species on a graphene support, according to X-ray absorption. The Raman spectra of the Pt-ISA/NG catalyst reveal three distinct peaks at 1325, 1580, and 2655 cm⁻¹, which are often referred to as the D, G, and 2D bands, as seen in Figure 11d. The G band, which is characteristic of a standard sp²-hybridized carbon network, is associated with the stretching mode of the C-C bond in graphitic structures. It is clear that few-layer graphene is present since the computed 2D/G intensity ratio is 0.57.

Furthermore, Zhang et al. [116] described a new method for synthesizing single iron atoms for CO₂ reduction. This method involves subjecting hemin and melamine molecules on graphene to extended heat pyrolysis, resulting in the production of strong and efficient single iron atoms. The individual iron atoms are incorporated into the graphene matrix. Analyzing the Raman spectra, particularly the intensity ratio between the D band (1360 cm⁻¹) and the G band (1590 cm⁻¹), enables us to evaluate the level of disorder in the graphitic systems. The ID/IG ratios of the samples H-M-G and H-M are determined to be 1.06 and 1.13, respectively, which are much greater than that of pure graphene (0.4). The rise in density is due to the presence of a large number of nitrogen dopants and the inclusion of individual Fe atoms in these samples. The exceptional CO₂-to-CO conversion efficiency is due to the existence of extremely effective FeN₅ active sites, which are scattered individually and supported by N-doped graphene. Additionally, there is an axial ligand coordinated with FeN. Furthermore, usages, advantages, and limitations of various characterization approaches used in graphene-based single-atom catalysts are represented in Table 2.

Characterization Techniques	Uses		Obtained Information		Advantages		Disadvantages		
FTIR	•	Characterization of surface adsorption and reactions.	•	Molecular vibrations, surface adsorbates, reaction kinetics.	•	Nondestructive. High sensitivity. Real-time monitoring.	•	Limited to surface analysis.	
HAADF-STEM	•	Structural characterization of SACs.	•	Atomic structure. Composition. Spatial distribution.	•	High-resolution atomic-scale imaging.	•	Complex sample preparation. Limited to thin samples.	
XAS	•	Determination of elemental composition and oxidation states of atoms in a material.	•	Reveals detailed electronic structure, oxidation states, and coordination environment.	•	High sensitivity to detect subtle changes in electronic and structural properties. Provides quantitative information about the concentration of elements.	•	Requires access to synchrotron radiation facilities for high-energy X-rays. Complex data analysis and interpretation.	
XPS	•	Surface elemental composition Oxidation states of atoms.	•	Chemical states, oxidation states, surface composition.	•	Elemental and chemical state analysis. High sensitivity.	•	Surface-sensitive technique, limited to top few nanometers.	
STM	•	Surface morphology and electronic structure observation.	•	Surface topography, atomic-scale imaging.	•	High-resolution real-space imaging.	•	Limited to conducting surfaces surface-sensitive technique.	
EDS	•	Elemental analysis. Identifying composition of microscopic areas.	•	Qualitative and quantitative elemental analysis. Elemental mapping. Distribution and concentration of elements.	•	Rapid analysis with minimal preparation. Wide elemental range. Nondestructive.	• •	Limited spatial resolution. Higher detection limits for light elements. Sample must be solid and vacuum-compatible.	
EELS	•	Analysis of thin films, interfaces, nanostructures. Used with TEM.	•	Electronic structure and bonding information. Chemical composition, sensitive to light elements.	• •	High sensitivity to light elements and bonding states. Detailed electronic structure information. High spatial resolution.	• •	Complex instrumentation and expertise required. Complex spectra interpretation. Samples must be thin and TEM compatible.	
Raman	•	Characterization of molecular vibrations, crystal structures, material properties.	•	Molecular and lattice vibrations (phonons). Information on chemical bonds and molecular symmetries.	•	Nondestructive, minimal preparation. Analyzes a wide range of materials, including liquids and solids. High specificity to molecular structures.	•	Fluorescence interference in some samples. Lower sensitivity compared to other techniques. Limited to vibrational modes changing polarizability.	

Table 2. The usages, advantages, and limitations of various characterization approaches used in graphene-based single-atom catalysts.



Figure 11. (**a**–**c**) Energy-dispersive X-ray spectroscopy (EDS) of C, N, and Mo elements. Reprint from reference [113]. (**d**) Raman spectra of Pt-ISA/NG catalyst. Reprint from reference [115].

4. Computational Study of Graphene-Supported Single-Atom Photocatalysts

Graphene is a two-dimensional lattice composed of carbon atoms, and its exceptional electrical, mechanical, and thermal properties have attracted a great deal of interest in materials research. More attention has recently been paid to investigating various potential applications of graphene based SACs. The combination of graphene and SACs has led to the emergence of a fascinating area of research: the computational study of graphene-supported single-atom photocatalysts [117].

The concept of single-atom catalysis represents a paradigm shift in catalytic science. Traditional heterogeneous catalysts often rely on the ensemble effects of nanoparticles, where active sites can be buried within the bulk of the material [118]. Over the other hand, SACs are made up of metal atoms that have been separated and then spread over a support material. This ensures that each and every atom participates to the catalytic process. Graphene, with its high surface area, exceptional conductivity, and ability to stabilize metal atoms, serves as an ideal substrate for these SACs. When utilized in photocatalysis, this synergy between graphene and SACs can result in unprecedented catalytic activities for light-driven reactions [119].

The computational study of graphene-supported single-atom photocatalysts involves a multidisciplinary approach. Quantum mechanical calculations [120], often employing

density functional theory (DFT) [121], are crucial for understanding the electronic structure and reactivity of these systems. Researchers investigate the interaction between the single metal atom and the graphene support, evaluating the adsorption energy, electronic states, and charge transfer. These factors collectively influence the stability and catalytic performance of the SAC. Additionally, simulations of photoexcitation processes provide insights into the catalyst's behavior under light irradiation [35]. In the realm of solar energy conversion, graphene-supported single-atom photocatalysts have been widely used. Many ecologically important processes are being investigated in these systems, including water splitting and carbon dioxide reduction. Computer simulations allow scientists to plan ahead for reactions, evaluate potential energy obstacles, and fine-tune catalyst structures for optimal performance [122].

4.1. Density Functional Theory (DFT)

Significant insights are obtained by using DFT in the study of electrical and catalytic properties of single-atom systems reinforced by graphene. The study makes use of intricate simulations to investigate the atomic level of charge transfer, electron concentrations, and contact interactions with the graphene substrate [123]. Through the examination of electron delocalization, charge buildup, and metal–support interactions, density functional theory (DFT) offers a full comprehension of the impact of individual atoms on the catalytic activity and reactivity of systems based on graphene [35]. The comprehension of this concept holds great importance in the advancement and optimization of highly efficient catalysts used in several fields, including energy conversion and storage.

Cao et al. [124] shown that the introduction of sodium (Na) leads to an improvement in the production of a ruthenium (Ru) catalyst that is attached to graphene oxide (GO) functionalized with sodium (GO_{Na}) at the atomic level. The electron densities of the Ru single-atom (Ru SA) and Ru nanoparticle (Ru NP) structures were examined using DFT computations. Differences in electron densities between the Ru surface-adsorbed (SA) and Ru nanoparticle (NP) systems were observed. The study determined that the average net electronic charges transferred from the Ru SA and Ru NP to GO_{Na} were 1.791801 e and 1.504535 e, respectively, as seen in Figure 12a,b. Negative values indicate the buildup of electrons. It is worth mentioning that GO_{Na} demonstrated a notable tendency to acquire a greater number of electrons from the Ru SA, resulting in a reduction in electron density of the Ru SA. The observed significant transfer of charge is likely attributed to the strong contact between the interfaces and the powerful interaction between supporting material and single atom.

With the exception of the interface, the amount of contact between Ru and the support material was rather low in the Ru NP scenario. Consequently, there was a modest amount of prominence in the charge transfer from the ruthenium nanoparticle to the support material. Furthermore, DFT calculations were obtained to comprehend the mechanism controlling the interaction between graphene oxide nanosheets (GO_{Na}) and ruthenium surface anchors (Ru SA). As shown in Figure 12c, the results obtained from the computer models of the HOMO and LUMO molecular orbitals suggest that electrons are transferred from the Ru SA to the GO_{Na} substrate by d- π conjugation. The initiation of electron delocalization in Ru SA was triggered by the occurrences of this phenomenon, leading to a subsequent drop in electron density inside Ru SA and an increase in photocatalytic activity. The results show a notable reduction in the absorption of intermediate hydrogen (H^{*}) species while concurrently accelerating the detachment of produced H₂ from the catalyst's surface.



Figure 12. (**a**) Ru NP/GO interface, and (**b**) Ru SA/GO_{Na} interface. (**c**) HOMO and LUMO orbital circulation of Ru SA/GO_{Na}. Reprint from reference [124].

Electronic Structure Band-Gap Modification

Catalysis and materials science both stand to benefit greatly from research into the electrical structure and control of band gaps in graphene-based single-atom catalysts. Catalytic processes rely heavily on the electrical properties of the catalyst, and our study aims to provide light on the intricate interaction between these two variables [125]. Through the use of computational techniques such as density functional theory (DFT), researchers are able to examine the impact of integrating individual atoms onto graphene surfaces on the electrical structure and band gap [126]. Having a comprehensive understanding of these factors offers valuable knowledge on the distribution and transfer of charges, as well as the overall reactivity. This study makes a valuable contribution to the development of catalysts that are more efficient and specifically designed for a range of applications, such as energy conversion and environmental cleanup [35].

For example, Rong et al. [127] used density functional theory (DFT) as a computational method to examine the electronic characteristics of single-atom Cu-doped ZnO material, which was supported by graphene, within the framework of a Cu-ZnO/GPET system. The calculations conducted in the study showed that the thermodynamic stability of the Cu-doped Cu1/ZnO configuration surpasses that of the undoped Cu1/ZnO configuration. Consequently, it is anticipated that the Cu-doped Cu1/ZnO configuration would prevail in the Cu-ZnO/GPET system. Projected density of states (pDOS) was performed for estimates Cu1/ZnO and Cu1/ZnO, as seen in Figure 13a,b, by optimizing the most stable doped and supported structures. The findings of the study indicate that the electronic d-states of the copper (Cu) atoms are positioned in greater proximity to the Fermi energy level in comparison to the zinc (Zn) atoms. Moreover, it is observed that there exist vacant Cu d-states, indicating that upon exposure to light, electrons produced by the photoexcitation



process might possibly become localized at the doped Cu atoms. This localization may result in a partial hindrance of the recombination between the photoexcited electrons and holes.

Figure 13. The projected density of states (pDOS) for the surface Zn and Cu atoms in two different models: (a) the doped Cu1@ZnO model and (b) the supported Cu1/ZnO model. (c) Band structure of pure ZnO and (d) band structure of the doped Cu1@ZnO model. Reprint from reference [127].

In order to further comprehend the electrical structure and variations in the band gap caused by the introduction of Cu, the researchers used the DFT + U methodology to calculate the band structures of both undoped ZnO and ZnO doped with Cu in its bulk form. The band gap of pure ZnO was determined to be 2.08 eV (as indicated in Figure 13c), and it decreased to 1.63 eV following Cu doping. In the arrangement with doping, the bands of Cu crossed the Fermi level, as seen in Figure 13d. This observation suggests the existence of unoccupied 3d states on the Cu atoms.

In another study, Talib et al. [128] conducted research where they used first-principles methods to investigate the bonding properties of single-atom catalysts (SAC) composed of chromium (Cr) on graphyne (GY). The figure displays the optimized structure of the most stable Cr-GY arrangement, as seen in Figure 14a. The Bader charge analysis revealed that the chromium (Cr) atom bonded to the GY surface had a positive charge of about +1.41e. This discovery indicates a significant movement of electric charge and a strong connection between the Cr atom and the GY surface. Figure 14b depicts the partial electron density differences (PEDD) plot, which showcases the movement of electron density from the Cr atom to neighboring C atoms, hence emphasizing the strong binding energy. The examination of the band gap indicated that the band gap in Cr-GY had a higher degree of scattering at the Fermi level in comparison to pure GY. This discovery indicates a significant similarity between Cr and GY, which is further supported by the plot of the projected density of states (PDOS). Furthermore, the spin-polarized partial density of states (PDOS) analysis, as seen in Figure 14c, revealed a notable correlation between the Cr-3d orbitals and the sp hybrid orbitals of GY. This observation implies a heightened degree of reactivity in close proximity to the Fermi level, which might possibly play a crucial role in the catalytic process.



Figure 14. (a) Computed structure of the Cr attachment to GY is presented, inclusive of top and side views. (b) The PEDD plot is visualized, with charge accumulation regions denoted in blue and charge depletion regions in yellow. (c) A spin-polarized projected density of states (PDOS) is examined, with particular emphasis on the Cr-3d (red), sp (green), and C-sp (blue) states. Reprint from reference [128].

4.2. Molecular Dynamics (MD) Simulation

MD simulations are a real computational methodology used for the examination of the atomic-level dynamic properties and structural stability of materials [129]. For example, Ali et al. [130] used MD simulations to assess the structural soundness of flawed and doped graphene as a base for single-atom catalysts (SACs). The objective of the work was to observe the behavior of Cu, Ru, and Pd atoms when they were placed on graphene with a single vacancy (m-VacG) at different temperatures, namely, 300 K, 500 K, 700 K, and 1000 K. The study was dedicated to the investigation of this behavior. It was proved via simulations that the supported metal atom structures displayed a high degree of stability for a period of time equal to five picoseconds (ps) at temperatures of three hundred and fifty, five hundred, and seven hundred degrees Celsius. There were only slight aberrations discovered when the temperature was raised to one thousand degrees Celsius.

In another study, Cao et al. [131] used ab initio molecular dynamics (AIMD) simulations to examine the mechanism behind the oxygen reduction process (ORR) on Mn_1N_4/DV graphene. When subjected to solvent surroundings, the active site Mn_1N_4 experiences a significant change in the way it adsorbs O₂. The shift from the superoxide state to the peroxide state is included within these alterations. An increase in the rate at which the electric charge moves from the substrate to oxygen is one of the two processes that contribute to this shift. The other mechanism is the establishment of hydrogen bonds between the species that have been absorbed and the water molecules that are present in the nearby aqueous layer.

4.3. Stability of Single Atom on Graphene-Based Support

The phenomenon of strong metal–support interaction (SMSI) is well acknowledged in the realm of heterogeneous catalysis, where it has a substantial influence on impeding the diffusion and aggregation of metal nanoparticles. The scope of surface science and materials interface (SMSI) has been broadened as a result of developments in research techniques, including robust interactions between metallic components and their corresponding substrates [132]. SMSIs are likely created due to electrical flaws and surface structural imperfections [133].

For instance, Back et al. [134] conducted a comprehensive investigation on various metal surface atoms (Co, Cu, Ag, Au, Ni, Os, Fe, Ir, Pd, Pt, Rh, and Ru) that were anchored onto defective graphene using DFT calculations. The results of the study revealed that Co, Fe, and Rh exhibited a preference for anchoring onto effective graphene with a single vacancy, whereas the other metal atoms demonstrated a stronger binding affinity towards

double vacancies (Figure 15a). The strong covalent bonds between SA and its graphene substrate are responsible for electron transfer. The transfer of electrons was made possible due to the robust electronic contact between the p-orbital of graphene and d-orbital of the metal atom. This interaction is responsible for the unique surface properties found in transition metals (Figure 15b). Additionally, the SACs' configuration exhibited distinct variations in product selectivity. The various surface areas feature distinct surface chemical and electrical structures, which serve as the underlying basis for substrate selection.



Figure 15. (a) Figure 14 illustrates the top view of M/sv-Gr and M/dv-Gr, with (a) representing the visual depiction. Additionally, (b) displays the binding energies of various transition-metal atoms with the sv-Gr and dv-Gr defect sites, shown by filled black circles and open blue circles, respectively. Reprint from reference [134]. (c) The optimal configurations for g-X-Pt compounds are as follows: a bifunctional fluorinated g-Pt-F₂ complex, a hydroxylated g-Pt-(OH)₂ complex, a nitrated g-(CN)₂-Pt complex, and a monofunctional hydrogenated g-Pt-H₂ complex. This is a reprint sourced from reference [135].

Langer et al. [135] investigated the contacts between graphene and platinum (Pt) single atoms. The graphene samples were covalently functionalized with several groups (-OH, -CN, -F, and -H), which acted as binding sites for the Pt atoms. This experimental setup is seen in Figure 15c. During the course of the study, it was noted that the platinum (Pt) atoms had a discerning capacity to cleave the chemical bonds linked to fluorine (F), hydroxyl (OH), and hydrogen (H) atoms that were bonded to the graphene substrate. However, this resulted in the creation of a linear arrangement in which the Pt atom was coordinated above the -CN group, leading to the development of a g-CN-Pt complex. The strategic placement of the Pt atom either immediately above or in close proximity to the -CN group served as an effective measure to inhibit any possible detrimental processes, such as particle agglomeration, diffusion away from the place, or leaching of Pt. This finding suggests that the influence of thermal effects on the material's long-term stability is improbable. Furthermore, the attachment of Pt atoms onto the graphene served to maintain the accessibility of the coordination sphere, which is favorable for catalytic performance.

4.4. Role of Computational Analysis for Predicting Reaction Mechanism

Computational analysis plays a crucial role in predicting reaction mechanisms in photocatalysis. By employing quantum chemistry and molecular dynamics simulations, researchers can unravel the intricate details of photon-induced chemical processes on catalyst surfaces. These computational tools enable the exploration of potential energy surfaces, identification of intermediates, and determination of reaction pathways [35]. Moreover, they shed light on the electric structures and charge migration dynamics involved, aiding in the design and optimization of photocatalysts. Computational analysis accelerates the discovery of efficient and sustainable photocatalytic materials and reactions, reducing the need for extensive experimental trial and error, and ultimately contributes to the advancement of renewable energy production and environmental remediation [121]. For example, Poldorn et al. [136] used DFT simulations to investigate the possible chemical reactions for the transformation of carbon dioxide (CO_2) into formic acid. The study specifically focused on determining whether the cis- or trans-configuration is involved in this process. Understanding the conductivity of single iron (Fe) or nickel (Ni) atoms constructed on graphene was the primary objective of this investigation. These graphene sheets were specifically labeled as Fe-N₃Gr or Ni-N₃Gr. The thorough explanation of the chemical pathways is explained in detail below.

4.4.1. Pathway 1

Adsorption and HCOO* Formation

Concurrently, at an initial adsorption energy of -1.17 electron volts (eV), molecules of carbon dioxide (CO₂) and hydrogen (H₂) adsorb onto the surface of iron trioxide (Fe-N₃Gr). When CO₂ and H₂ molecules come into contact with Fe-N₃Gr, the carbon atom in CO₂ interact with the hydrogen atom (H1). An intermediate species known as HCOO* is formed as a consequence of this interaction. At this point in time, an activation energy (Ea) concentration of 0.57 electron volts is required according to the TS1-Route A framework. The hydrogen bond length grows from 0.81 to 1.56 angstroms over this time, while the distance between the carbon atoms in the adsorbed CO₂ and H1 decreases from 2.37 to 1.50 angstroms.

HCOO* Reorientation and Pathway Division

Following the initial generation of HCOO*, the reaction might proceed along two separate routes. The aforementioned processes are designated as Route A1 and Route A2, whereby each pathway yields distinct products, namely, cis-HCOOH and trans-HCOOH, respectively. The energy transformations linked to these pathways exhibit distinct variations. The reaction denoted as Route A1 is characterized by an endothermic nature, as it has a reaction energy (Er) value of 0.04 electron volts (eV). Conversely, Route A2 is classified as exothermic, as it exhibits an Er value of -0.12 eV.

Rate-Determining Steps

The production of cis-HCOOH in Route A1 is governed by a rate-determining step that requires an activation energy of 1.01 eV. Conversely, in the case of Route A2, the step that determines the rate is the formation of HCOO* with an activation energy of 0.57 eV. The results indicate that the formation of trans-HCOOH is more energetically and reactively favorable than the formation of cis-HCOOH on the Fe-N₃Gr surface.

Dominant Reaction

As a result of these observations, it is concluded that CO_2 hydrogenation on the Fe-N₃Gr surface predominantly leads to the production of trans-HCOOH (Route A2). When compared to Route A1, where cis-HCOOH is formed, this alternative is more efficient from a thermodynamic and kinetic viewpoint (as seen in Figure 16).



Figure 16. The energy profiles (in electron volts, eV) for the catalytic reaction pathways of carbon dioxide (CO_2) hydrogenation to produce formic acid on a catalyst consisting of iron anchored within nitrogen-doped graphene sheets (Fe-N₃Gr) elucidated through computational modeling. Reprint from reference [136].

4.4.2. Pathway 2

Adsorption

The process starts with CO₂ and H₂ molecules being adsorbed together on the Ni-N₃Gr surface. This adsorption is accompanied by energy of -0.87 eV (Figure 17).



Figure 17. The energy profiles (in electron volts, eV) for the catalytic reaction pathways of carbon dioxide (CO_2) hydrogenation to produce formic acid on a catalyst consisting of iron anchored within nitrogen-doped graphene sheets (Ni-N₃Gr) elucidated through computational modeling. Reprint from reference [136].

Formation of HCOO* Intermediate

Moving forward, there is a transition state, TS1-Route B, which facilitates the creation of an intermediate species known as HCOO* on the Ni-N3Gr surface. This step requires an activation energy (Ea) of 0.37 eV. This activation energy is notably lower compared to the crucial step in Route A2, which was observed to be 0.57 eV.

Interaction with Remaining Hydrogen Atom

Following the formation of the HCOO* intermediate, the next stage involves the interaction between this intermediate and the remaining hydrogen atom, setting the foundation for two possible paths: Route B1 and Route B2. These pathways eventually lead to the production of two forms of formic acid: cis- and trans-HCOOH.

Route B1—Formation of cis-HCOOH*

The formation of cis-HCOOH* (FA-Route B1) takes place on the Ni-N3Gr surface in Route B1. The progression involves traversing a transitional state referred to as TS2-Route B1, which requires an activation energy (Ea) of 0.80 electron volts (eV). Following this, the process of cis-HCOOH* transitioning into the gaseous phase occurs, necessitating an energy of desorption (Edes) equal to 0.74 electron volts (eV).

Route B2—Formation of trans-HCOOH*

In an alternate reaction route, the intermediate $HCOO^*$ (referred as Route B) undergoes a chemical alteration with the remaining hydrogen atom (H₂) present on the surface of Ni-N₃Gr. this reaction results in the production of trans-HCOOH^{*} (Route B2). During this particular phase, there occurs a transition state denoted as TS3-Route B2, which is distinguished by an exceptionally low activation energy (Ea) value of 0.16 eV. Significantly, this particular number is much more diminutive in comparison to the value observed on the Fe-N₃Gr surface.

Formic Acid Desorption and Reusability

It is noteworthy to mention that the adsorption energy of formic acid on the Ni-N₃Gr surface is around -0.67 eV. The aforementioned number indicates that the detachment of formic acid from the Ni-N₃Gr surface occurs spontaneously, hence allowing the catalyst to be used again in future catalytic cycles.

The complex system included in Route B involves an in-depth exploration of the CO_2 hydrogenation process for the synthesis of formic acid. This process takes place on the surface of Ni-N₃Gr via the use of an intermediate HCOO* species, which ultimately leads to the creation of both cis- and trans-HCOOH structures. The reaction pathway exhibits distinct energy profiles and structural configurations, whereby the advancement of the reaction is governed by diverse transition states and activation energies (as represented in Figure 17).

5. Factors Effecting Photocatalytic Activity of Graphene-Based Single Atom Photocatalysts

5.1. Effect of Electron Density

Electron density plays a pivotal role in photocatalysis by influencing the generation, transfer, and utilization of charge carriers. The consensus is that the photocatalytic performance is heavily influenced by the metal core and its local coordination. Due to the redistribution of electron density caused by the introduction of metal, the majority of electrons gather around the metal and its surrounding atoms. Therefore, significant attempts have been made to modify the metal center and/or ligands in order to enhance the effectiveness of CO_2 and H_2 photoreduction. Through extensive investigation, it has been shown that the process of electron transfer is highly influenced by the size of metal nanostructures and the specific local coordination. Wu et al. [70] observed that electrons were moved from individual Pt atoms to a carbon support that was doped with sulfur. They

also found that the direction of electron transfer would be reversed after Pt nanoclusters were loaded. The surface electron density has a substantial impact on the photocatalytic efficiency. Based on the idea of Au-anchored CdS, Cao et al. [137] provided a fundamentally new method for surface electron density modulation. Crucially, the surface electron density can be controlled by altering the size of Au nanostructures. Reducing Au nanoclusters to individual atoms allows for faster photoelectrons transport to the surface, which in turn increases the number of electrons accessible for CO₂ reduction due to the high hybridization of the Au 5d and S 2p orbits. The product production rate of AuSA/Cd1-xS is at least 113 times higher than that of pure Cd1-xS, which is a noteworthy improvement. Prior research indicates that the bonding between adsorbed CO₂ molecules and metal sites is rather weak due to the fact that the resulting metal-C or metal-O connections are less strong than the extremely stable C-O bonds in the CO_2 molecule. This results in the facile cleavage of metal-C or metal-O bonds during the reaction, impeding the subsequent conversion of CO₂. Based on the aforementioned factors, it can be inferred that manipulating the dimensions of metal nanostructures and/or the nature of vacancies might potentially lead to the concentration of electrons at locations other than metal nanostructures. This, in turn, is expected to enhance the process of CO₂ adsorption and conversion.

In this process, light excites electrons in the photocatalyst, altering its electron density [132]. This promotes efficient electron–hole separation, enhancing redox reactions at the catalyst's surface. Optimal control of electron density facilitates higher photocatalytic activity and selectivity, thus underscoring its significance in harnessing solar energy for sustainable chemical processes. Cao et al. [124] conducted a study whereby they used DFT simulation to demonstrate that a strong metal–support contact between graphene and Ru SA. This process significantly decreases the electron density of Ru SA. This electron transfer is responsible for the reduction of electron density, which enhances the photocatalytic activity.

5.2. Interaction and Charge Transfer in Graphene Single-Atom Catalysts

Strong metal–graphene interactions can significantly enhance photocatalytic activity. When single atoms are anchored onto graphene surfaces with a high degree of interaction, charge transfer and synergistic effects are promoted. This leads to improved separation and utilization of photoinduced electron–hole pairs, augmenting catalytic efficiency. The metal–graphene interface serves as a favorable site for intermediate adsorption and reaction, reducing energy barriers [138]. Additionally, the strong interaction stabilizes metal atoms, preventing aggregation and maintaining high surface area. Thus, the synergy between metal and graphene creates a platform for efficient light absorption, charge transport, and catalysis, making such composites promising candidates for advanced photocatalytic applications [139].

For instance, Gao et al. [140] fabricated a photocatalyst composed of individual cobalt (Co) atoms integrated into partially oxidized graphene (Co1-G) nanosheets (NSs) with the purpose of facilitating the conversion of carbon dioxide (CO₂) into carbon monoxide (CO). Graphene has many advantageous characteristics for various applications. Firstly, it exhibits a substantial surface area, allowing for increased interaction with other substances. Secondly, its flexible nature enables it to effectively accept a significant amount of metal loading. Thirdly, graphene offers specialized locations that may serve as anchors for Co SAs (cobalt single atoms). Lastly, it demonstrates high carrier mobility, facilitating efficient electron transfer processes. The analysis of Co1-G reveals that the cobalt (Co) surface atoms (SAs) are uniformly distributed inside a graphene matrix and are coordinated with carbon (C) and oxygen (O) atoms. Additionally, their results revealed that the transfer of charge from cobalt to graphene in Co1-G single atoms increases the photocatalytic activity.

In another work, Ali et al. [130] performed a comprehensive analysis using firstprinciples methodology to examine the process of CO_2 hydrogenation on graphene surfaces with an extraordinary concentration of faults. They revealed that the combination of metal (Cu, Pd, and Ru) single atoms into graphene with an extraordinary density of faults leads to an enhancement in its catalytic performance for the conversion of CO_2 to formic acid. The aforementioned investigations provide evidence that the integration of metal surface atoms (SAs) with defects leads to a substantial improvement in charge separation during catalytic processes.

5.3. Effect of N-Doping in Graphene-Based Single-Atom Photocatalysts

The incorporation of nitrogen dopants into graphene-based single-atom catalysts (SACs) has a profound impact on their photocatalytic activity, leading to enhanced performance and unique properties. Due to its ideal electrical structure and abundance of active sites, nitrogen-doped graphene is an excellent support material for fundamentally distributed metal catalysts [141].

Zhou et al. [88] documented the achievement of synthesizing nitrogen-doped graphenebased Pd single-atom catalysts (SACs) (Pd1/N-graphene) using freeze-drying techniques. They emphasized the notable impact of nitrogen dopants on the modulation of photocatalytic activity. Nitrogen atoms on the graphene lattice exhibit a strong capability to coordinate with Pd²⁺ ions, thereby facilitating the precise dispersion of Pd atoms. This interface not only soothes the Pd atoms but also provides a direct pathway for charge transfer, promoting efficient photocatalysis. The nitrogen dopants introduce electronic modifications to the graphene structure, creating localized states within the band gap that enhance light absorption and extend the spectral response range. This results in improved light utilization efficiency and increased generation of electron–hole pairs, which are crucial for photocatalytic reactions.

5.4. Effect of Active Sites in Graphene-Based Single-Atom Photocatalysts

Active sites in graphene-based single-atom photocatalysts play a pivotal role in dictating their photocatalytic efficiency, selectivity, and stability [142]. The precise control over the nature and distribution of these active sites enables tailoring of these materials for specific applications, making them promising candidates for advanced photocatalysis [143]. An important factor in the reduction of carbon dioxide and production of hydrogen is the specific surface area of photocatalysts based on single-atom graphene. This increases the number of active sites for adsorption and activation of molecules, improves light absorption, and allows for efficient charge transfer, all of which greatly improve the photocatalytic efficiency [35]. The reduction and hydrogen evolution processes are enhanced when materials with a high surface area are used because they expose more catalytic sites, which allow for increased contact with CO₂ or water molecules. In addition, graphene's high conductivity allows for fast electron movement, which reduces recombination losses and boosts activity generally [144]. The improved interaction and structural integrity of these catalysts lead to better photocatalytic activity and stability, which in turn leads to increased quantum efficiency and more effective use of photogenerated carriers, according to reported studies.

In the case of CO_2 photoreduction, the effectiveness of catalysts in the photoreduction of CO_2 is influenced by a range of parameters, such as CO_2 adsorption, electron transfer rates, intermediate production, intermediate binding energies, and product desorption. The role of single-atom catalytic (SAC) active sites, composed of individual metal atoms, is crucial in influencing the interactions between reactants and intermediates on the surface of the catalyst [145]. Hence, it is essential to possess a sufficient quantity of active sites to allow the adsorption of CO_2 molecules and stabilize intermediates like *CO and *COOH on the catalyst's surface. This eventually controls the catalyst's performance and its ability to produce desired products with selectivity.

For example, Zhang et al. [146] aimed to provide a complete explanation about of the importance of atomic-level reactive sites in the process of CO_2 photocatalysis. They classify catalytic active sites into four separate categories: (i) single atoms of metal (SAs), (ii) vacancies, (iii) surface functional groups, and (iv) Lewis pairs. Several physicochemical changes, including shifts in chemical valence, electron density, and ionic radius, result from metal atom integration into a catalyst's semiconductor framework. The upshot is that

catalysts with metal atoms on their surfaces are more likely to have active sites that boost photocatalytic activity.

In addition, Yi et al. [87] demonstrated that nitrogen-doped graphene (NG) exhibits a significant specific surface area and remarkable electrical conductivity. This property enables NG to establish a strong interface with TiO₂, effectively acting as an "electron trapping" mechanism. Therefore, nitrogen-doped graphene (NG) enables the effective transportation of electrons from the semiconductor titanium dioxide (TiO_2) to the individual cobalt (Co) atoms. In addition, the cobalt (Co) atoms present in the N-doped graphene (NG) matrix are both isolated and consistently distributed. These atoms exhibit the capacity to capture electrons and function as highly efficient catalytic sites for the conversion of hydrogen ions (H^+) into hydrogen gas (H_2) . The researchers demonstrated this phenomenon by augmenting the quantity of individual cobalt atoms, which in turn led to an increase in the number of active sites inside the photocatalyst. As a result, the integration of the Co-NG co-catalyst into the Co-NG/TiO₂ composite demonstrates significant improvements in many simultaneous processes, including greater separation of charge carriers, quicker transportation of electrons, and increased efficiency of photocatalysis. These approaches involve tailoring the catalyst's properties to match the requirements of the desired photocatalytic reaction, ultimately leading to more efficient and effective photocatalytic processes.

5.5. Photocatalytic Applications of Graphene-Based Single-Atom Photocatalysts

5.5.1. Photocatalytic CO₂ Reduction Application

Graphene-based single-atom photocatalysts have shown great potential for CO_2 reduction. The unique structure and properties of graphene allow efficient light absorption and charge transfer, enabling the conversion of CO_2 into valuable chemical compounds, such as carbon monoxide or methane [147]. The single-atom configuration provides enhanced catalytic activity and selectivity, allowing for improved CO_2 conversion rates. Furthermore, graphene's high stability and durability make it a promising material for long-term CO_2 reduction applications. This innovative approach holds promise for mitigating climate change by utilizing CO_2 as a valuable resource [148].

Mechanism of CO₂ Photoreduction

Photocatalysis has been proven as a viable method for activating and converting carbon dioxide into valuable chemical compounds. Carbon dioxide adsorption onto a photocatalyst surfaces is the most efficient method for lowering the energy barrier for this conversion. The result is an increase in carbon dioxide's reactivity due to the bending of its linear structure. This leads to the transformation of carbon dioxide's linear structure into a bent configuration, enhancing its reactivity. This alteration occurs due to the decrease in the LUMO energy level of carbon dioxide upon bending [149].

The process initiates with a one-electron transfer subsequent to the development of carbon dioxide bound to the surface of the photocatalyst. This adsorbed carbon dioxide then triggers subsequent chemical reactions [150]. These reactions predominantly encompass transfers of electrons or protons, the breaking of carbon-oxygen (C-O) bonds, and the formation of new carbon-hydrogen (C-H) bonds. The eventual distribution of products in these chemical reactions hinges upon multiple factors, including the quantity and potential of the charge carriers involved, operational conditions, and the reducing agent nature that was employed. In the context of the carbon dioxide reduction reaction (CO₂RR), a photocatalyst performance is gauged by its ability to effectively capture light, facilitate the movement and separation of charges, and channel them towards the reduction reaction [151]. To achieve an optimal reduction of CO_2 through light-driven processes, a photocatalyst must possess a narrower energy band gap and exceptional light-absorbing characteristics spanning the visible, infrared, and ultraviolet ranges. Moreover, it must exhibit a valence band (VB) level that is situated below the oxidation potential of water, while its conduction band (CB) level should be positioned above the reduction potential of electrons produced when light is absorbed [152].

The process of photocatalytic reduction of carbon dioxide (CO_2RR) relies on the transfer of a single electron, which requires a significant potential of 1.9 volts. This high potential is necessary owing to the intrinsic stability of the CO_2 molecule. The sequence of the reaction is hindered by the structural differences between linear and bending carbon dioxide, which lead to an increased energy state. Nevertheless, it is feasible to reduce the necessary energy threshold for the CO_2 reduction reaction (CO_2RR) by using a multielectron process in conjunction with proton involvement. Based on empirical evidence, it has been shown that photocatalysts have the ability to use ultraviolet (UV) light in order to promote the reduction of carbon dioxide via the involvement of multiple electrons and protons. This process leads to the production of hydrocarbon molecules, namely, C1 (methane), C2 (ethane), and C3 (propane) [153]. Equations (1)–(5) presented in this study provide a detailed representation of the electron and proton reduction and oxidation processes that are crucial for the production of the principal products described earlier.

$$CO_2 + 2H^+ + 2e^- + 2H_2O \rightarrow HCOOH + CO + H_2O \text{ (Formic acid)}$$
(1)

$$CO_2 + 4H^+ + 4e^- + 2H_2O \rightarrow HCHO + H_2O$$
 (Formaldehyde) (2)

$$CO_2 + 6H^+ + 6e^- + 3H_2O \rightarrow CH_3OH + H_2O \qquad (Methanol) \qquad (3)$$

$$CO_2 + 8H^+ + 8e^- + 4H_2O \rightarrow CH_4 + 2H_2O$$
 (Methane) (4)

$$CO_2 + 12H^+ + 12e^- + 6H_2O \rightarrow C_2H_5OH + 3H_2O$$
 (Ethanol) (5)

CO₂ conversion into a wide range of compounds may be heavily influenced by factors such as electron flow and the availability and choice of photocatalyst.

For example, graphene has demonstrated its potential as an effective photocatalyst for converting carbon dioxide into useful chemicals. This is achieved by combining graphene with a single atom to create a composite material. The photocatalytic carbon dioxide (CO₂) reduction method utilizing a graphene-based single-atom photocatalyst involves multiple sequential phases. In the initial stage, electrons in a photocatalyst consisting of a single atom and made of graphene are energized by photons. These electrons then undergo a transfer process from the valence band (VB) to the conduction band (CB) [135]. This transfer results in the creation of holes in the VB, which occurs as a consequence of the interaction with visible light, as represented by Equation (8). During the second step, the photoexcited electrons are effectively confined by a single atom, hence minimizing the charge carrier recombination (Equation (6)).

In the subsequent stage, the photogenerated electrons in the conduction band proceed to react with CO_2 , resulting in the production of benign byproducts such as hydrogen, carbon monoxide, and other fuel products (as shown in Equation (7)). Simultaneously, water undergoes oxidation by interacting with the holes present in the valence band, leading to the generation of oxygen (Equations (8) and (9)).

graphene/single atom photcatalyst +
$$hv \rightarrow h^+ + e^-$$
 (6)

 $e^- + single atom \rightarrow single atom (e^-) (electrom trapping)$ (7)

$$CO_2 + single atom (e^-) \rightarrow CH_4 + CO + COOH + CH_3OH$$
 (8)

$$H_2O + h^+ \to O_2 \tag{9}$$

For instance, Gao et al. [140] reported the discovery of a significant catalytic system for the transformation of carbon dioxide (CO_2) using single-atom cobalt (Co) sites that are attached to partly oxidized graphene nanosheets. The catalyst is formed by the immobilization of individual cobalt (Co) atoms onto the surfaces of partly oxidized graphene nanosheets. This technique, referred to as Co1-G, is achieved using a thermal treatment method, as seen in Figure 18a. Oxygen-containing moieties (functional groups) at the surface of graphene oxide act as anchoring sites for metal ion attachments; they also help to avoid agglomeration to large particles. A visual representation of the process is illustrated in Figure 18b,c, wherever the graphene material facilitates the establishment of linkages between light-absorbing components and single-atom catalytic sites. This facilitates the efficient transfer of electrons that have been stimulated by photons.



Figure 18. (a) Synthesis of Co1-G. (b,c) Charge transfer mechanism of Co1-G and CO₂ photoreduction into CO. Reprint from reference [140].

The research results presented in this study exhibit a noteworthy level of catalytic efficiency, as shown by a turnover number of 678 and a considerably increased turnover frequency of 3.77 min^{-1} , specifically in relation to the production of carbon monoxide (CO). The values given above surpass the capacity of photocatalysts currently used in heterogeneous systems. The research offers novel perspectives on the strategic configuration of catalytic sites within the realm of photocatalytic carbon dioxide (CO₂) conversion, with a particular focus on the impact of charge kinetics in connecting traditional heterogeneous and homogeneous photocatalytic systems. However it was concluded that graphene-based single-atom photocatalysts efficiently capture light-generated electrons, enabling CO₂ reduction and potential sustainable energy applications.

5.5.2. Photocatalytic Hydrogen Production

Graphene-based single-atom photocatalysts have emerged as promising materials for efficient hydrogen (H_2) production through photocatalytic water splitting. These innovative catalysts consist of single metal atoms, such as platinum (Pt), dispersed on a graphene

matrix [154,155]. Graphene possesses distinctive attributes such as its exceptional electrical conductivity, expansive surface area, and remarkable strength. When these properties are paired with the catalytic capabilities of individual metal atoms, graphene becomes an optimal medium for the creation of H_2 .

Mechanism of Photocatalytic Hydrogen Production

Photocatalytic hydrogen (H_2) production has been recognized as a highly advantageous method in the realm of renewable energy research. This approach holds great potential for addressing global energy challenges and alleviating environmental concerns [156]. The photocatalytic process of hydrogen (H_2) evolution occurs in a series of three consecutive steps.

Excitation of the electrons in the valence band (VB) occurs during the initial phase of the process, which happens whenever a photocatalytic absorbs photons with energy levels that are higher than the material's band gap. The electrons then proceed to the conduction band (CB). Hole formation occurs simultaneously inside the valence band as a consequence of the process of absorption. To proceed to the subsequent step, Equation (10), it is necessary to isolate the electron–hole pairs generated inside the semiconductor material. After that, the individual charge carriers move in the direction of the surface of the semiconductor material they made contact with [157].

During the last stage, the electrons in the conduction band (CB) of the material actively participate in the reduction of adsorbed hydrogen ions (H⁺) to produce molecular hydrogen (H₂) (Equation (11)). Simultaneously, the presence of holes in the valence band (VB) assumes a crucial function in facilitating the process of water molecule oxidation, resulting in the production of molecular oxygen (O₂) (Equation (12)) [158].

Photocatalyst + hv
$$\rightarrow$$
 h⁺_{VB} + e⁻_{CB} (10)

$$\mathrm{H}^{+} + \mathrm{e}_{\mathrm{CB}}^{-} \to \mathrm{H}_{2} \tag{11}$$

$$H_2O + h_{VB}^+ \to O_2 \tag{12}$$

In order to ensure the successful execution of the hydrogen evolution reaction (HER) using a normal hydrogen electrode (NHE), it is critical that the conduction band (CB) energy level remains below 0 V (E (H⁺/H₂)). Furthermore, for the purpose of promoting the reduction reaction of H₂O, it is essential that the energy level of the valence band (VB) surpasses 1.23 V (E (O₂/H₂O)).

The production of hydrogen (H₂) using photocatalysts containing non-noble metals encounters notable challenges, primarily arising from their poor reactivity to visible light, quick recombination of charge carriers generated by light, slow surface reactions, and significant thermodynamic energy barriers. Several approaches have been used to overcome these obstacles, such as modifying the energy band arrangement, producing heterojunctions, and increasing the catalytic activity. An effective strategy to tackle these challenges involves the immobilization of single-atom co-catalysts onto graphene. In the last several decades, there has been a significant use of noble metals, including ruthenium (Ru) [159], palladium (Pd) [160], rhodium (Rh) [161], silver (Ag) [162], and platinum (Pt) [163], as very effective co-catalysts in promoting the generation of hydrogen (H₂).

For example, it has been shown that graphene may serve as a highly effective photocatalyst for the conversion of carbon dioxide into valuable compounds after its integration with a single atom to form a composite material. The photocatalytic H_2 production mechanism by a graphene-based single-atom photocatalyst includes many stages. In the first stage, photoexcited electrons in the graphene-based single-atom photocatalyst transfer from the VB to the CB, leaving holes in the VB, after interaction with visible light (Equation (13)). In the second stage, the single atom tightly traps the photoexcited electrons, reducing the possibility of charge carrier recombination (Equation (14)) [158]. In the next step, these photoexcited conduction-band electrons then react with H⁺ ions and generate hydrogen fuel, (Equation (15)), and water is oxidized by reacting with holes present in the VB to generate oxygen (Equation (16)) (Figure 18).

graphene based single atom
$$+ hv \rightarrow h^+ + e^-$$
 (13)

$$e^{-} + single atom \rightarrow single atom (e^{-}) (electrom trapping)$$
 (14)

$$H^+ + \text{single atom } (e^-) \rightarrow H_2$$
 (15)

$$H_2O + h^+ \to O_2 \tag{16}$$

Graphene's ability to integrate with individual atoms produces active spots that boost light absorption and power water splitting. The nature of single-atom photocatalysts ensures maximum utilization of the metal atom, enhancing catalytic efficiency [105]. Additionally, the graphene matrix acts as an electron mediator, facilitating charge separation and promoting a reduction in protons to generate H_2 . The use of graphene-based single-atom photocatalysts for H_2 production offers several advantages, including high efficiency, improved stability, and reduced cost compared to conventional catalysts [164]. This advancement holds significant potential for renewable energy technologies, as it provides a sustainable and efficient method for producing H_2 , which can be utilized as a clean fuel or stored for future energy use.

For instance, Yang et al. [165] used a freeze-drying process to synthesi single atoms of Fe and Co that were scattered over nitrogen-doped graphene. The catalysts exhibited notable efficacy in the photocatalytic hydrogen evolution procedure when used with mesoporous graphitic carbon nitride (mpg- C_3N_4). The increased level of activity may be ascribed to two main factors: the thin structure of mpg- C_3N_4 enables enhanced absorption and active site availability, hence minimizing the recombination of charge carriers. Additionally, nitrogen-based modification in the graphene surface derived from NG provides a plentiful number of coordination sites, therefore guaranteeing a consistent binding of iron (Fe) and cobalt (Co) atoms. The performance of the (Fex, Coy)-NG catalysts for hydrogen production was assessed by the researchers, with the Fe and Co atom ratios being varied. The hydrogen generation rate (1958 μ mol g⁻¹) was much greater for the optimum combination (5 wt% (Fe_{0.2}, Co_{0.8})-NG/mpg-C₃N₄) than for the metal equivalents (5 wt% Fe and Co-NG/mpg-C₃N₄). The enhanced photoactivity seen may be ascribed to the synergistic effect between iron (Fe) and cobalt (Co).

Likewise, Zhao et al. [105] synthesized N-doped graphene-based single nickel atoms (Ni-NG), a durable and efficient co-catalyst for photoelectrochemical hydrogen evolution (PHE). The Ni-NG/CdS composite photocatalyst exhibited a 3.4-fold increase in PHE activity compared to NG/CdS, although containing just 0.0013 wt% nickel. The Ni-NG/CdS composite has been well recognized as a very efficient co-catalyst, despite not being composed of noble metals. It has been shown that Ni-NG and CdS composites have a remarkable ability to prevent electron–hole pair recombination and boost proton reduction. During the hydrogen evolution process, the Ni-NG/CdS composite has a lower activation energy barrier, which contributes to its improved performance. To achieve effective hydrogen synthesis using solar energy, the research suggests developing long-lasting and highly efficient co-catalysts without the usage of noble metals.

Yi et al. [87] presented a new photocatalyst comprising TiO_2 nanobelts and N-doped graphene around a single cobalt atom (Co-NG). The work presents evidence of the effective co-catalytic function of Co-NG in the photocatalytic hydrogen (H₂) generation process including TiO_2 . The enhanced photocatalytic efficacy may be ascribed to the collaborative interplay between the distinct cobalt atom and the nitrogen-doped graphene. The cobalt atom is essential in facilitating the reduction in H⁺ ions, while the nitrogen-doped graphene effectively behaves as an electron acceptor. Furthermore, the use of the Co-NG co-catalyst demonstrates efficient suppression of charge carrier recombination, leading to enhanced

longevity of these charge pairs, as seen in Figure 19a,b. The Co-NG system has shown a remarkable rate of hydrogen evolution at an ideal loading of 3.5 weight percent (wt%) and estimated as 677.44 μ mol h⁻¹g⁻¹ while exposed to simulated sunlight conditions (AM 1.5 G), as represented in Figure 19c,d.



Figure 19. (**a**,**b**) Represent the charge transfer mechanism of Co-NG co-catalyst. (**c**,**d**) represent the weight percent (wt%) of hydrogen evolution from Co-NG. Reprint from reference [87].

In another study, Cao et al. [124] exhibited that altering graphene oxide with sodium (GO_{Na}) improves the production of ruthenium (Ru) single-atomic catalysts. The strong metal–support contact allowed d-conjugation of Ru single atoms (Ru SA) to GO_{Na} , reducing Ru SA electron density. The reduced electron density weakened H⁺ intermediate adsorption and accelerated H₂ desorption. Hence, the Ru SA/GONa catalyst exhibited remarkable effectiveness, with a hydrogen production rate of 24.2755 mmol g⁻¹ h⁻¹. The use of Eosin Y light harvesting in the photocatalytic hydrogen production process resulted in an impressive apparent quantum efficiency of 65.2% at a specific wavelength of 520 nm, hence demonstrating a notable level of effectiveness. Furthermore, this approach reached a remarkable level of efficiency, setting a new record in this field. The achievement has been rendered feasible by the use of Ru SA/GO_{Na}.

Raja et al. [166] effectively synthesized a robust photocatalyst with the specific objective of facilitating hydrogen (H₂) production and the breakdown of ofloxacin (OFL). The catalyst used in this study utilized a support material consisting of a blend of TiO₂ and rGO. To improve its efficiency, single copper/tungsten atom oxide (SCu/WAO) sites were

included as co-catalysts. The catalyst exhibited significant performance, as shown by a large hydrogen generation rate of 14.32 mmolg⁻¹h⁻¹. Remarkably, it outperformed noble metal catalysts and showed long-lasting efficiency under solar radiation. This photocatalyst holds promise for renewable H₂ production, offering a potential alternative to current noble metal catalysts.

Yang et al. [155] achieved the effective synthesis of photocatalytic materials by the combination of GQDs and single platinum atoms (Pt_{SAs}) with cadmium sulfide (CdS) nanosheets. The use of platinum-based solid acids (Pt_{SAs}) in conjunction with graphene quantum dots (GQDs) resulted in a notable enhancement in the efficacy of photocatalytic processes. The aforementioned results were supported by the achievement of a significant hydrogen generation rate of 13,488 µmol $h^{-1}g^{-1}$ and a maximum apparent quantum proficiency of 35.5%. The usage of GQDs expanded the photoresponsiveness of cadmium sulfide (CdS) to include the whole visible light spectrum, hence facilitating enhanced dissociation of electron–hole pairs. Simultaneously, platinum–silica composite catalysts (Pt_{SAs}) served as efficient locations for promoting proton reduction in the photocatalytic process.

Dao et al. [167] proposed a novel Z-scheme ternary heterojunction to increase the efficiency of photocatalytic hydrogen evolution (PHE). This catalyst comprised 2D α -Fe₂O₃, nitrogen-doped graphene (NGr), and single-atom platinum (Pt_{SAs}) co-catalyst components. The 2D α -Fe₂O₃/NGr₃-Pt_{SAs} photocatalyst exhibited exceptional performance by obtaining a high PHE rate of 6.4 µmolmgcat⁻¹h⁻¹ visible light irradiation. It is possible that the greater efficiency is related to the direct development of a core–shell structure in two dimensions. This structure offers a bigger surface area, which helps to absorb more light. This, in turn, promotes efficient separation and transfer of charges. The effectiveness of the catalyst is further augmented by the existence of active platinum-supported acid sites.

Liu et al. [102] presented a study focusing on the use of graphene-based Ni single atoms (Ni SA-NG) for hydrogen (H₂) production within the context of a SrTiO₃(Al)/CoOx photocatalyst, with the goal of replacing precious metals. The observed photocatalyst shows exceptional effectiveness in the process of photocatalytic water splitting. According to the findings of the experiment, the rate of hydrogen (H₂) generation was about 498 mmol g⁻¹ h⁻¹, whereas the rate of oxygen (O₂) production was approximately 230 mmol g⁻¹ h⁻¹. The implementation of the photocatalyst had a significant influence on the efficacy of charge production and separation in the context of photocatalysis, principally ascribed to the establishment of Ti-O-C bonds. These bonds served as effective pathways for the transfer of electrons. Furthermore, Ni SA-NG introduced highly active sites that greatly accelerated the rate of H₂ production on the photocatalytic surface.

Table 3 provides an overview of the use of graphene-based single-atom photocatalysts to provide precise control over electron-trapping states, with the objective of enhancing photocatalytic hydrogen (H₂) generation.

Catalyst	Substrate	Single Atom	Synthesis Method	Reaction Conditions for Synthesis	Light Source	Application	Conditions for Photocatalytic Reaction	Stability	Product Yield Rate	Reference
Co1–G	Graphene sheets	Со	Sonication	Temperature 550 °C 3 h Ar protection	300 W xenon lamp	CO ₂ reduction	solvent (30 mL acetoni- trile/triethanolamine/ H ₂ O)	88% efficiency after 5 reaction cycles	678 μ mol h ⁻¹ g ⁻¹	[140]
(Fe _{0.2} , Co _{0.8})- NG/mpg-C ₃ N ₄	N-doped graphene	Fe, Co	Impregnation technique	Sonication, room temperature	Visible light	H ₂ generation	Catalyst + solvent (TEOA)	Stable up to 5 cycles	1958 μ mol g ⁻¹	[165]
Ni-NG/CdS	N-doped graphene	Ni	In situ	NH3 treatment at 750 °C	300 W xenon lamp	H_2 generation	Photocatalyst + 10 mL 1.0 M aqueous (NH ₄)2SO ₃	Stable after 3 photocatalytic reaction cycles	1351.1 μ mol h ⁻¹	[105]
Co-NG/TiO ₂	N-doped graphene	Со	Freeze-drying	Stirring for 5 h room temperature	300 W xenon lamp	H ₂ generation	25 mg photocatalyst + 70 mL H ₂ O + 50 mL of ethanol	-	677.44 μ mol h ⁻¹ g ⁻¹	[87]
Ru SA/GO _{Na}	Na graphene oxide	Ru	In situ	Room temperature	300 W xenon lamp	H_2 generation	5.0 mg catalyst + solvent (0.5 mL water, 0.5 mL ethanol)	-	$24.2755 \text{ mmol g}^{-1} \text{ h}^{-1}$	[124]
TiO ₂ -SCu/WAO- rGO	Reduced graphene oxide	Cu	In situ	Temperature 180 °C 12 h	300 W xenon lamp	H ₂ generation	Photocatalyst + water	65% efficiency after 5 cycles	$14.32 \text{ mmol g}^{-1} \text{ h}^{-1}$	[166]
CdS/GQDs/Pt _{SAs}	Graphene quantum dots	Pt	In situ	Room temperature	300 W xenon lamp	H_2 generation	50 mg catalyst + solvent (water + ethanol)	Stable after 5 reaction cycles	13,488 μ mol h ⁻¹ g ⁻¹	[155]
Ni SA- NG/SrTiO ₃ (Al)/CoO _x	N-doped graphene	Ni	Ultrasonication	190 °C for 24 h + annealing at 900 °C for 2 h in Ar atmosphere	200 W xenon lamp	H ₂ generation	50 mg photocatalyst + 100 mL H ₂ O	Stable after 4 photocatalytic reaction cycles	498 mmol $g^{-1} h^{-1}$	[102]
$\begin{array}{l} \alpha \text{-} Fe_2O_3\\ @NGr_3Pt_{SAs} \end{array}$	N-doped graphene	Pt	Ultrasonication	Temperature 180 °C 24 h	Visible light	H_2 generation	Photocatalyst + solvent (water + ethanol)	Stable after 5 photocatalytic reaction cycles	$6.4 \ \mu molmg^{-1} \ h^{-1}$	[167]
Co-NG/CdS	N-doped graphene	Со	Stirring	Room temperature	300 W xenon lamp	H ₂ generation	Photocatalyst + 100 mL 1.0 M aqueous (NH ₄) $2SO_3$ solution	Stable after 3 photocatalytic reaction cycles	1382 μmol h ⁻¹	[168]

Table 3. Graphene-based single-atom photocatalyst for photocatalytic CO₂ reduction and H₂ production application.

6. Conclusions and Future Perspectives

The purpose of this study is to conduct an in-depth analysis of the progress made in using graphene-based materials as the principal substrate for developing durable singleatom-based photocatalysts. Graphene, due to its exceptional characteristics and adjustable surface chemistry, presents itself as an optimal substrate for facilitating the presence of individual metal atoms, thereby yielding photocatalysts that exhibit excellent activity and selectivity. This review offers a brief summary of the latest progress and future possibilities in the area of photocatalytic carbon dioxide (CO_2) reduction and hydrogen (H_2) production. It notably emphasizes the use of graphene-based single-atom photocatalysis. Within the realm of photocatalytic CO_2 reduction and H_2 generation, the current study presents a detailed examination of the techniques of manufacturing, characterization, and application of single-atom photocatalysts based on graphene. In addition, this research offers detailed knowledge of the effectiveness of using first-principles density functional theory, together with theoretical and computational modeling techniques, for the analysis of single-atom photocatalysts derived from graphene. Utilizing a material based on graphene demonstrates the capacity to enhance light absorption and facilitate electron mobility. Furthermore, it acts as a reliable material for anchoring individual metal atoms, which impeding their clustering and eventually improving the stability of the catalyst. To optimize the use of single-atom photocatalysts, this section examines the existing limitations and prospective outlook of these catalysts, hence offering insights into future research activities (as shown in Figure 20):

- Single-atom photocatalysts often make use of very rare and distinctive metals. A more efficient and effective solution to this problem would include enhancing the performance of metal atoms so that they are more useful in photocatalytic applications. The full exploitation of the benefits afforded by metal single atoms has the potential to transform their unique function in photocatalytic systems of the next generation. Once cost-effective production of single-atom photocatalysts is realized, they may play a vital role in renewable energy production and other applications.
- Although there has been a substantial amount of study conducted lately on creating single-atom photocatalysts, the challenge of producing photocatalysts with a high metal concentration (>10 wt%) remains a serious issue. Enhancing the metal input content to an appropriate extent has the potential to further improve the photocatalytic proficiency. However, current single-atom-based photocatalysts are unstable because of high reactivity of single metal atoms that result in rapid reactions with ambient reactants to form undesirable species. Therefore, it is essential to conduct research and advance innovative approaches for the controlled production of SACs with elevated metal concentration and long-lasting properties.
- The use of computation-guided methodologies in theoretical investigations is a crucial technique in the systematic examination of electron configurations, adsorption of species, and other characteristics shown by single-atom photocatalysts. Moreover, this study provides useful information for developing single-atom photocatalysts. This includes the discovery of optimal loading sites and the determination of the appropriate metal composition on the semiconductor material. The thorough knowledge of the operation of photocatalysts has been a persistent challenge in the field of theoretical modeling. Material simulations may provide crucial insights into single-atom photocatalysts, potentially improving research in the area of photocatalysis.
- Research on SACs for photocatalysis is still limited, especially when compared to the more thorough examinations conducted on SACs for electrocatalysis. Research into SACs for photocatalytic water splitting has so far concentrated on the hydrogen evolution half-reaction but has paid less attention to the oxygen generation half-reaction. The much greater energy barrier associated with oxygen synthesis primarily impedes the achievement of photocatalytic water splitting for hydrogen evolution and oxygen synthesis. The advancement of single-atom catalysts (SACs) with appropriate characteristics for generating oxygen throughout the process of water splitting has the

potential to have a revolutionary impact on the area of photocatalytic water splitting. This implies that utilizing single-atom photocatalysts has significant potential.

- Moreover, the focus of study has mostly revolved around a restricted range of semiconductors, namely, TiO₂ and g-C₃N₄, as substrates. Consequently, it is imperative to investigate other semiconductor systems.
- Nitrogen-doped graphene (NG) is often used in single-atom photocatalysts, where the
 nitrogen atoms present in NG are commonly classified into three categories: graphitic,
 pyrrolic, and pyridinic nitrogen. The identification of these three different types of
 nitrogen species is heavily reliant on the use of XPS analysis. However, the semiquantitative investigation that relies on XPS is susceptible to significant mistakes,
 hence posing challenges in obtaining precise results. Hence, it is essential to use more
 effective methodologies for quantifying the quantities of distinct nitrogen atoms in
 N-doped graphene.
- Despite the extensive research into nitrogen-based photocatalysts, few studies have investigated how different kinds of nitrogen atoms affect the catalyst's photocatalytic performance. It is crucial to possess a comprehensive comprehension of the diverse nitrogen atom kinds' contributions to the performance of photocatalysis. This involves examining the potential for regulating or achieving dominance of a certain nitrogen atom type, with the aim of surpassing 80% nitrogen content in NG. Furthermore, the determination of whether the performance contributions of nitrogen atoms of the same type in various application scenarios, such as hydrogen production and CO₂ reduction, are comparable, and the manipulation of the spatial arrangement of nitrogen atoms, including their positions at the edges and within the graphene plane, requires both theoretical investigation and experimental analysis.



Figure 20. Future perspectives of the graphene-based single-atom photocatalyst.

The factors listed above seem superficial in light of the quick progress observed inarea of photocatalysis research. Single-atom photocatalysts, generated from graphene derivatives, provide excellent potential for significantly enhancing the effectiveness of solar energy conversion into chemical energy if they are strategically implemented and exploited. This study aims to give a thorough examination of graphene and N-doped graphene to guide and inform future developments in graphene-based single-atom photocatalysts. This overview also aims to delve into the applications of graphene derivatives outside of photocatalysis, such as electrocatalysis, supercapacitors, and solar cells.

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