Ni@NiO Core—Shell Structure-Modified Nitrogen-Doped InTaO₄ for Solar-Driven Highly Efficient CO₂ Reduction to Methanol

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Supporting Information

ABSTRACT: This investigation demonstrates the photocatalytic properties and activities of N-doped InTaO₄ photocatalysts, which were prepared by impregnating Ni and the use of a modified Ni@NiO core—shell nanostructure-cocatalytic method for the reduction of CO₂ to methanol. X-ray absorption spectroscopy (XAS) clearly indicates the oxygen vacancies and mechanism of a series of InTaO₄-based photocatalysts. Nitrogen doping produces visible-light-responsive photocatalytic activity and further enhances absorbance. The cocatalytic method not only dramatically enhances absorbance, but also efficiently avoids electron—hole recombination that would otherwise be caused by electrons and holes separated from the crystal. The photocatalytic activity that was determined by the methanol yield demonstrates that N-doped samples give approximately twice the yield of undoped ones, whereas the cocatalytic method gives about triple the yield. A mechanism is aided in attempts to elucidate the correlation between structures and activities.

INTRODUCTION

Since the amount of CO₂ in the global atmosphere has increased as the human race has advanced technologically, numerous studies have been concentrated on reducing that amount of CO₂. Of many different methods developed so far, the reduction of CO₂ with H₂O under irradiation of aqueous suspension systems involving a variety of semiconductor powders with catalytic activities to generate organic compounds such as methanol was regarded as a potential avenue to facilitate CO₂ conversion into useful energy fuels. Hereafter, there were growing researches in studying photocatalytic reduction of CO₂ by utilizing functional materials such as semiconductor powders, micropores and mesopores in zeolites with titanium oxide, and cocatalysts. Although different catalysts had been synthesized to convert CO₂ under photocatalytic reaction, all of them only could catalyze substances in aqueous suspension conditions by absorbing ultraviolet (UV) light. However, sunlight was composed of a 5% quantity in UV light less than a 45% quantity in visible light, and therefore the design of photocatalysts absorbing visible light was a solution to this urgent demand. InTaO₄ reportedly exhibits outstanding photocatalytic reduction of CO₂ under visible light irradiation. Tantalum oxides have structural regularities such as layered and tunneling structures, in which octahedral TaO₆ units have microporous structures, and it seems to be important to develop new photocatalytic materials. In addition, the bond angle of M—O—M in InTaO₄ might be easy for the movement of photogenerated electron—hole pairs because of an ideal bond angle of 180°, promoting the enhancement of photocatalytic efficiency.

However, little research has been focused on the reduction of the band gap to absorb more visible light for InTaO₄ material. It has been confirmed that the valence bands of oxynitride-based materials are composed of N 2p- and O 2p-orbitals, leading to more negative valence band levels and smaller band gaps compared to conventional oxide semiconductors, enhancing the further visible-induced photocatalytic reaction. Thus, the N-doped method is introduced to cause a decrease in band gap. Moreover, the method of cocatalytic sensitization was performed to prevent electron—hole recombination. NiO was reportedly an efficient cocatalyst for the photocatalytic system. Never-theless, the conduction band of InTaO₄ (E_CB = −0.8 V vs NHE) is lower than that of NiO (E_CB = −0.96 V vs NHE), so the electron transfer from InTaO₄ to NiO would be hindered. To solve this obstruction, the Ni@NiO core—shell structure is modified for this design. The metallic Ni layer in the double-layered structure assists the transfer of photogenerated electrons in the conduction bands for InTaO₄ photocatalyst to the NiO surface, allowing electrons to react with reactants effectively.

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Besides, comprehensive structural characterization of photocatalytic materials is crucial. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are powerful tools for probing nanomaterials, but the characterization of atomic surroundings and chemical bonding by using these two tools is still limited. In contrast, X-ray absorption spectroscopy (XAS) can provide accurate information about chemical surroundings of nanomaterials. X-ray absorption near edge spectroscopy (XANES) can identify the vacant extent of orbitals and can be used to derive effective atomic valence. Extended X-ray absorption fine structure (EXAFS) is a short-range probe of structure and can elucidate the characteristics of chemical bonding, which supports understanding the formation of molecular bonding and the local structure in noncrystalline and crystalline materials. The use of monochromatic radiation makes EXAFS element selective and, therefore, very suitable for examining samples that contain more than one metal element, or substrate lattices, which interfere with diffraction measurements. This study demonstrates the photocatalytic effect by doping nitrogen and sensitizing cocatalysts in InTaO₄ material and elucidates the relationship after relative modification by using XAS.

**EXPERIMENTAL SECTION**

**Chemicals and Materials.** Indium oxide (In₂O₃, 99.999%), tantalum oxide (Ta₂O₅, 99%), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99%), and sodium borohydride (NaBH₄, 98%) were obtained from Cerac, Aldrich, Merck, and Acros Organics, respectively. They were used without further purification. The water used throughout the experiment was of reagent grade, produced by using a Milli-Q SP ultrapure water purification system from Nihon Millipore Ltd., Tokyo, Japan.

**Fabrication Method of Nitrogen-Doped InTaO₄.** The starting materials, In₂O₃ and Ta₂O₅, were mixed in a stoichiometric molar ratio of 1:1 and ground uniformly in a mortar. They were put in an alumina crucible and then sintered in air at 1100 °C for 12 h. Crystalline InTaO₄ was thus synthesized by the above solid-state reaction and ground to a fine powder for further use. In the second step for nitrogen doping, InTaO₄ samples were sintered in an atmosphere of ammonia (NH₃) at 800 °C for 0.2 h under 450 mL·min⁻¹. Eventually, the InTaO₄-N photocatalyst was synthesized after the aforementioned fabricating process.

**Fabrication of Ni@NiO Core—Shell Cocatalysts.** Ni, 3.2 wt %, was loaded on InTaO₄-N by impregnation from an aqueous Ni(NO₃)₂ solution under sonication for 30 min, followed by reduction by 2.55 mM NaBH₄, added dropwise at 500 rpm. The mixed solution became gray and was filtrated with deionized water. Then it was dried at 90 °C for 12 h and sintered in air at 200 °C for 1 h. Finally, the Ni@NiO/InTaO₄-N photocatalyst was obtained after the above treatments.

**Characterization of photocatalyst.** The nitrogen and nickel contents of photocatalysts were determined by both elemental analysis (EA), performed by using a HERAEUS VarioEL-III analyzer, and energy-dispersive X-ray analysis (EDX), performed using a JEOL JSM-6700F field emission scanning electron microscope (FE-SEM) that was equipped with an EDS. The Ni@NiO core—shell structure was examined by using JEM-2010F field emission transmission electron microscope (FE-TEM). The crystallographic structures of a series of photocatalysts were analyzed by X-ray powder diffraction (XRD) by using an XPert PRO diffractometer Cu Kα radiation (λ = 1.5418 Å). UV—visible diffuse reflectance spectroscopy (UV—visible DRS) was performed by using a Varian Cary spectrophotometer 100 in transmission mode, ranging from 200 to 800 nm at wavelength. The surface characterization of the synthesized samples was conducted by X-ray photoelectron spectroscopy (XPS, PHI Quantera) using Al Kα radiation (λ = 8.3406 Å).

**Photocatalytic Reaction Testing.** Photocatalytic reactions were carried out in a continuous flow reactor. The catalyst powder (0.1 g) was added to a reactant solution (50 mL of deionized water) in a window-type irradiation cell that was made of Pyrex glass (200 mL). It was magnetically stirred at a constant rate of 200 rpm, dispersing the powder homogeneously in the solution. To remove the oxygen from the solution, pure carbon dioxide (CO₂) was added continuously to the solution for 10 min. The flow rate of CO₂ was kept at 3 kg·cm⁻² at 25 °C during the experiment. The light source was a Xenon lamp, and the light was filtered through PE30BF filters, allowing only visible light from 390 to 770 nm to pass with a fixed intensity of 100 mW for 2 h. Two milliliters of liquid was extracted from the top of the solution for analysis every 30 min. The methanol yield was determined by using China Chromatography 2000 gas chromatograph that was equipped with a flame ionization detector (FID).

**XAS Data Analysis.** The Ta LIII-edge (9881 eV) XAS spectra and the Ni K-edge (8333 eV) XAS spectra were obtained in transmission mode and fluorescence mode at room temperature, respectively, at the BL01C1 beamline facility of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The backscattering amplitude and phase shift functions for specific atom pairs were calculated ab initio by using the FEFF7 code. The EXAFS data were analyzed by using an analytical package called “REX2000,” coded by Rigaku. The raw X-ray absorption data were first pretreated by using standard procedures, including pre-edge and postedge background subtraction, normalization with respect to edge height, and Fourier transformation. The Fourier transformed k³-weighted EXAFS spectra, k³x(k) ranged from 3 to 13.8 in a k range, to evaluate the contribution of each bonding pair to the Fourier transform (FT) peak. XANES peak ratio was fitted by using the aforementioned software to verify the Ni to NiO ratio of Ni@NiO core—shell cocatalysts.

**RESULTS AND DISCUSSION**

**Structural Analysis via XRD.** Figure 1 presents the XRD pattern of InTaO₄-N-based samples. The pattern of the as-prepared InTaO₄ sample matches the normal Joint Crystal of Powder Diffraction (JCPD, file no. 25-0391). As displayed in the inset of Figure 1, InTaO₄ is composed of Ta₂O₅ and In₂O₃ octahedra, such that the individual [In₂O₃] octahedral chains are linked by Ta₂O₅ octahedra in a three-dimensional network. Samples that had been treated in NH₃ were identical to as-prepared InTaO₄, and XRD revealed no other nitrogen-containing compound, except for TaON (denoted as #) originated from nitridation of unreacted Ta₂O₅ (denoted as *) in as-prepared InTaO₄. In TaON, NH₃ did not evidently change the XRD peak position. The peak (29.355°) intensities of InTaO₄-based samples were decreased after nitrogen doping, evidencing the replacement of oxygen by doping nitrogen. This result is consistent with the HNb₃O₈-N previously synthesized by Li et al. The modification of an Ni@NiO core—shell structure did not yield any Ni or NiO diffraction peaks that matched the JCPD standard files, since the Ni@NiO core—shell cocatalysts may be amorphous, no any peaks can match well, so with NiO and Ni phases, respectively.
InO$_6$ and TaO$_6$ octahedral networks. cocatalysts deposited on InTaO$_4$-N for InTaO$_4$-based samples (Figure 1). The band gaps of the InTaO$_4$-N samples was 2.28 eV, resulting in deeper color for samples under Ni@NiO core modification. The band gaps of the material was effectively reduced when it reacted with NH$_3$ to form oxynitrides. The Ni@NiO/InTaO$_4$-N catalysts exhibit a greater absorbance than the N-doped catalysts. As shown in Figure 2, the as-prepared InTaO$_4$ sample was yellowish, while the InTaO$_4$-N samples were brownish and the Ni@NiO/InTaO$_4$-N samples were gray. The strong absorption in visible region results in deeper color for samples under Ni@NiO core—shell modification. The band gaps of the InTaO$_4$-N samples was 2.28 eV, calculated from the UV—visible spectra (Figure 2). The extension of the absorption of light from the UV to the visible range is associated with both the doped nitrogen atoms and the oxygen vacancies in the lattice, because the nitrogen atoms produced the local states close to the valence band edge and the oxygen vacancies gave rise to the local states to the conduction edge.  

Optical Analysis via DRS. The optical properties of the InTaO$_4$-based samples were investigated by UV—visible DRS (as shown in Figure 2). The absorption edges of the InTaO$_4$-N catalysts shifted to remarkably longer wavelengths than that of the as-prepared InTaO$_4$ catalyst, leading to obvious response in these N-doped samples. Since the potential energy of N 2p-orbital is higher than that of the O 2p, the band gap of the material was effectively reduced when it reacted with NH$_3$ to form oxynitrides. The Ni@NiO/InTaO$_4$-N catalysts exhibit a greater absorbance than the N-doped catalysts. As shown in the inset in Figure 2, the as-prepared InTaO$_4$ sample was yellowish, while the InTaO$_4$-N samples were brownish and the Ni@NiO/InTaO$_4$-N samples were gray. The strong absorption in visible region results in deeper color for samples under Ni@NiO core—shell modification. The band gaps of the InTaO$_4$-N samples was 2.28 eV, calculated from the UV—visible spectra (Figure 2). The extension of the absorption of light from the UV to the visible range is associated with both the doped nitrogen atoms and the oxygen vacancies in the lattice, because the nitrogen atoms produced the local states close to the valence band edge and the oxygen vacancies gave rise to the local states to the conduction edge.  

Excitation from such local states to the conduction band is consistent with the “add-on shoulder” on the absorption edge of the UV—visible spectrum. Moreover, the steep and almost parallel absorption edges of the InTaO$_4$-N catalysts shifted to remarkably longer wavelengths than that of the as-prepared InTaO$_4$ catalyst, leading to obvious response in these N-doped samples. Since the potential energy of N 2p-orbital is higher than that of the O 2p, the band gap of the material was effectively reduced when it reacted with NH$_3$ to form oxynitrides. The Ni@NiO/InTaO$_4$-N catalysts exhibit a greater absorbance than the N-doped catalysts. As shown in the inset in Figure 2, the as-prepared InTaO$_4$ sample was yellowish, while the InTaO$_4$-N samples were brownish and the Ni@NiO/InTaO$_4$-N samples were gray. The strong absorption in visible region results in deeper color for samples under Ni@NiO core—shell modification. The band gaps of the InTaO$_4$-N samples was 2.28 eV, calculated from the UV—visible spectra (Figure 2). The extension of the absorption of light from the UV to the visible range is associated with both the doped nitrogen atoms and the oxygen vacancies in the lattice, because the nitrogen atoms produced the local states close to the valence band edge and the oxygen vacancies gave rise to the local states to the conduction edge.  

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To elucidate the chemical states of nitrogen doping, XPS measurements were conducted to investigate all samples. In particular, an XPS peak at approximately 400 eV (N 1s) was confirmed. The deconvolution of N 1s and Ta 4p$_{3/2}$ core levels was carried out due to their close binding energy, displaying changes of species with and without N dopants. As shown in Figure S1, the peaks close to 404 eV are ascribed to Ta contribution and the peaks close to 401 eV are assigned to adsorbed nitrogen. The peaks appearing at 399 eV are characteristic of substitutional nitrogen after nitrogen doping. The smaller shift toward higher binding energy (404.5 eV) in Ni@NiO/InTaO$_4$-N for Ta analysis could be imputed to the decreased outer electron densities of Ta. This energy shift can be explained as the bigger electronegativity (Ni: 1.91 versus Ta: 1.5), originating from deposition of Ni@NiO nanoparticles on the surface. Comparing from the above results, it should be mentioned that the oxygen atoms could be replaced by the nitrogen atoms in the process of nitrogen doping and the sensitizing effect for Ni@NiO nanoparticles.

Morphological Analysis of InTaO$_4$ Samples. Figure 3a presents a typical FE-SEM image of as-prepared InTaO$_4$, while Figure 3b and 3c show typical FE-SEM images of InTaO$_4$-N and Ni@NiO/InTaO$_4$-N, respectively. Comparing from the former two images reveal that neither the size nor the shape of InTaO$_4$-N samples changed at all upon treatment in flowing NH$_3$. However, numerous irregular particles were deposited on the surface of InTaO$_4$-N after deposition of cocatalysts. The TEM image in the insets of Figure 3c clearly demonstrates the characterization of core and shell structure, ranging from 30 to 40 nm in size. The EDX spectra of the Ni@NiO core—shell catalyst revealed an atomic composition of only Ni, In, Ta, and O (Supporting Information S2, in which nitrogen signal is neglected) by using EDX. The EA result shows that the N contents of InTaO$_4$-N was 0.42(3) wt %. The EDX and EA elemental analyses agreed to closely with each other, confirming the elemental composition.

Evaluation of Photocatalytic Activity via GC. When the energy of incident light exceeds the band gap of a photocatalyst in a photocatalysis process, the electrons in the valence band are excited to the conduction band, leaving holes in the valence band. The electrons and holes are transferred to the surface of the photocatalyst. As a result, the InTaO$_4$ samples that were fabricated by the as-prepared, N-doped, and modified Ni@NiO core—shell methods were irradiated under visible light (λ ranges from 400 to 800 nm) to investigate the photocatalytic activity of InTaO$_4$-N samples. The photocatalytic activity was evaluated by measuring the concentration of 4-nitrophenol (4-NP) in a suspension of InTaO$_4$-N particles in a methanol solution containing 4-NP. The concentration of 4-NP was monitored at λ = 400 nm, and the reaction was carried out under illumination of visible light (λ > 400 nm) for 3 h. The results show that the InTaO$_4$-N samples exhibited a higher photocatalytic activity than the as-prepared InTaO$_4$, indicating that the nitrogen doping and modification of the Ni@NiO core—shell catalysts have a significant positive effect on the photocatalytic activity of InTaO$_4$-N samples.

Figure 2. DRS of an NH$_3$ treatment and Ni@NiO cocatalysts deposited on InTaO$_4$-N for InTaO$_4$-based samples. Inset shows the colors of samples.

Figure 3. FE-SEM images of InTaO$_4$ samples: a) as-prepared InTaO$_4$, b) InTaO$_4$-N, and c) Ni@NiO/InTaO$_4$-N. Inset shows the TEM image of Ni@NiO/InTaO$_4$-N.
from 390 to 770 nm) in the presence of a mixture of CO₂ and H₂O to yield methanol. As shown in Figure 4, the rate of the photoformed product increases linearly with the Vis-irradiation time, and the reaction stopped immediately when the irradiation was ceased. The formation of the reaction product was not detected under dark conditions. The reaction rate varied with the species of photocatalyst. A comparison of the total rates of methanol formation shows that the photocatalytic activity depends on the photocatalysts, according to be in the following order: as-prepared InTaO₄ < InTaO₄-N < Ni@NiO/InTaO₄-N. Among these photocatalysts, the Ni@NiO/InTaO₄-N exhibits the highest rate of formation of methanol. Annealing in NH₃ dramatically increases the methanol to approximately double that of the as-prepared InTaO₄ sample. Of special interest is the comparison of the photocatalytic reaction rates of the N-doped and modified Ni@NiO core–shell catalysts with that of the as-prepared InTaO₄ catalyst. Clearly, the photocatalytic reaction rates achieved by using the N-doped and modified Ni@NiO core–shell catalysts as a function of reaction time, and normalized to unit mass (gram) of the catalysts are much higher than that achieved using the as-prepared InTaO₄ catalyst. Because of their narrower band gap and stronger absorbance, the samples that were annealed in NH₃ and by the modified Ni@NiO core–shell structure absorbed more energy to catalyze the reaction. The energy of the N 2p-orbital is higher than that of O 2p, so the band gap was effectively shortened by using this N-doped method. However, the cocatalytic method not only provides reaction centers, which effectively transfer the electrons from the surface of catalysts, but also enhances the light absorbance. On the basis of these methodological improvements, the annealing of catalysts in NH₃ and the modified Ni@NiO core–shell structure can be utilized efficiently to increase methanol yield in the photocatalytic reduction to methanol. Thus, proper treatment can promote the photocatalytic reaction.

**Structural Analysis via XAS.** To confirm the electronic states and the bonding atoms of the series of InTaO₄-based samples, XAS analyses were conducted. Since XAS is sensitive to the atomic bonding environment and can detect even tiny changes in it, it is a powerful approach for analyzing the electronic states and bonding atoms. The local structures were examined by comparing the Ni K-edge and Ta L₃-edge X-ray absorption spectra with those of the metal foil. The reactivity to d-band vacancies could be attributed to the modification of the electronic structure for metal. To elucidate the d-orbital vacancies of InTaO₄-based
The relative comparison was determined by XANES. Figure 5a presents normalized X-ray absorption near edge structure (XANES) spectra of a series of InTaO₄-based samples. The inset clearly shows Ta 5d-orbital vacancies that correspond to the intensity of the white line, as determined by a comparison with Ta foil and Ta₂O₅. Nitrogen doping generates hole states in the O 2p band and lowers donation electrons back from O to Ta, such that fewer electrons occupy the Ta 5d-orbitals, enhancing the intensity of white line in InTaO₄-N compared to that in as-prepared InTaO₄. The area of the LIII threshold resonance line is proportional to the number of vacant d-electron states, instructing the distribution of vacant d-electron association. Moreover, Ni@NiO/InTaO₄-N exhibits greater intensity of white light than that of InTaO₄-N. The vacancies of the orbitals respond to the electronic states of the surrounding atoms, and this phenomenon may be ascribed to the interaction between the central atom and the neighboring ones. Due to the larger electronegativity of Ni than that of Ta, more electrons can be lengthened from Ta 5d-orbital, resulting in more vacant orbitals. Figure 5b presents Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectra of a series of InTaO₄-based catalysts. The strong peak scattering at 1.5 Å in the figure is characteristic of the Ta—O bond. Nitrogen doping broadens Ta—O scattering peaks, indicating that some of the O (O—Ta—O) is replaced by N (N—Ta—O). To determine the effects of N-doping, the structural parameters are obtained by EXAFS fitting and fixing Ta—O coordination numbers. Debye—Waller factors increase if only the Ta—O path is considered (Supporting Information, Table S1) to confirm the effect of N replacement. Figure 6a presents normalized X-ray absorption near edge structure (XANES) spectra of the modified Ni@NiO core—shell catalysts as compared to the Ni foil and NiO. The specific structure cannot be clearly characterized by diffraction in this region, and thus the XAS technique is important for revealing the Ni@NiO core—shell structure. Since the spectrum (Figure 6a) shows the mixture features of metallic and oxidized nickel for Ni@NiO/InTaO₄-N, these nanoparticles must have a mixed valence. The composition of Ni and NiO are 46.11(1) and 53.89(2), confirmed by XANES peak fitting. Figure 6b presents Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) spectra of Ni@NiO core—shell catalysts. The Ni—Ni (Ni foil) and Ni—Ni (NiO) bonds scatter at 2 Å and 2.8 Å, respectively, directly revealing the modified Ni@NiO core—shell structure, which is consistent with the XANES results. Hence, the above observation confirmed the N-doped effect and modified Ni@NiO core—shell effect, demonstrating the local structure of the photocatalysts transitioned from the N-doped structure to the Ni@NiO core—shell one.

Mechanism. Based on the above observations, a model of the catalytic mechanism about a series of InTaO₄-based catalysts, including relative band gap diagrams (Scheme 1), is proposed to define the process. In the photoreaction, the carbon source is CO₂, H₂CO₃, and CO₃²⁻, which reacts with H₂O to form the hydrocarbon fuels, CH₃OH. In the beginning, untreated commercial
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Scheme 1. Mechanism for Photoreduction of CO2

Elemental analysis of Ni@NiO–InTaO4-N photocatalyst was conducted by using an EDS (S2). Table S1 lists structural parameters of InTaO4-based samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES


■ ASSOCIATED CONTENT

5 Supporting Information. Emission spectrum employed, XPS spectra of N1s and Ta4p3/2 in InTaO4-based samples (S1).


■ CONCLUSION

In summary, a series of InTaO4-based samples were successfully synthesized by using N-doping, while their structures and activity were also demonstrated. XANES data clearly verify those variations in electronic structure and the extent of orbital vacancies. EXAFS data characterize the effect of introducing N. According to Ta LIII-edge XANES, the 5d-orbital vacancies increase, and photocatalytic activity is improved, according to GC. The Ni@NiO core–shell cocatalysts play a crucial role in the further enhancement of photocatalytic activity, owing to the difference between the atomic electronegativity, which may offer a new reaction center transferred from the surface of InTaO4 substance. The bifunctional N-doped and cocatalytic treatments can enhance the photocatalytic activity. XAS results were obtained to elucidate the proper mechanism of this treatment. Although this study concerned the InTaO4-based system, we believe this strategy can be extended to other photocatalytic systems.