

Article

Synergistic Effect on Photocatalytic Activity of Co-Doped NiTiO₃/g-C₃N₄ Composites under Visible **Light Irradiation**

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Received: 3 November 2020; Accepted: 14 November 2020; Published: 16 November 2020



Abstract: Co-doped NiTiO₃/g-C₃N₄ composite photocatalysts were prepared by a modified Pechini method to improve their photocatalytic activity toward methylene blue photodegradation under visible light irradiation. The combination of Co-doped NiTiO₃ and g-C₃N₄ and Co-doping into the $NiTiO_3$ lattice synergistically enhanced the photocatalytic performance of the composite photocatalysts. X-ray photoelectron spectroscopy results for the Co-doped NiTiO₃/g-C₃N₄ composite photocatalysts confirmed Ti-N linkages between the Co-doped NiTiO₃ and g-C₃N₄. In addition, characteristic X-ray diffraction peaks for the NiTiO₃ lattice structure clearly indicated substitution of Co into the NiTiO₃ lattice structure. The composite structure and Co-doping of the C-x composite photocatalysts (x wt % Co-doped NiTiO₃/g-C₃N₄) not only decreased the emission intensity of the photoluminescence spectra but also the semicircle radius of the Nyquist plot in electrochemical impedance spectroscopy, giving the highest k_{app} value (7.15 × 10⁻³ min⁻¹) for the C-1 composite photocatalyst.

Keywords: NiTiO₃; g-C₃N₄; composite photocatalyst; recombination; photodegradation; charge separation efficiency

1. Introduction

Graphitic carbon nitride $(g-C_3N_4)$ is a metal-free polymeric semiconductor having high thermal and chemical stability with good electronic and optical properties [1,2]. Its bandgap of ~2.7 eV is appropriate for absorption of visible light. Due to these features, $g-C_3N_4$ has been widely applied as a potential photocatalyst for environmental remediation and artificial photosynthesis [3]. However, g- C_3N_4 also has some drawbacks as a photocatalyst, including fast recombination of photo-induced electron-hole pairs and a low specific surface area [3–5]. To overcome these weaknesses, many researchers have tested a range of solutions.

In recent years, composite materials prepared from $g-C_3N_4$ have been widely used for photocatalysis under visible light irradiation owing to their efficient charge separation of photo-excited electron-hole pairs and a narrow band gap [4,6-14]. Metal oxide photocatalysts, such as TiO₂ and ZnO, have been individually studied and as inorganic components in $g-C_3N_4$ composite photocatalysts [4,6–9]. For example, when ZnO, a UV-responsive photocatalyst, was combined with $g-C_3N_4$ as a composite photocatalyst, photocatalytic activity was improved by enhanced electron-hole separation through the Z-scheme mechanism [8,9]. Inorganic materials used in composite photocatalysts have been extended to double metal oxides, such as $NiTiO_3$, which can be prepared by wet methods and has a



narrow bandgap responsive to visible light irradiation [10–15]. In comparison with the performance of individual photocatalytic components, the composite photocatalyst (NiTiO₃/g-C₃N₄) had a much higher photocatalytic activity toward photodegradation of dye pollutants [12,14], H₂ production [10], and nitrobenzene removal [15]. Further modification of the NiTiO₃/g-C₃N₄ composite photocatalyst was achieved by doping heteroatoms into the NiTiO₃ lattice structure [13]. Molybdenum (Mo) doping was used to modify the structural, electrical, and optical properties of NiTiO₃ [13,16], resulting in a high photocatalytic activity [13]. In a previous study, cobalt (Co) has been used as a heteroatom dopant, substituting Ni sites of the NiTiO₃ lattice, suggesting potential for use as a dopant for NiTiO₃/g-C₃N₄ composite photocatalysts [16].

In this study, we prepared Co-doped NiTiO₃/g-C₃N₄ composite photocatalyst by a modified Pechini method to reveal the effects of Co-doping into the NiTiO₃ lattice and compositing with g-C₃N₄ on photocatalytic activity for methylene blue (MB) photodegradation. The composite photocatalysts were characterized with the use of X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, field-emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), ultra violet (UV)/visible absorption spectroscopy, photoluminescence (PL) spectroscopy, and electrochemical impedance spectroscopy (EIS). The heteroatom, Co, was doped into the NiTiO₃ lattice structure to modify the optical and electrochemical properties of the NiTiO₃/g-C₃N₄ composite photocatalysts had a higher photocatalytic activity than NiTiO₃/g-C₃N₄ composite or Co-doped NiTiO₃/g-C₃N₄ composite photocatalysts, which we attribute to the high charge separation efficiency of Co-doped NiTiO₃/g-C₃N₄ composite photocatalysts.

2. Results and Discussion

2.1. Morphological and Structural Properties

A detailed description of the prepared materials in this study is listed in Table 1. The samples denoted as N-*x*, C, and C-*x* in Table 1 represent pure or Co-doped NiTiO₃, pure g-C₃N₄, and composites of g-C₃N₄ and N-*x*, respectively.

Sample	Description	d (nm) ^a	Eg (eV) ^b	${ m k_{app}} imes 10^3$ (min $^{-1}$) ^c	R ²
N-0	Pure NiTiO ₃	32.39	2.97	0.34	0.989
N-1	Co-doped NiTiO ₃ (Co = 1%)	35.06	2.76	3.17	0.990
N-3	Co-doped NiTiO ₃ (Co = 3%)	36.54	2.91	1.95	0.995
С	Pure $g-C_3N_4$	-	2.65	0.44	0.983
C-0	$g-C_3N_4/N-0$ composite	21.62	2.67	0.79	0.984
C-1	g-C ₃ N ₄ /N-1 composite	27.32	2.53	7.15	0.992
C-3	$g-C_3N_4/N-3$ composite	33.83	2.45	5.66	0.987

Table 1. Physicochemical	properties and p	photodegradation rate constants	of the prepared	photocatalysts.
5			1 1	1 2

^a Average crystallite sizes estimated using the Scherrer equation on the basis of the (1 0 4) diffraction; ^b Band gap calculated from UV–Vis spectra; ^c Apparent rate constant of MB photodegradation reactions.

The phase structure of as-prepared g-C₃N₄ (C), Co-doped NiTiO₃/g-C₃N₄ composites (C-*x*), and Co-doped NiTiO₃ oxides (N-*x*) were characterized by XRD. All composites and oxides had typical diffraction peaks of the NiTiO₃ ilmenite phase with the space group R3 (JCPDS 33-0960), (Figure 1). Peaks at 24.02°, 32.98°, 35.56°, 40.74°, 49.32°, 53.86°, 62.34°, 64.00°, and 71.46°, correspond to (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (0 1 8), (1 2 4), (3 3 0), and (1 0 10) planes, respectively. No diffraction peaks attributed to Co-containing phases were detected, indicating that cations in the lattice were substituted by Co without affecting the crystal structure. However, doping of Co ions induced a 0.1° shift of the characteristic peak positions to higher diffraction angles and the peak width narrowed owing to a change in the NiTiO₃ crystallite size [13,17,18]. The Scherrer equation was employed to estimate the average crystallite sizes (d₍₁₀₄₎) from the (1 0 4) diffraction plane (Table 1). For both the oxide and composites families, the crystallite size increased as the Co content was increased.

This result is consistent with FE-SEM observations of the photocatalysts (Figure S1, see Supplementary Materials). In theory, doping of Co cations is regulated by Pauling's rule, which means that Co can enter the NiTiO₃ lattice by replacing Ni octahedral sites [19]. In addition, the characteristic XRD peaks of $g-C_3N_4$ at 13.1° and 27.2°, which are indexed as the (1 0 0), and (0 0 2) planes, respectively, were difficult to identify in the x-ray diffraction (XRD) patterns of the composite photocatalysts because of their relatively low intensity, suggesting that the compositing led to a high dispersion of C_3N_4 in the composite photocatalysts.



Figure 1. XRD patterns of the prepared photocatalysts.

FT-IR spectra of the prepared materials are shown in Figure 2. Characteristic vibrational peaks attributed to $g-C_3N_4$ were observed in all three C-*x* composites, consistent with previous reports [12]. A sharp peak at 807 cm⁻¹ is assigned to bending vibration of heptazine rings on $g-C_3N_4$ [20]. A series of peaks ranging from 1225 to 1636 cm⁻¹ are assigned to typical stretching modes of aromatic C-N and C=N in tri-s-triazine rings. Furthermore, there is a broad band in the range of 3000–3600 cm⁻¹ assigned to the stretching vibrations of N-H bonds, associated with primary and secondary amino groups, and of O-H groups from adsorbed water [12]. The major phase of NiTiO₃ oxides (N-*x*) was identified in all N-*x* samples based on characteristic vibrational bands corresponding to oxygen-metal bonds at 451 cm⁻¹ (Ti-O-Ni stretch), 551 cm⁻¹ (Ni-O stretch), 655 cm⁻¹ (Ti-O stretch), and 731 cm⁻¹ (O-Ti-O bend) [17]. The Co doping induced no change in the FT-IR spectra, indicating that no CoO_x phases formed in either the oxides or the composites.

2.2. Electrical and Optical Properties

The interfacial electronic states of the prepared catalysts were further investigated by XPS analysis. We examined the C 1s and N 1s core-level spectra for $g-C_3N_4$ and the composites (Figure 3a,b) to identify the electrochemical state of $g-C_3N_4$. For pure $g-C_3N_4$, the N 1s spectra in Figure 3a should be fitted by three peaks [21,22]. The peaks at 397.6 and 398.4 eV derive from sp^2 -hybridized

nitrogen atoms (C=N-C), and tertiary nitrogen (N-C₃), respectively. The peak at 399.7 eV is assigned to amino groups (C-N-H). In the composite, another small peak appeared at 396.5 eV, in addition to above-mentioned peaks, corresponding to Ti-N linkages between NiTiO₃ and g-C₃N₄ [13]. The C-1 composite photocatalyst had a higher amount of nitrogen involved in Ti-N bonding than C-0 and C-3, based on the area ratio of the Ti-N peak and the total N 1s peaks. Thus, the C-1 composite had stronger interactions between the inorganic (NiTiO₃) and organic (C₃N₄) components than the remaining composites. In the C 1s spectra (Figure 3b), peak fitting revealed features at 284.1, 285.5, 287.4, and 288.8 eV, which we assign to external carbon contamination, C-NH₂, C-(N)₃ coordination, and N-C=N in the aromatic rings of g-C₃N₄ in the four samples, respectively [23].



Figure 2. FT-IR spectra of the prepared photocatalysts.

The XPS data for metal components in the oxides and the composites are shown in Figure 3c,d. The XPS data of Ni 2p (Figure 3c) had doublets at 854.9 and 872.5 eV corresponding to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ states, respectively. Broad peaks at ca. 861 and 878 eV represent Ni²⁺ satellites [24,25]. In the Ti 2p XPS data (Figure 3d), peaks of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ at 458.6 and 464.4 eV correspond to the Ti⁴⁺ oxidation state, and those at 457.5 and 463.1 eV are assigned to Ti³⁺ [13]. In addition, the appearance of Ti-N features in the composites reconfirmed the presence of Ti-N bonding and a relatively high Ti-N atomic percentage in the C-1 composite photocatalyst compared with other composite photocatalysts. The formation of the Ti-N linkages between the NiTiO₃ lattice and g-C₃N₄ can decrease the recombination rate of the photo-generated charges in the composite photocatalysts owing to high charge separation efficiency. As a result, the Co-doped NiTiO₃/g-C₃N₄ composite photocatalysts can have a high photocatalytic activity. Notably, at higher Co contents, the binding energies of the Ni $2p_{1/2}$ and Ti 2p peaks slightly shifted, suggesting electronic interactions between the structured oxides and the doped Co component [17].



Figure 3. XPS data of (a) N 1s, (b) C 1s, (c) Ni 2p, and (d) Ti 2p for the prepared photocatalysts.

Optical properties of photocatalysts are important to their performance; hence, the light absorption of the prepared materials was measured by UV-visible diffuse reflectance spectra (Figure 4a). The band gap—an important factor in evaluating the photoactivity of semiconductors [26]—was estimated from the following formula,

$$(\alpha h \upsilon)^n = k(h \upsilon - E_g), \tag{1}$$

where α , k, h ν , and E_g are the absorption coefficient, a constant related to the effective masses associated with the conduction and valence bands, the absorption energy, and band gap, respectively (Table 1 and Figure S2, see Supplementary Materials). Each of the prepared catalysts had a visible light response owing to band gaps within the range of 2.45–2.97 eV. The band gaps of the composites were lower than those of the oxides (Figure S2), suggesting interactions between the individual components. This same phenomenon has been previously reported [13].



Figure 4. (a) UV–Vis absorption spectra, and (b) PL spectra of g-C₃N₄ and C-x composites.

The interfacial charge transfer process has an important role in photocatalytic performance. Therefore, we measured the PL emission spectra to investigate the recombination process of photo-induced charge pairs. Similar to pure $g-C_3N_4$, all the composites had a broad peak ca. 460 nm with a tail extending to 600 nm in Figure 4b. However, the PL emission intensity for the composites was lower than that of pure $g-C_3N_4$, indicating faster photoelectron transfer within the composites, when Co was doped into the lattice structure. The higher PL intensity of C-3 compared with C-1 might be explained by aggregation of Co and weak interfacial effects, which accelerated the recombination rate of electrons and holes.

To further examine the charge transfer separation and photogenerated exciton separation efficiency of the prepared catalysts, we performed EIS (Figure 5). In general, the smaller the semicircle radius in the EIS Nyquist plot, the lower the recombination rate. The semicircular radius (Figure 5) increased in the order, C-x < N-x < C, indicating that charge transfer processes in the composite photocatalysts were promoted by Co doping. The Co dopant in the composite photocatalysts acted as an impurity state, which accepted electrons excited from the conduction band, to decrease the recombination rate. Therefore, on the basis of the above PL and EIS results, we confirm that Co-doping of the composite photocatalysts improved the efficiency of the charge separation process of photo-induced electrons and holes.



Figure 5. EIS Nyquist plot of the prepared photocatalysts.

2.3. Photocatalytic Performance

In this study, the performance of the prepared photocatalysts was evaluated by the MB photocatalytic degradation tests under visible light irradiation, and corresponding results are shown in Figure 6 and Table 1. A pseudo-first-order model was used to better understand the reaction kinetics of the MB degradation [27], where the apparent rate constant, k_{app} , was calculated from the slope of the plot *t vs* ln(*C*/*C*₀) by the equation,

$$\ln(C/C_0) = -k_{\rm app}t \tag{2}$$

where C_0 and C are the concentrations of MB initially and at a given time, respectively. The concentrations were measured by UV-Vis spectra for MB (Figure S3, see Supplementary Materials). The determination coefficients (R² values) for the linear regression were higher than 0.97, indicating that the photodegradation reaction rate constants of all reactions followed an apparent-first-order reaction model [23]. A blank test confirmed that MB was stable under visible light in the absence of the photocatalysts over the same period of time with rate constant $k_{app} = 0.01 \times 10^{-3} \text{ min}^{-1}$. The apparent rate constants of pure g-C₃N₄ (C) and NiTiO₃ (N-0), and their composite (C-0) were relatively low with the values of 0.44×10^{-3} , 0.34×10^{-3} , and $0.79 \times 10^{-3} \text{ min}^{-1}$, respectively, which were similar to results of a previous study [13]. The rates for the Co-doped NiTiO₃ oxide (N-*x*) were higher at $3.17 \times 10^{-3} \text{ min}^{-1}$ for N-1 and $1.95 \times 10^{-3} \text{ min}^{-1}$ for N-3. Furthermore, the Co-doped composites (C-1 and C-3) had outstanding photocatalytic activity with k_{app} values of $7.15 \times 10^{-3} \text{ min}^{-1}$ for the latter. This performance was approximately 3 times as high as that of the oxide catalysts at the same Co-doping content, indicating a synergistic effect between the Co doping and the g-C₃N₄ coupling.



Figure 6. (a) Photocatalytic degradation of MB (initial concentration = 10 ppm) fitted to the apparent-first-order kinetics model. (b) Trend of the photodegradation rate constant as a function of the Co content.

3. Materials and Methods

3.1. Materials

In this study, dicyandiamide (DCDA 99%), titanium *n*-butoxide (Ti(OC₄H₉)₄ \ge 97%), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O 98%), and nickel nitrate hexahydrate (NiNO₃·6H₂O 98%) were obtained from Sigma-Aldrich Korea (Gyounggi, South Korea). Anhydrous ethyl alcohol (C₂H₅OH 99.9%) was supplied from Samchun Pure Chemical Company Ltd. (PyoungTaek, Korea). Citric acid monohydrate (C₆H₈O₇·H₂O 99.5%) was supplied from OCI Company Ltd. (Seoul, Korea). Distilled water was used for all of solution preparation.

Bulk g-C₃N₄ was synthesized from DCDA. A 5-mg portion of DCDA was ground for 10 min, and the obtained fine powder was transferred to a crucible boat before being placed in the middle of a tube furnace. The tube was purged with N₂ gas to remove air and humidity for 1 h, and then heated to 550 °C for 4 h (ramping rate = 10 °C/min) to initiate the thermal polymerization. Next, the yellow solid sample was washed and centrifuged several times with an ethanol/distilled water mixture. The resultant sample was dried at 80 °C for 15 h and finally ground to a fine powder in a mortar. Bulk g-C₃N₄ is denoted as C.

Pure NiTiO₃ and Co-doped NiTiO₃ were prepared by modified Pechini method. A mixture of 0.75 g citric acid and 100 mL ethanol was magnetically stirred for 15 min at room temperature. Cobalt nitrate hexahydrate was added and the mixture continuously stirred to achieve a homogeneous mixture for 30 min. Afterwards, titanium *n*-butoxide and nickel nitrate hexahydrate were dropped into the mixture, which was then stirred for 1 h to obtain a transparent green solution. The amounts of precursors were calculated on the basis of the nickel and titanium molar ratio of 1:1. The obtained solution was then transferred to a Teflon-lined autoclave for further solvothermal treatment at 160 °C for 6 h (ramp rate = 2 °C/min). The resultant solid was collected and washed several times with ethanol by centrifugation, then completely dried at 80 °C in air and calcinated at 600 °C for 5 h (ramp rate = 2 °C/min). Pure NiTiO₃ is denoted as N-0. The Co-doped NiTiO₃ is denoted N-*x*, where *x* is the Co weight percent (wt %) over the total weight of Co-doped NiTiO₃ (*x* = 0, 1, 3).

The composite photocatalysts were synthesized by mixing N-*x* with DCDA in a mortar for 10 min at a weight ratio of 1:1 and then the mixtures were transferred to a crucible boat covered with aluminum foil. The samples were calcinated in the N₂ atmosphere of the tube furnace at 500 °C for 4 h (ramping rate = 10 °C/min). The obtained dark yellow solids were washed and centrifuged, dried at 80 °C for 15 h, and finally ground again into powder. These composite photocatalysts are denoted as C-0, C-1, and C-3.

3.3. Characterization Techniques

The morphologies of all photocatalyst samples were analyzed by field-emission scanning electron microscopy (FE-SEM; JSM-600F JEOL, Tokyo, Japan). XRD, Rigaku D/MAZX 2500 V/PC high-power diffractometer, Rigaku Corp., Tokyo, Japan) with a Cu Ka X-ray source operating at a wavelength of $\lambda = 1.5415$ Å was used to determine the crystalline structures of the obtained samples in the range of 10° – 90° at a scan rate of 2° (20)/min. Functional groups of the prepared photocatalysts were characterized with a Fourier transform infrared (FT-IR, Nicolet 380 spectrometer, thermo Scientific Nicolet iS5 with an iD1 transmission accessory, Waltham, MA, USA). Elemental compositions and electronic states of the elements were examined by XPS, Thermo Scientific K-Alpha system, Waltham, MA, USA). The optical properties of the photocatalysts were analyzed by ultraviolet–visible diffuse reflectance (UV–Vis, Analytik Jena SPECORD 210 Plus 190 spectroscope, Jena, Germany) and photoluminescence measurements (PL, Agilent Cary Eclipse fluorescence spectrophotometer, Santa Clara, CA, USA) at room temperature with a 473-nm diode laser. Electrochemical impedance spectroscopy measurements (EIS, BioLogic Science Instruments VSP, Seyssinet-Pariset, France) were conducted with the use of an electrochemical analyzer in a three-electrode quartz cell with 1 M NaOH electrolyte solution to study the recombination of the photogenerated charged carriers. A 3-W visible light bulb was used as the visible light source. A Ag/AgCl electrode and platinum wire were used as the reference electrode, and counter electrode, respectively.

3.4. Photocatalytic Tests

Photocatalytic activities were studied in the degradation of methylene blue in an aqueous solution (MB, Riedel-de Haen, Germany; initial concentration $C_0 = 10$ ppm). A 50 mL portion of MB solution containing 10 mg of the prepared photocatalyst was magnetically stirred for 30 min at room temperature

in a dark chamber to obtain an equilibrium adsorption state. The solution was irradiated for 180 min by four surrounding visible-light bulbs (model GB22100(B)EX-D, Eltime, 100 W). The concentration of MB was measured with a UV–Vis spectrometer (SPECORD 210 Plus spectroscope, Analytik Jena, Germany) at $\lambda_{max} = 664$ nm. For each analysis point, a 1 mL portion of MB solution was collected by syringe with polytetrafluoroethylene membrane filter 0.2 µm (Whatman GmbH, Dassel, Germany).

4. Conclusions

In this study, Co-doped NiTiO₃ oxides (N–*x*) and Co-doped NiTiO₃/g-C₃N₄ composites (C-*x*) were successfully synthesized by the modified Pechini method. The results of various characterization methods and photocatalytic MB degradation reactions under visible light irradiation indicate that Co doping in composite photocatalysts enhanced the interaction between inorganic (NiTiO₃) and organic (g-C₃N₄) components in the composites through the formation of Ti-N linkages and an impurity state for better charge transfer efficiency. The photocatalytic activity and separation efficiency of the photogenerated electrons in the photocatalysts followed the order of C-*x* > N-*x* > C.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/11/1332/s1, Figure S1: FE-SEM images of N-1, N-3, C-1, and C-3; Figure S2: Calculated band gap of photocatalysts as a function of Co wt %; Figure S3: UV-Vis spectra of MB photodegraded with C-1 photocatalyst as a function of reaction time.

Author Contributions: D.Q.D. performed the experiments and wrote a draft of the paper; T.K.A.N. performed the experiments and contributed to data analysis; T.-T.P. contributed to data collections; E.W.S. supervised the work and polished the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2018R1A2B6004219 and No. 2020R1A4A4079954).

Acknowledgments: In this section you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

Conflicts of Interest: The authors declare no conflict of interest.

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