Review
Nanoparticle–Hydrogel Based Sensors: Synthesis and Applications

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Abstract: Hydrogels are hydrophilic three-dimensional (3D) porous polymer networks that can easily stabilize various nanoparticles. Loading noble metal nanoparticles into a 3D network of hydrogels can enhance the synergy of the components. It can also be modified to prepare intelligent materials that can recognize external stimuli. The combination of noble metal nanoparticles and hydrogels to produce modified or new composite materials has attracted considerable attention as to the use of these materials in sensors. However, there is limited review literature on nanoparticle–hydrogel-based sensors. This paper presents the detailed strategies of synthesis and design of the composites, and the latest applications of nanoparticle–hydrogel materials in the sensing field. Finally, the current challenges and future development directions of nanoparticle–hydrogel-based sensors are proposed.

Keywords: hydrogels; sensors; nanoparticle; preparation methods; composite materials

1. Introduction

A hydrogel is a 3D network gel structure composed of cross-linked polymers. It looks like a solid material but absorbs and retains water, which makes the hydrogel appear soft and moist. Based on the composition and arrangement of polymers, hydrogels exhibit a wide range of structural, mechanical, and chemical properties. Biological tissues are made of hydrogels composed of protein and polysaccharide networks, which enable the organism’s solidity and maintenance of life activities. Therefore, hydrogels have attracted much attention in biological applications, such as tissue engineering, drug delivery, and wound dressings [1–3]. In addition, hydrogels are highly sensitive to stimuli, such as pH, temperature, light, electric field, and solvents [4–7]. Therefore, hydrogels have a wide range of applications in sensors and electrode materials [8–10]. Since the advent of nanomaterials, hydrogels have shown many unique physical and chemical properties because of their surface effect, small size effect, and quantum effect. Noble metal nanoparticles (NMNPs), such as gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), platinum nanoparticles (PtNPs), and palladium nanoparticles (PdNPs), have been extensively investigated in recent years. They have become the most attractive nanomaterials owing to their unique properties, such as corrosion resistance, oxidation resistance, high surface volume ratio, and easy synthesis and functionalization [11,12]. With the progress of nanoscience, the shape, size, and properties of NMNPs can be fine-tuned by controlled synthesis. Therefore, NMNPs have a wide range of applications in biomedicine, chemical catalysis, and energy materials [13–15].

With the development of the two materials, the innovative combination of hydrogels and NMNPs has been proposed. The porous structure of hydrogels can disperse and load NMNPs and can effectively reduce the aggregation of NMNPs. Additionally, the homogeneous hydrogel system can overcome the limitation of the slow reaction rate of NMNPs [16,17]. Furthermore, NMNPs can bring unique physical and chemical properties to hydrogel composites. For example, the conductivity of metal particles can facilitate
the transmission of electrical signals, and the antibacterial properties of silver are widely used in biomaterials. Hydrogels combined with NMNPs have unique properties beyond each single component and overcome the limitations of hydrogels, such as the lack of mechanical strength and biological activity [18,19]. Research activity about the composites has been executed over the past decade. Composite materials are often used in medical and biological fields, while there is still a lack of review with regard to their use in the field of sensors. Here, recent research on the development of NMNPs and hydrogel composites is summarized. This review focuses on the synthesis method and sensor applications of the composites.

2. Synthesis and Design of the Composite

The NMNP–hydrogel composite consists of a polymer matrix and NMNPs embedded in the matrix. The synthetic routes of the composite can be roughly divided into ex situ and in situ synthetic routes. For ex situ synthetic routes, the synthesis and combination of NMNPs with hydrogel are separately carried out. A simple ex situ synthesis method is to directly mix NMNPs into hydrogels and bind them together via cross-linking agents. For in situ synthetic routes, the NMNP precursor, usually a metal salt solution, is introduced into the hydrogel or mixed with the hydrogel precursor solution. The reduction of the metal nanoparticles (NPs) precursor to NPs could occur in the hydrogel or in the hydrogel precursor solution. Based on these routes, the methods of preparing NP–hydrogel composites include the cross-linking method, the swelling and shrinking method, the in situ reduction method, and the one-step method. Typical examples are listed in Table 1. Some synthetic methods and related research are introduced below.

<table>
<thead>
<tr>
<th>Method</th>
<th>Hydrogel</th>
<th>Nanoparticles</th>
<th>Size of NPs</th>
<th>Ref.</th>
</tr>
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<tr>
<td>Cross-linking method</td>
<td>chitosan-g-PNVCL</td>
<td>Au</td>
<td>20 nm</td>
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<tr>
<td></td>
<td>Carrageenan-gelatin</td>
<td>Ag</td>
<td></td>
<td>[21]</td>
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<tr>
<td></td>
<td>smart GNP</td>
<td>Au</td>
<td>13 nm</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>PAAM</td>
<td>Au</td>
<td>13 nm</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>PAM</td>
<td>Au/Pt</td>
<td>12 nm/3 nm</td>
<td>[24]</td>
</tr>
<tr>
<td>Swelling and shrinking method</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>In situ reduction method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical reduction</td>
<td>agar/CMC</td>
<td>Ag</td>
<td>7 nm</td>
<td>[25]</td>
</tr>
<tr>
<td></td>
<td>CNCs/guar gum</td>
<td>Pd</td>
<td>3 nm</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>LCG</td>
<td>Ag</td>
<td>9.5 nm</td>
<td>[27]</td>
</tr>
<tr>
<td>Self-reduction</td>
<td>PSiNPs</td>
<td>Au</td>
<td>10–20 nm</td>
<td>[28]</td>
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<td></td>
<td>D-gel</td>
<td>Au</td>
<td>8 nm</td>
<td>[29]</td>
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<tr>
<td></td>
<td>CNCC-AHB</td>
<td>Pd</td>
<td>9 nm</td>
<td>[30]</td>
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<td>Physical reduction</td>
<td>microgels</td>
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<td>20 nm</td>
<td>[31]</td>
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<tr>
<td></td>
<td>dextran-graft-polyacrylamide copolymers</td>
<td>Ag</td>
<td></td>
<td>[32]</td>
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<td></td>
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<td>Au</td>
<td>7 nm</td>
<td>[33]</td>
</tr>
<tr>
<td>One-step method</td>
<td>RGOH</td>
<td>Au</td>
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<td>[34]</td>
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<td>10.1 nm/9.6 nm/7.6 nm</td>
<td>[35]</td>
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<tr>
<td></td>
<td>hydrogel</td>
<td>Ag</td>
<td>2.47 nm</td>
<td>[36]</td>
</tr>
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</table>

2.1. Cross-Linking Method

The cross-linking method is an ex situ method that uses a synthetic route. NMNPs and hydrogel are prepared separately in a sequential order. The prepared NMNPs are incorporated into the hydrogel precursor, and a cross-linking agent is added to form composite materials. The NPs and hydrogel precursor solution are crosslinked, which results in the encapsulation of the NPs in the hydrogel. This method is widely used in the synthesis of hydrogel composites. Compared with biological macromolecules, such as proteins and polysaccharides, smaller NPs can form hydrogels more easily, and
natural macromolecules have good biocompatibility and non-toxicity, which also provides a multifunctional platform for tissue engineering. Hydrogels with good biocompatibility are often used in the biomedicine field. Recently, Preethi et al. [37] prepared a galacto-xyglucan semi-interpenetrating hydrogel using acrylamide as the crosslinker. Acrylamide can promote gelation and improve the mechanical properties of the hydrogel. The composites prepared after the further incorporation of AgNPs demonstrated good antibacterial potential and wound healing ability in vitro and in mouse model studies. Another study [38] combined prepared Ag/carrageenan with gelatin hydrogel and glutaraldehyde to obtain a hybrid hydrogel with good antibacterial activity. In other studies [20, 21], AuNPs were coated with chitosan as the matrix, and the obtained polymer materials had good antibacterial activity and could be applied to wound dressings. As shown in Figure 1 [22], in contrast to conventional polymer hydrogels, the researchers used modified AuNPs as large-scale multifunctional crosslinking agents to fabricate a robust and smart nanocomposite hydrogel. The functionalized AuNPs were modified with N,N-bis(acryloyl)cystamine (BACA) and were chemically bound in the network. The modified AuNPs could form a well-defined hyperbranched network and a large number of dynamic thiolate-gold (RS-Au) bonds to provide the hydrogel with self-healing ability. The hydrogel achieved rapid self-healing within 1 min under near-infrared irradiation with an optimal efficiency close to 96%. The photothermal properties of AuNPs enable the polymer to be reversibly turned on/off under external stimuli, which could rebuild the polymer network between damaged fragments and provide the possibility of self-healing. However, the AuNPs modified with N,N-methylene-bis-acrylamide were physically doped in the hydrogel network, and the resulting composites had poor mechanical strength and self-healing properties. NPs with uniform size and shape could be obtained by shape-controlled synthesis with the cross-linking method. The method is easy to perform, because the preparation and combination of NPs and hydrogels are performed separately. However, NPs tend to be unevenly distributed in hydrogels and aggregate or agglomerate; therefore, high NP loadings are difficult to achieve.

Figure 1. Schematic Illustrations of Gold-Thiolate Interaction-Triggered Self-Healing Nanocomposite Hydrogels (a) Schematic structure of gold NPs and a list of co-monomers used for polymerization of hydrogels. (b) Schematic formation of GNP hydrogel with modified gold NPs as large crosslinkers in the in situ free-radical polymerization. (c) Schematic mechanism for dynamic and reversible RS–Au bonding with NIR laser irradiation (808 nm) [22]. Copyright Elsevier, 2017.

2.2. Swelling and Shrinking Method

The swelling and shrinking method is also an ex-situ synthetic route. The prepared NPs are incorporated into the hydrogel based on a “breathing” mechanism, where shrunken hydrogel can swell in an aqueous solution containing NMNPs. Pardo-Yissar et al. [23]
prepared an AuNPs–PAAM hydrogel composite to study solvent-switchable electronic properties. The “breathing” mechanism of introducing NPs into hydrogel consists of three steps and is repeated several times to obtain the desired NP density (Figure 2). The swollen gel was placed in acetone, causing hydrogel collapse and water expulsion (“breathing-out”). Then, the shrunken hydrogel was placed in an aqueous solution of AuNPs to swell the hydrogel, which took in (“breathing-in”) the solution, including the suspended NPs. Finally, the hydrogel was washed well with water to remove weakly surface-adsorbed NPs. By these steps, the AuNPs were incorporated into the hydrogel network. The interfacial electron transport resistance of swelling polymers decreases with the increase in the number of AuNPs. The polymer has a resistance of 40 kΩ when it expands and 0.4 kΩ when it shrinks. This low resistance is attributed to the electrical connection between the AuNPs in the polymer. The shrinking low-resistance material is conducive to interface electron transfer. Therefore, the NPs fixed in the polymer hydrogel allow the external control of interface conductivity by switching them between electrical communication and non-communication states. Using the “breathing” mechanism, AuNPs and PtNPs were also introduced into polyacrylamide (PAM) hydrogel [24]. The PAM hydrogel was prepared within the pore of an anodic aluminum oxide template by electropolymerization. Other studies found that the number of AgNPs loaded into AgNP–hydrogel composites using this method increased as the number of breathing-in–breathing-out cycles increased [39]. This method can synthesize ideal composites through the shrinkage properties of hydrogels, but it has high requirements for solvents. Moreover, it easily causes agglomeration when the NMNP concentration is too high, and NMNPs leak out of the hydrogels when the concentration is too low. Therefore, this method is rarely used in the synthesis of NP–hydrogel composites.

Figure 2. Construction of Au nanoparticles and hydrogel composite by switching between its swollen and shrunken states [23]. Copyright © 2001 John Wiley and Sons.

2.3. In-Situ Reduction Method

In the in-situ reduction method, the precursor salt solution of NPs is reduced instantaneously in the hydrogel after being added into the hydrogel by volume swelling or direct addition. The reduction method plays an important role in in-situ reduction methods. The in-situ method is a two-step synthesis process. First, the NP precursor solution is added to the hydrogel matrix, and then the solution is reduced in situ into the hydrogel polymer matrix to form NPs. This method is easy to implement on less reactive noble metals.

2.3.1. Chemical Reduction

Chemical reducing agents, such as sodium borohydride or sodium citrate, are often used for in-situ synthesis of NPs in a liquid phase system. For example, NaBH₄ can be used for the in-situ reduction of AgNO₃ adsorbed into the active sites of hydrogels [40]. The prepared hydrogels were immersed in silver nitrate and transferred to NaBH₄ solution to promote the reduction of Ag⁺ to AgNPs, which produced AgNPs@hydrogel with antibacterial activity. Moreover, the effect of surfactants on AgNP loading was also studied. Studies have shown that adding surfactant, especially rarasaponin, can effectively improve
the AgNP loading of the hydrogel dressing by adsorption. The immersing method [41] and the stacking method [25] can also be used as in-situ reduction methods with NaBH₄. Wang et al. [26] prepared a thermally responsive hydrogel by loading PdNPs with an average size of about 3 nm on cellulose nanocrystals (CNCs) through a two-step process, in which CNCs were used as the carrier and stabilizer to fix PdNPs. As shown in Figure 3a, after PdCl₂ was mixed with the CNC suspension, NaBH₄ was added drop by drop to reduce Pd²⁺ in the solution, and PdNPs@CNCs were obtained after freeze-drying. NaBH₄ was added to the solution with guar gum and added again to hydrolyze it to form sodium metaborate, which acted as a cross-linking agent for gelation. The hydrogel showed a rapid sol–gel transition process during the heating and cooling cycles; the hydrogel changed to a sol state above 70 °C and could be used for catalytic reaction and turned to a gel state below 20 °C so that PdNPs could be reused (Figure 3b). Zhang et al. [27] used lignin in lignocellulose hydrogel (LCG) as the reductant and capping agent to synthesize Ag-L NPs/LCG, which exhibited good catalytic activity and high antibacterial ability. Lignin can adsorb Ag⁺ and can effectively fix and disperse AgNPs after in-situ reduction. The particle size of AgNPs can be controlled by adjusting the lignin content; the higher the lignin content, the smaller the particle size. Furthermore, kappa-carrageenan [42], curcumin [43], and ethylene glycol [44] can also be used as reducing agents during in-situ restoration.

Figure 3. Schematic of thermo-responsive PdNPs@ CNCs/guar gum hydrogel catalyst system (a): (i). Formation of PdNPs@ CNCs composites (ii). Preparation of PdNPs@ CNCs/guar gum hydrogel. (b) Thermo-responsive guar gum hydrogel: hydrogel transferred to sol state at high temperature (over 70 °C), and returned to gel state when cooled down (below 20 °C). (c) Boron-based crosslinking in the Guar gum hydrogel matrix [26]. Copyright Elsevier, 2019.

2.3.2. Self-Reduction

NMNPs can also be obtained without adding an external reductant. For example, a certain component in hydrogels can be used to reduce metal ions in situ. For example, as a part of the carrier, treated porous silicon nanoparticles (PSiNPs) can be added to HAuCl₄ solution to reduce Au³⁺ and synthesize PSiNPs@Au nanocomposites [28]. CS/PSiNPs hydrogels were constructed by adding PSiNPs into the CS solution, and their potential applications in future clinical local cancer treatment were demonstrated. Polysaccharides can be used as a capping and reducing agent in AuNP synthesis. The hydrophilic sites in
polysaccharides can form complexes with Au (III) and coordinate with reduced Au (0) to stabilize them. A related study [45] reported an in-situ AuNP synthesis into pectin solutions to yield pectin-capped AuNPs/chitosan hydrogel composites. Zhao et al. [29] embedded AuNPs into D-sorbitol hydrogel (D-gel) by the in-situ reduction method and obtained D-gel@AuNPs with good electrocatalytic activity. Due to the ligand metal interaction between gold ions and gel fibers, AuNPs reduced by hydrazide functional groups in D-gels at room temperature are uniformly dispersed in the dendritic fiber branches of the gels. A study on the in-situ synthesis of PdNPs [30] showed that after PdCl$_2$ was adsorbed into the cationic nanocellulose (CNCC) and alginate hydrogel, the carbonyl group in the hydrogel induced Pd$^{2+}$ to Pd$^{0}$, and CNCC acted as the support/stabilizer and reductant.

2.3.3. Physical Reduction

In addition to in-situ reduction with chemical reagents, reduction with physical methods (such as light, heat, and UV light) is also an important synthetic method that can effectively avoid the introduction of extra ions. As shown in Figure 4, Kim et al. [31] synthesized and grew AuNPs by photoreduction and thermal reduction under UV irradiation, and the AuNPs synthesized by this method were highly concentrated and uniformly embedded in the microgel matrix without aggregation. The water-in-oil emulsion droplets were prepared by a microfluidic device, and then the gold precursor and hydrogel precursor were irradiated to form a complex, which was reduced to AuNPs by the ketone radicals generated by the photolysis of the photo initiator. The irradiated droplets changed from pale yellow to violet red, indicating AuNP formation. Heat treatment can further grow or newly form AuNPs, which makes the droplets turn dark red and shifts the absorption peak of the spectrum from 400 nm to 522 nm and then to 565 nm. The obtained microgels can be used for the direct detection of small molecules in mixtures with high sensitivity and reproducibility.

Another survey [32] on AgNP reduction by in-situ UV irradiation showed that the size and number of AgNPs increased with increase in the irradiation time. Some other physical in-situ reduction methods have also been introduced. For the glow discharge method [46], high-energy argon can be used as an electron source to reduce Au ions to AuNPs in water. Another device is also used to immobilize AuNPs in the aqueous phase of the hydrogel monomer and then cross-link AuNPs to obtain a composite hydrogel [33]. For the atmospheric pressure microplasma method [47], AuNPs and AgNPs were successfully synthesized in situ in polyvinyl alcohol (PVA) hydrogels, providing a feasible technology for the preparation of NP–hydrogel composites. Due to the porous structure of hydrogels, these pores can serve as templates for NP synthesis, fixing the corresponding size of the NPs. However, the shape and size distribution of the synthesized NPs is difficult to control. The in-situ method can fundamentally solve the problem of particle precipitation, but the connection between NPs and the hydrogel network is lower, which means the combination of NPs and the hydrogel network is not sufficiently tight.

2.4. One-Step Method

In the one-step method, the precursor of inorganic salt solution is mixed with the hydrogel precursor solution. The method can further simplify the synthesis steps. NPs are formed by reduction, and the hydrogel cross-linking. In some cases, the components of the hydrogel or hydrogel precursor could act as reducing agents for noble metals. He et al. [48] adopted a green and cheap one-step method with tannic acid (TA) as the reducing agent and stabilizer for AgNPs. TA also acted as a cross-linking agent for PVA. The 3D PVA/TA network was obtained by connecting TA with PVA by hydrogen bonds and was further used as a carrier for immobilizing Au@AgNPs. The one-step hydrothermal method is often used to synthesize composite hydrogels because of its simplicity and environmental friendliness. In Soysal group’s work [49], glycine was added to a dispersion of silver nitrate in graphene oxide and was used as a nitrogen source and a reducing agent for graphene oxide and AgNO$_3$. The nanocomposites obtained by hydrothermal
treatment had good catalytic activity for the reduction of 4-nitrophenol and methylene blue. Similarly, the study of loading AuNPs into modified graphene oxide hydrogels according to a one-step hydrothermal method can be used for sensitive NO₂ and NH₃ monitoring [34]. The one-step electrodeposition method can also be used to synthesize composite materials [50], which can further be used as electrochemical sensing materials for sensitive glucose determination, because Pd has good activity for the electrocatalysis of glucose oxidation.

Figure 4. Production of plasmonic microgels. (a,b) Schematics of the microfluidic device and optical microscopy (OM) image showing the formation of monodisperse emulsion droplets at the cross-junction in the device. (b) Series of drawings showing the formation of hydrogel and gold nanoparticles in a water-in-oil droplet by UV irradiation and the growth of the gold nanoparticles by thermal treatment. (c) OM images of emulsion droplets as-prepared (left panel), microgels transferred in water after UV irradiation (middle panel), and microgels transferred in water after UV irradiation and thermal treatment (right panel). (d) Magnified OM images of droplets and microgels in panel (c). (e) Absorbance spectra of the droplets as-prepared (black curve), microgels formed by UV irradiation (blue curve), and microgels formed by UV irradiation and thermal treatment (red curve) in the oil phase [31]. Copyright 2020, American Chemical Society.

Some examples of one-step synthesis use physical techniques. As shown in Figure 5 [35], a one-step laser-induced method has been developed to prepare various NMNP–3D graphene nanomaterials. The prepared metal precursor chitosan hydrogel ink was coated on the film, and the composite was obtained after laser induction. The treated NMNPs were evenly distributed on the graphene surface. The electrode prepared by this method can be used as a flexible impedance immunosensor for detecting E. coli, which has great potential. In another study [36], the hydrogel precursor was mixed with AgNO₃
and irradiated under a UV lamp for 10 h to obtain an Ag–hydrogel composite. UV light serves as the reductant for Ag and the crosslinker of hydrogel. The average particle size of ultrafine silver particles obtained by reduction is only $2.47 \pm 0.26$ nm and they are evenly dispersed in the hydrogel network. The one-step method can further simplify the steps of the composite synthesis, so it is fast and cost effective. One-step synthesis by the physical method is economical and efficient, and the introduction of toxic crosslinking and reducing agents can be avoided.

Figure 5. Schematic illustration of the formation process of metal nanoparticle–LIG hybrid nanocomposites using the one-step laser induction method [35]. Copyright Elsevier, 2020.

3. Sensor Applications of the Composite

The NMNP–hydrogel composite could be used as a sensing device based on the plasmonics of NMNPs, the stimulus-responsiveness of the hydrogel, or a combination of these factors. Hydrogels are sensitive to physical, chemical, and biochemical stimuli (Figure 6); therefore, the structure of hydrogels changes when stimuli are applied [51]. These changes can be transformed into detectable optical, electrical, or chemical signals, which can be used to manufacture sensors, biological probes, and other devices. According to the response of hydrogels to different stimuli, the corresponding sensors, such as strain sensor, biosensor, colorimetric sensor, and pH sensor, also have different sensing mechanisms [52–54]. Compared with traditional sensors, the shape and volume of hydrogels are variable, and the hydrogel structure can be changed according to the change of the solvent; thus, hydrogel sensors have attracted extensive attention in recent years [55,56]. As an important part of building composites, NMNPs can improve the performance of sensor composites. For example, the superior ductility of noble metals can be applied to strain sensors. Moreover, noble metals as good conductors can also improve the electrical conductivity of hydrogels to generate detectable electrochemical signals, fabricating electrochemical sensors. Furthermore, different noble metals also provide different properties, such as nano-gold showing different colors at different sizes, while silver has good antibacterial properties and can be applied to various colorimetric sensors and biosensors [57–59]. Different types of NMNPs–hydrogel composite sensors are introduced below.

3.1. Strain Sensor

Strain is the local relative deformation of an object under the action of external force. A device that detects strain through resistance change is called a strain sensor. Hydrogels have unique advantages in the fabrication of strain sensors owing to their variability and biocompatibility. The applications of conductive hydrogels to smart sensors, such as wearable sensors, electronic skin, and artificial organs, have been widely discussed. However, traditional hydrogels have poor durability and poor mechanical properties [60,61]. Therefore, combining NMNPs with hydrogels has become a development direction for conductive hydrogels. For example, gold has stable properties and good ductility, and silver has excellent antibacterial and conductive properties. They are often incorporated into hydrogel matrices and used in strain sensors [62].
Wang et al. [63] composited AgNPs into chemically crosslinked hydrogels for strain sensors. AgNPs were prepared by the solid-state reduction of hydroxyethyl cellulose (HEC). Silver nitrate was reduced by hydroxyl groups after mixing with HEC. The mixture turned from white to pale yellow during the grinding process and turned yellow after a period of time. The hydrogen bonds formed by the hydroxyl groups on the HEC chain and the amide groups on the PAM could be broken and reorganized during the stretching process, which enabled hydrogels with high tensile strain (704.33%) and low tensile stress (0.12 MPa). The tensile strain and tensile stress of the hydrogel after adding AgNPs were higher than those of the original hydrogel, which might have been due to the fact that the AgNPs covered a part of the HEC chains and limited the formation of hydrogen bonds. Based on the antibacterial ability of silver, silver was subjected to an antibacterial test, and the effect was remarkable. Therefore, this research is expected to be applied to electronic devices, such as flexible antibacterial strain sensors. Another study [64], synthesized a multifunctional silver nanocomposite hydrogel through free radical polymerization, which was dynamically connected by hydrogen bonds, and the assembled wearable sensor could monitor and distinguish various human joint movements and tiny physiological signals. The effect of the size of the AgNPs added into the composites was also investigated. A study on the incorporation of AgNPs with different sizes (3–40 nm) into hydrogels showed that the ultimate tensile strength of the composites decreased with increase in the size of the AgNPs [65]. Another research showed that with the increase in the size of the AgNPs, the storage modulus of the composite hydrogels initially increased and then decreased [66].

In recent years, self-healing hydrogels have attracted much attention as materials that can be applied to wearable sensors, such as smart skin, and many studies have incorporated NMNPs into hydrogel matrices to increase their mechanical properties and self-healing
properties. Lin et al. [67] prepared a PB-Ag/TA@CNCs biomimetic hydrogel, based on Ag/TA@CNCs, by dynamic cross-linking. The composite hydrogel was obtained by adding borax after stirring Ag/TA@CNCS and PVA. The AgNPs obtained by the reduction of TA-modified CNCs could enhance the conductivity ($4.61 \text{ Sm}^{-1}$) and stretch ability ($>4000\%$) of the composite and provided excellent antibacterial properties. The dynamic borate ester bonds and hydrogen bonds between Ag/TA@CNCS and PVA helped provide fast (within 10 min), high-efficiency (98.6\%), and repeatable self-healing ability. Moreover, it could also enhance the mechanical properties of the nanocomposite hydrogel. The tensile strength and strain of the hydrogel after TA modification were increased to 246.1 kPa and 4106.4\%, respectively. As shown in Figure 7, the tensile stress of the cut hydrogel recovered to 83.7\% after 10 min of healing, and increasing the content of Ag/TA@CNC could improve the self-healing efficiency, which confirmed the role of dynamic bonds. Based on the composite material, the authors fabricated a flexible self-healing capacitive sensor that can quickly sense a wide range of motion, which is expected to promote the development of flexible, wearable, self-healing electronic devices. Another study on self-healing hydrogel composites [68], prepared a dynamic supramolecular hydrogel based on AgNPs, PVA, and other materials by the freezing/thawing method, and the hydrogel could still recover high electrical conductivity (~100\%) and mechanical properties (88\%) when chopped, and could be applied to electronic skin to monitor human movement in real time. The collagen-based hydrogel prepared by Zhang et al. [69] also showed strong adhesion to the skin and exhibited excellent hemostatic properties in animal experiments. In addition, studies have been conducted on adding AuNPs to composite materials for strain sensors [70–72]. The photothermal effect of AuNPs enables the hydrogel to respond to a variety of stimuli, such as light, heat, motion, and diverse movements, and has a wider range of applications.

Figure 7. (a) Demonstration of the self-healing ability of PB-Ag/TA@CNC4 in an ambient environment. (b) Tensile stress–strain curves of the PB-Ag/TA@CNC hydrogels with different contents of Ag/TA@CNC before and after healing for 10 min. (c) Original stress, healed stress and corresponding self-healing efficiency of the PB-Ag/TA@CNC hydrogels. Reproduced from Ref. [67] with permission from the Royal Society of Chemistry.

### 3.2. Colorimetric Sensor

Colorimetric sensors are widely used in target detection because of their simplicity and portability. The core component is to convert complex stimuli, such as temperature and pH, into visible color changes [73]. The quality factor of colorimetric sensors is closely related to the stimulus response of the sensor material. NMMNs have unique advantages in the field...
of colorimetric sensing. Localized surface plasmon resonance (LSPR) means that when the light is incident on the NMNPs and the incident photon frequency matches the overall vibration frequency of the NMNPs or metal conduction electrons, the NMNP has a strong absorption effect on the photon energy, and the phenomenon of local surface plasmon resonance occurs. At this time, a strong resonance absorption peak appears in the spectrum, resulting in color changes [74,75]. In addition, NMNPs can bring good biocompatibility and catalytic performance [76,77] when combined with the hydrogel matrix, which can be applied to some color reactions.

Embedding 2D AuNP arrays on the surface of hydrogel films can fabricate colorimetric sensors with good reversibility and reproducibility [78]. The gap of AuNP array changes with hydrogel swelling and shrinking, which leads to change in the diffraction peak. The color of the composite changes from iridescence to purple to golden yellow to red, which displays changing water content from less to more. In addition, to the color change caused by physical scale, chemical reactions can also cause color changes. As shown in Figure 8, Ma et al. [79] synthesized AuNPs on g-C$_3$N$_4$ nanosheets in the hydrogel as the binding sites of cancer marker antibodies/antigens. The nanosheets immobilized in the 3D porous microcrystalline cellulose (MCC) hydrogel could reduce the diameter and distribution of AuNPs and made them uniformly dispersed. Moreover, the hydroxyl groups in MCC could reduce AuCl$_4^{-}$ to AuNPs in situ. Incubating the antibody/antigen with the hydrogel would “turn off/on” the catalytic sites in the hydrogel, whereas the remaining catalytic sites could be determined by reducing 4-nitrophenol (yellow) to 4-aminophenol (colorless). Therefore, qualitative and quantitative antibody monitoring could be represented by the color changes during the reaction. This colorimetric immunoassay holds promise for the detection of cancer markers. In the studies of separately detecting total volatile basic nitrogen [80] and mercury content [81], the concentration of the detected substance could be quantified through the color change of the colorimetric sensor, and the color information could be digitized through a smart phone to achieve simple, fast, and portable detection. Among the NMNPs doped into the hydrogel matrix, AgNPs [82] and PdNPs [83] are also mentioned, in addition to the most commonly used AuNPs. As a display method, colorimetric sensing is often used to detect chemical substances, such as glucose and ions in sewage, owing to its easy observation characteristics.

![Figure 8](image-url)
3.3. Electrochemical Sensor

As another quantifiable form, electrical signals are widely used in the field of sensors because of their easy transmission and control. As the derivative equipment, electrochemical sensors have high sensitivity and fast execution speed; therefore, they are often used in the fields of wearable sensors and chemical detection \[84,85\]. NMNPs have excellent electrocatalytic activity and good biocompatibility. Additionally, the large specific surface area of NPs can improve sensor sensitivity. Therefore, NMNPs are widely doped into the hydrogel matrix for electrochemical analysis \[86\].

Cao et al. \[87\] incorporated AuNPs into graphene hydrogel nanocomposites by the hydrothermal method to construct an AuNP–GH composite, which was modified on a glassy carbon electrode (GCE) to detect indole 3-acetic acid (IAA) and salicylic acid (SA). The amperometric responses to IAA and SA at various electrodes by chronoamperometry are shown in Figure 9. Compared with bare, GO, and AuNs electrodes, strong responses were observed on GH and AuNP–GH electrodes, and the strongest response was observed on AuNP–GH, indicating that it had better electrocatalytic activity. The authors also studied the differences in the activity of the hydrothermal samples at different temperatures, and the results showed that the best activity occurred at 140 °C. When IAA and SA were added continuously, they showed a wide linear range with detection limits of 0.21 and 0.22 µM, respectively, which could be applied to the detection of IAA and SA in spiked samples. Another study \[88\], used graphene hydrogel as the matrix, and its surface-enhanced Raman scattering (SERS) properties, after adding AgNPs, were used to amplify the photoelectrochemical performance and accelerate the transfer rate of photogenerated electron–hole pairs, and a photoelectrochemical sensor was established for thrombin determination. AuNP-based hydrogels can also be used to detect dopamine (DA) \[89\]. AuNPs provide electrocatalytic ability, and ciprofloxacin provides antibacterial activity. DA was oxidized to dopamine quinone under the action of hydrogel-modified GCE. Compared with the hydrogel without AuNPs, the oxidation peak potential decreased from 0.42 V to 0.32 V, and the response time was within 1.0 s. The antibacterial electrochemical sensor based on this construction is expected to detect tar in the human body without infection. The study \[90\] on the construction of an electrochemical sensor on a carbon paste electrode for 4-nitroaniline detection discovered that, compared with the bare carbon paste electrode, the as-prepared electrode exhibited a 422 mV reduction in over-potential in the cyclic voltammetry test and better catalytic activity in the chronoamperometry test. Furthermore, it showed good reproducibility and repeatability in the differential pulse voltammetry test. In other studies \[91,92\], NMNP–hydrogel composites were synthesized by electrochemical deposition and electropolymerization and applied to electrochemical sensors. The obtained electrode materials had good electrocatalytic activity and could be used to detect drug flutamide and hydrogen peroxide, respectively.

3.4. Biosensor

Hydrogels are used in biosensors because of their biocompatibility and hydrophilicity. Their porous structure and soft properties can simulate the physiological environment and increase the loading capacity. The sensing process begins with the interaction between the hydrogel and the analyte, which then transmits and gives a detectable signal. \[93\] Recently, new conductive hydrogels with conductive additives, such as NPs, graphene, and conductive polymers, have attracted much attention \[17,94\]. For example, the addition of NMNPs can improve the sensitivity, mechanical strength, and biodegradation resistance of hydrogels, which makes the study of more diverse biosensors possible.

During the formation of polyaniline (PAni) conductive polymer hydrogel \[95\], the protonation of aniline by amino trimethylene phosphonic acid (ATMP) provided the conductivity of the hydrogel while retaining the chelating abilities. The ABEI-Ag@PAni-ATMP hydrogel was constructed after doping with AgNPS. Furthermore, xanthine oxidase (XOD) was immobilized in the hydrogel to construct a xanthine biosensor. The hydrogel could promote rapid electron transfer between the electrode and XOD active sites; the conduc-
tivity detection limit of the sensor was as low as 9.6 nM, and the linear range was wide (0.01–200 µM). Therefore, it has great application potential. Many studies have investigated glucose biosensors as an energy-supplying substance for life. Glucose sensors can be broadly classified into the presence and absence of the enzyme. As a component of the composite, NMNPs are used to improve the immobilization process or electrocatalytic activity [96]. Bagal-Kestwal et al. [97] connected Tamarindus indica seed–shell NPs and glucose oxidase on the surface of AgNPs and constructed a hydrogel polymer with a locust bean gum as the shell. A polymer-modified copper-micromesh grid electrode could be used as a platform for the glucose biosensor. The assembly drawing of the sensor, the cross-sectional view of a single polymer, and the photo of the actual electrode are shown in Figure 10. The probe had good repeatability, high specificity, and sensitivity for glucose detection, and the detection limit was 1.0 nM, which could be applied to the detection of ultralow glucose in the saliva and could be used to detect blood glucose after further modification. Non-enzymatic glucose nano-sensors can also detect the concentration by the degree of coloration to solve the problem of unstable enzyme reaction [98,99]. Based on the LSPR effect of AuNPs, glucose concentration could also be reflected according to the changes of wavelength and color [100,101]. The in situ-prepared AuNPs were doped into the hydrogel matrix [29], and the resulting composite could detect glucose and exhibit good electrocatalytic performance. In addition, the biosensors based on NMNP–hydrogel composite were also used for the detection of digoxin [102], sucrose [103], miRNA [104], and other substances.

Figure 9. Amperometric responses towards IAA (a) and SA (c) on various electrodes in 0.1 M PBS with a pH value of 2.5. The corresponding values of the steady current towards IAA (b) and SA (d) on various electrodes. The concentration of the added IAA and SA was 20 µM. The working potentials for IAA and SA were set at 0.8 V and 1.25 V, respectively. Reproduced from Ref. [87] with permission from the Royal Society of Chemistry.
3.5. Molecular and Ionic Detection

In recent years, analyte-responsive hydrogels have become a new technology and received extensive research attention. Molecular sensors can respond to surrounding target molecules and detect, or even quantify, their concentrations. Hydrogel sensors work through molecular recognition by interacting with analytes through chemical reactions or covalent bonds and then converting the signals into detectable signals, such as optical or volume changes [93]. After amplifying the detection response, the sensors can detect a low concentration of analytes. Many hydrogels have been developed for the detection of analytes, such as gases, biomolecules, and inorganic ions [105–107]. The NPs on the carrier can provide greater specific surface area and sensitivity, whereas metallic nanostructures have been used to amplify the Raman spectra of molecules near the surface, which, in turn, can be used for small-molecule detection. This kind of sensor has portability and rapidity and can be used for pollutant detection and environmental monitoring [108,109].

In a study [34], using composite materials to detect gases, the researchers synthesized a kind of AuNP-modified reduced graphene oxide (RGO) hydrogel with 3D porous structure by a simple one-step hydrothermal method and used the hydrogel for monitoring NO\textsubscript{2} and NH\textsubscript{3}. The addition of AuNPs could improve the responsiveness of NO\textsubscript{2} and NH\textsubscript{3}. Density functional theory calculation showed that the binding energy of NO\textsubscript{2}–Au was higher than that of NO\textsubscript{2}–RGO. Therefore, theoretically, AuNPs have strong binding sites for NO\textsubscript{2} molecules. The gas sensor based on this exhibited high sensitivity and had a low detection limit, as well as having excellent selectivity and reversibility. Microgels with AuNPs as the active sites can also be used to detect small molecules in albumin solution [31]. The high loading of AuNPs enhances the detection sensitivity, and their even distribution provides high signal uniformity and reproducibility. The authors took the detection of pyocyanin as an example and prospect for its wider application. Composite hydrogels are commonly used as colorimetric sensors to detect ions. As a kind of heavy metal ion, mercury ions do great harm to the environment. Sharma et al. [110] coated AgNPs with chitosan and capped the composite with thiol by a simple amide coupling reaction; the obtained hydrogel could overcome the interference of Cu\textsuperscript{2+} and Fe\textsuperscript{3+} and achieved the highly specific detection of Hg\textsuperscript{2+}. The presence of Hg\textsuperscript{2+} caused the NPs in the gel to agglomerate (Figure 11), and the change in morphology might be attributed to the difference in the redox potentials of Hg(II)/Hg couple (0.85 V) and Ag(I)/Ag couple (0.8 V). The disappearance of particle morphology resulted in a decrease in LSPR and a blue-shift.
in the UV–Vis spectrum, and the color of the gel changed from yellow (colloidal AgNPs) to colorless. The composite hydrogel had fast detection speed and a low detection limit (5 ppm) for Hg\(^{2+}\) and could conveniently and accurately determine Hg\(^{2+}\) in drinking water. Another study [111] constructed a capsule sensor, which could be used for colorimetric detection with various LSPR active metal NPs. For example, Hg\(^{2+}\) concentration could be quantified by adding lysine-modified AuNPs to its core, and Pb\(^{2+}\) could be detected by adding citrate-terminated AuNPs.

![Figure 11. SEM images of Mod-Ch-Ag NPs (a) before and (b) after addition of Hg\(^{2+}\) ions [110]. Copyright Elsevier, 2018.](image)

### 3.6. Temperature, pH, and Humidity Sensor

In addition to the above categories of sensors, some other common sensors are briefly introduced below. Most of the thermally responsive hydrogels have temperature-responsive functional groups, which can be used to prepare temperature-sensitive hydrogels by establishing and weakening dynamic hydrogen bonds. Some hydrogels that contain crystal structures can also transmit signals by changing their crystal arrangement according to temperature [112]. The pH-sensitive hydrogel can change its volume according to the pH change of the environment. The polymer contains weak acidic groups or basic groups, which can be more ionized in the higher or lower pH environments and, thus, change the volume and refractive index of the hydrogel. The sensor based on the polymer has a wide measurement range and high sensitivity; therefore, this sensor is widely used [113]. The hydrogel humidity sensor also utilizes the property of swelling after absorbing substances. The change in physical shape changes the optical path or reflectivity, and the signal is amplified and then recorded as the humidity changes [114].

In a study of temperature sensors, the researchers incorporated functionalized AuNPs into poly(N-isopropylacrylamide-co-hydroxyethylmethacrylate)/poly(N-isopropylacrylamide) (P(NIPAM-co-HEMA)/PNIPAM) semi-interpenetrating hydrogel network through a cross-linking agent. PNIPAM acted as the thermal response component in the hydrogel matrix [115]. The hydrogel shrank and the density of AuNPs per unit volume increased with an increase in temperature, resulting in enhanced electrical conductivity. The obtained composite could detect mechanical strain and temperature change and could be applied to strain/thermal dual sensors. The thermal sensor could detect ambient temperature (0–70 °C) while having a fast response and recoverability. Therefore, they designed an intelligent thermal switch to protect electronic components, which could prevent electronic equipment from being damaged by high temperature during operation. Another study [116], showed that the addition of AgNPs exhibited a higher phase volume transition temperature. The SERS effect refers to the phenomenon that the Raman scattering signal of adsorbed molecules is greatly enhanced owing to the enhancement of the electromagnetic field on the sample surface or near surface in the excitation region of some specially prepared metal surfaces or sols. A pH sensor was prepared according to this principle [117]. The pH-sensing material constituting the sensor was a hydrogel composed of multilayer microcapsules, in which AgNPs played a SERS-sensitive role. This material was sensitive
in the pH range of 6.5–9.7, and urea concentration could also be differentiated after the addition of urease.

Furthermore, pH sensors with AuNPs as the response material can also use SERS as the detection mechanism [118]. Jung et al. [119] used the swelling and shrinking properties of chitosan hydrogel to add MNP to construct a colorimetric humidity sensor. As shown in Figure 12, the membrane pores formed by disordered AgNPs were smaller than the mean free path of permeating gas; therefore, the gas could quickly penetrate the hydrogel through the gap of the top metal NP layer, and the hydrogen bonds between chitosan could make it absorb large amounts of water and increase the thickness of the hydrogel, which reduced the refractive index. The change in refractive index caused a change in the reflection spectrum, making the multilevel SiO$_2$ layer on the bottom reflector show different colors. The response time of the designed humidity sensor was reduced to less than 140 ms, which was about 104 times faster than conventional ones. This design concept can also be extended to various optical sensors to detect various gases, such as hydrogen and nitrogen.

Figure 12. Graphical illustration of MNHM etalon and its ingredients. (a) Schematics of MNHM etalon under the humid and dry state of the surrounding. (b) Ligand exchange of AgNPs-OLA transformed to AgNPs-SCN. The aggregated nanoclusters form membrane pores that aid the penetration of gas into the hydrogel layer. Gray circle, Ag NP; dot with zigzag tail, OLA ligand; dot with straight tail, SCN ligand. (c) Swelling/contraction of chitosan hydrogel under the change of humidity condition. Yellow line, chitosan network; blue dot, water molecule; green dashed line, hydrogen bonding between the chitosan network and water molecules [119].
4. Conclusions and Outlook

This review focused on the current status and progress of NMNPs and hydrogel composites from the perspective of synthesis and sensing applications. Little research has been conducted on composite materials before 2010, but in the last decade, especially in the last three years, an increasing number of articles have been published on the development of nanoscience and material characterization techniques. In the context of composite synthesis, including ex-situ and in-situ syntheses, synthesis methods can be divided into the cross-linking method, the swelling and shrinking method, the chemical or physical in-situ reduction method, and the one-step synthesis method, according to the state and reduction mode of NMNPs and hydrogels. The development of analysis and synthesis technology has made it possible to embed NMNPs with more uniform distribution and smaller particle size into hydrogels. Some unique properties of NMNPs, such as electrocatalysis and antibacterial properties, can add new properties to the composites and facilitate their wider use. Moreover, hydrogel-based sensors have made great progress in various application fields. The chemical diversity and biocompatibility of hydrogels enable them to be applied in many fields, such as health detection, substance detection, and temperature sensing. NMNP-doped hydrogel sensors have also become a new research direction. Composite materials combined with hydrogels have excellent applications in the fields of strain sensors, colorimetric sensors, biosensors, and electrochemical sensors owing to the unique LSPR, SERS, and electrocatalytic properties of NMNPs. The addition of NMNPs enhances the mechanical strength and electrical conductivity of the composite materials, making rapid and accurate analysis possible.

However, despite the sensors based on NMNP–hydrogels having great prospects and progress, some challenges still need to be solved. At present, the main bottlenecks, which require future research and development, are as follows: (1) the NPs in the complex matrix are unevenly dispersed and prone to agglomerate; (2) the size and shape of NPs are difficult to control. From the perspective of the future, we should focus on the following: (1) developing some hydrogel materials with simple synthesis steps to reduce the use of toxic and polluting chemicals; (2) manufacturing reusable nanomaterial hydrogels; (3) striving to produce various multifunctional sensors to perform different complex actions; (4) conducting interdisciplinary research to develop the preparation and applications of nanomaterial hydrogels in extensive fields.

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