Synthesis and Characterization of WO₃/CeO₂ Heterostructured Nanoparticles for Photodegradation of Indigo Carmine Dye

Duangdao Channei, Kantapat Chansaenpak, Sukon Phanichphant, Panatda Jannoey, Wilawan Khanitchaidecha, and Auppatham Nakaruk*

ABSTRACT: WO₃/CeO₂ heterostructured nanocomposites containing different WO₃ ratios (0.1, 0.3, 0.5, and 1.0 wt %) were synthesized by a precipitation method. The coupling of CeO₂ and WO₃ with a high specific surface area noticeably enhanced the photocatalytic activity of indigo carmine (IC) degradation under visible-light irradiation. The degradation rate constants (k) of 0.5 wt % WO₃/CeO₂ nanocomposites reached 4 and 5 times higher than those of CeO₂ and WO₃, respectively. Regarding the experimental results, the X-ray diffraction (XRD) patterns of the CeO₂ spherical nanoparticles and rod-shaped WO₃ were assigned to the cubic fluorite and orthorhombic phase structures, respectively. The increasing photocatalytic activity of nanocomposite samples could be attributed to the heterojunction of the photocatalysts with efficient charge separation and strong oxidative ability, which were confirmed by the photoluminescence spectra and diffuse reflectance spectrometry. The staggered heterojunction of the nanocomposite promoted efficient electron transfer and suppressed the recombination of photogenerated electrons and holes during the process.

1. INTRODUCTION

Over the past decades, photocatalysis has attracted increasing interest in environmental and energy applications. Cerium dioxide or ceria (CeO₂) is one of the most widely used photocatalysts due to its particular characteristics including, nontoxicity, good stability, low cost, and favorable band edge positions compared with that of TiO₂ as a benchmark photocatalyst. However, the disadvantages of CeO₂ include limited photocatalytic activity due to its wide band gap (3.2 eV only active in the UV region) and the high recombination of photoexcited electrons and holes. To maximize the lifetime of these charges, doping CeO₂ with transition metal ions or making CeO₂ as a nanocomposite material can be considered as the one approach to modify the CeO₂ photocatalyst.

Various narrow band-gap semiconductor materials, which are active under visible light, have been studied extensively for the photocatalytic decomposition of organic pollutants such as Bi₂O₃, BiVO₄, CdS, Ag₃PO₄, and graphene quantum dot nanocomposite metal oxide. Hsieh et al. had prepared mesoporous Bi₂O₃/CeO₂ microspheres using hydrothermal treatment; the data showed that it could enhance photocatalytic activity under visible light in the degradation of the orange azo dye from efficient electron transfer inside the hybrid catalyst. In addition, Wetchakun et al. also reported on CeO₂-based nanocomposites combined with BiVO₄; the BiVO₄/CeO₂ nanocomposites were revealed to extend visible-light absorption compared to blank CeO₂. The nanocomposites of metal oxides have shown significant potential as a visible-light-driven photocatalyst for the photodegradation of a mixture of dyes. For example, the photocatalytic degradation of methylene blue (MB) using a CdS/CeO₂ heterojunction under visible light was evaluated by Channei et al.; the data indicated that MB azo dye was degraded to 70% within 2 h of irradiation time, which exhibited about 7-fold enhancement in photocatalytic activity compared to blank CeO₂. The enhancement of photocatalytic efficiency was due to a charge carrier in the staggered heterojunction of the CeO₂/CdS nanocomposite. Further, Yang et al. reported on the photocatalytic degradation of novel Ag₃PO₄/CeO₂ nanocomposites for colorless phenol degradation. The superior photocatalytic activity of the nanocomposite compared to blank Ag₃PO₄ and CeO₂ under both visible-light and UV-light irradiation could be attributed to the...
efficient separation of electron–hole pairs at the interfaces of the constructed Ag3PO4/CeO2 nanocomposites. Apart from this, tungsten oxide (WO3) has also been frequently recognized as a visible-light-driven photocatalyst for this application. However, the rapid recombination of the photogenerated charges due to the narrow band gap (~2.6 eV) of WO3 still significantly diminishes its photocatalytic efficiency. The major challenge associated with photocatalysis is slowing down the recombination rate of photoinduced electron–hole pairs.

Therefore, incorporating other semiconductors like CeO2 with WO3 could increase its photoresponse in visible-light reactions. Therefore, this study aimed to develop the influence of WO3 on CeO2 with different amounts of WO3 contents to achieve better charge separation and thus improving the photocatalytic performance of both CeO2 and WO3 toward indigo carmine (IC). The possible mechanism of the WO3/CeO2 system as a visible-light photocatalyst was proposed to understand the oxidation process in the WO3/CeO2 heterojunction. The role of WO3 contents in the CeO2/WO3 nanocomposite system and changes in structural, optical, and surface properties were analyzed by X-ray diffraction instrument (XRD), diffuse reflectance spectra (DRS), photoluminescence (PL), scanning electron microscope (SEM), and Brunauer–Emmett–Teller (BET) theory.

2. EXPERIMENTAL SECTION

2.1. Synthesis of WO3 Nanorods. The acid precipitation method was carried out for the synthesis of WO3 nanorods. For typical synthesis, 0.015 mol sodium tungstate dihydrate was dissolved in a solution of 20% ethylene glycol and stirred magnetically at room temperature for 1 h. After that, 10 M HCl was added dropwise to the previous solution to give a purple slurry, which then turned yellow. Third, the yellow precipitate was separated, washed several times with DI water, and dried at 80 °C for 6 h in a muffle furnace to produce WO3. The summarized chemical reaction is exhibited below (eqs 1 and 2).

\[ \text{Na}_2\text{WO}_4 + 2\text{HCl} \rightarrow \text{WO}_2(\text{OH})_2 + 2\text{NaCl} \]  
\[ \text{WO}_2(\text{OH})_2 + 500{\degree}\text{C} \rightarrow \text{WO}_3 + \text{H}_2\text{O} \]  

2.2. Synthesis of Blank CeO2 Nanoparticles. Blank CeO2 nanoparticles were prepared by the precipitation technique as follows. First, 0.01 mol cerium (III) nitrate hexahydrate and a 20% ethylene glycol solution were mixed at a temperature of 50 °C for 1 h, according to our previous report. Second, about 30 mL of a NaOH solution (0.04 mol) was added dropwise to the previous solution to give a purple slurry, which then turned yellow. Third, the yellow precipitate was separated, washed several times with DI water, and dried at 80 °C for 12 h in a hot-air oven. CeO2 nanoparticles were formed after calcination at 500 °C for 6 h as below (eqs 3 and 4).

\[ \text{Ce(NO}_3)_3 + 2\text{NaOH} \rightarrow \text{Ce(OH)}_3 + \text{H}_2\text{NO}_3 \]  
\[ \text{Ce(OH)}_3 + 500{\degree}\text{C} \rightarrow \text{CeO}_2 + \text{H}_2\text{O} \]  

2.3. Synthesis of CeO2/WO3 Nanocomposites. For the synthesis of WO3/CeO2 heterostructure nanocomposites, as-prepared WO3 powder of different concentrations (0.1, 0.3, 0.5, and 1.0 wt %) was added to the above-prepared solution of cerium (III) nitrate hexahydrate and 20% ethylene glycol solution. The remaining preparation steps were the same as the procedure for the synthesis of blank CeO2.

2.4. Characterization. Crystallographic structures were detected by an X-ray diffraction instrument (XRD, Philips X’PertMPD) over a range of 10–80°. The morphologies were studied using a scanning electron microscope (SEM, JSM–6335F, JEOL) and a transmission electron microscope (TEM, JSM-2010, JEOL). The specific surface area was determined from N2 adsorption/desorption isotherms based on the Brunauer–Emmett–Teller (BET) theory (Micromeritics TriStar II 3020). The photoluminescence (PL) spectrophotometer excited with a 350 nm light source was used for analyzing the emission wavelength (Fluoromax-4 Horiba JobinYvon). Optical studies were performed using diffuse reflectance spectra (DRS) on a UV–vis spectrophotometer (Shimadzu, UV-3101PC).

2.5. Photocatalyst Characterization. The photocatalytic performances of CeO2, WO3, and WO3/CeO2 nanocomposites were tested by the degradation of indigo carmine (IC) under visible light. The light source used for the irradiation experiment was a 54 W halogen lamp. The prepared catalyst (0.1 g) was mixed with 3 ppm of an IC aqueous solution (50 mL). The suspension was stirred magnetically at room temperature for 30 min under dark conditions to ensure the absorption/desorption equilibrium of dye adsorbed on the catalyst surface. About 5 mL of the suspension was withdrawn at given time intervals (15, 30, 45, 60, 75, 90, 105, and 120 min) and centrifuged at a speed of 6000 rpm for 5 min to separate the nanoparticles. Subsequently, the supernatant of the IC solution was further recorded for the difference in the absorbance at a fixed wavelength of 612 nm using a double-beam UV–vis spectrophotometer (Shanghai Mapada Instruments Co., Ltd.). The absorbance intensity at different times was converted to the IC remaining concentration at different times using a calibration curve.

3. RESULTS AND DISCUSSION

Powder X-ray diffraction (XRD) was used to analyze the phase purity and crystallinity of the synthesized photocatalysts. The XRD patterns of the as-synthesized catalysts are shown in Figure 1. The experimental XRD pattern of CeO2 agrees with the JCPDS card no. 34-0394. The crystal planes of CeO2 with a cubic structure are observed at 2θ values of 28.5, 33.2, 47.3, 56.3, 69.5, 76.8, and 79.1° corresponding to the 111, 200,
220, 311, 400, 331, and 420 planes, respectively. The peaks of WO₃ are seen at 2θ values of 23.3, 24.5, 26.5, 28.9, 34.1, 41.7, 50.2, 55.8, 62.5, and 76.6° corresponding to the 002, 020, 120, 112, 202, 222, 400, 142, 340, and 116 planes, respectively, which corresponded to JCPDS no. 01-083-0951 of a monoclinic phase. For WO₃/CeO₂ nanocomposites, the addition of WO₃ did not change the XRD profile of the diffraction pattern of CeO₂. No separate peaks of the WO₃ phase and no shift of the CeO₂ peak were observed, which could be attributed to the low amounts of WO₃ contents.

The surface morphology of the as-synthesized WO₃, CeO₂, and WO₃/CeO₂ nanocomposite catalysts were investigated using SEM, as presented in Figure 2. The typical SEM images at a magnification of 30 000× for blank WO₃ showed uniform rod-like shapes with a length of around 200 nm and a width of around 50 nm, while blank CeO₂ indicated an aggregation of sphere-like particles with an average particle size of less than 100 nm. Due to the small amount of WO₃ that was added in the nanocomposites, all nanocomposite samples had the same morphology as the spherical CeO₂.

As shown in the inset of WO₃ for the detailed morphology under higher magnification, it presented large textural porosity, which is related to high specific surface areas. The data presented in Table 1 summarize that blank WO₃ showed the highest BET surface area (SSA$_{BET}$) of 166.23 m²/g, while the SSA$_{BET}$ of CeO₂ was about 23.43 m²/g. The addition of WO₃ to CeO₂ resulted in a significant increase in the specific surface area of nanocomposite samples compared to CeO₂. This suggests that WO₃ could improve the photocatalytic performance of CeO₂ since the catalyst of a large surface area leads to higher adsorption and enrichment of organic pollutants on the photocatalyst surface.

Table 1. Surface Properties of WO₃ and CeO₂ Compared to WO₃/CeO₂ Nanocomposites

| sample | BET surface area, SSA$_{BET}$ (m²/g) | pore volume (cm³/g) |
|--------|-------------------------------------|---------------------|
| CeO₂   | 23.43                               | 0.03                |
| 0.1 wt % CeO₂/WO₃ | 33.88                             | 0.22                |
| 0.3 wt % CeO₂/WO₃ | 37.34                             | 0.22                |
| 0.5 wt % CeO₂/WO₃ | 45.35                             | 0.11                |
| 1.0 wt % CeO₂/WO₃ | 45.76                             | 0.14                |
| WO₃    | 166.23                              | 0.32                |

The results of light absorbance characteristics are plotted in Figure 4b. It can be seen that CeO₂ exhibited an absorption edge in the UV region at 370 nm, while the spectral pattern of blank WO₃ catalysts demonstrated strong adsorption for the visible-light region with the onset absorption edges of 440 nm, as presented in Table 2. It is obvious from the UV–vis absorption spectra that the addition of WO₃ to CeO₂ resulted in a significant increase in the specific surface area of nanocomposite samples compared to CeO₂. This suggests that WO₃ could improve the photocatalytic performance of CeO₂ since the catalyst of a large surface area leads to higher adsorption and enrichment of organic pollutants on the photocatalyst surface.

Figure 2. SEM images of WO₃, CeO₂, and WO₃/CeO₂ nanocomposites.

Figure 3. TEM images of (a) CeO₂, (b) WO₃, and (c) CeO₂/WO₃ nanocomposites.

Figure 4. a) UV–vis reflection spectroscopy (DRS). The corresponding absorption spectra for blank WO₃, CeO₂, and nanocomposite photocatalysts were then converted from reflectance (R) using the Kubelka–Munk functions given by

\[ F(R) = \frac{(1 - R)^2}{2R} \]  

The results of light absorbance characteristics are plotted in Figure 4b. It can be seen that CeO₂ exhibited an absorption edge in the UV region at 370 nm, while the spectral pattern of blank WO₃ catalysts demonstrated strong adsorption for the visible-light region with the onset absorption edges of 440 nm, as presented in Table 2. It is obvious from the UV–vis
absorption spectra of WO₃/CeO₂ photocatalysts that the absorption edges of such nanocomposites showed a shift toward a longer wavelength to the visible region with an increase in WO₃ contents compared to blank CeO₂.

According to the Tauc plots (as shown in Figure 4c), the adsorption function was plotted versus photon energy (hν) and the intercept of the tangent to hν-axis determines an approximation of the band-gap energy. The results showed that the band-gap energies of blank CeO₂ and WO₃ were 3.20 and 2.55 eV, respectively. Such a decrease in the band-gap energy, as well as a red shift of the absorbance edges toward longer wavelengths with the increase in the WO₃ ratios in nanocomposite samples, indicated better visible-light-harvesting ability than CeO₂.

The recombination rate of photoinduced charge carriers (electrons and holes) in the nanocomposite photocatalyst compared to WO₃ and CeO₂ was investigated by photoluminescence emission spectra (PL), as shown in Figure 5. The strong emission PL intensity was found in blank WO₃ and CeO₂ due to the rapid recombination rate of charge carriers, while the lower PL peak intensity of WO₃/CeO₂ nanocomposites was much lower than the blank samples in the order 0.1 < 0.3 < 0.5 < 1.0 wt % WO₃. Thus, this PL experiment could confirm the WO₃/CeO₂ hybrids, which is favorable for charge separation. The photoinduced electron from CB of CeO₂ is trapped by the lower CB of WO₃, leading to decreased involvement in the recombination of electrons and holes.

Figure 6a presents the photodegradation efficiency of IC in terms of Cₜ/C₀, as a function of visible-light irradiation. When the amount of the WO₃ content increases, the photodegradation efficiency of all nanocomposite samples increases compared to blank CeO₂ (9%) and WO₃ (7%). Otherwise, the excess doping of WO₃ to 1.0 wt % might act as a recombination center, which decreases the photocatalytic activity. It has to be noted that the chemical kinetics explains how fast is the rate of the chemical reaction. As shown in Figure 6b, the linear line provides a good fitting of the experimental data within the first 60 min. The initial rapid rate of degradation may be due to the availability of more active sites on the photocatalyst for dye molecules present in the solution. The later slow degradation rate part of the curve may
be because no more active sites on the surface are available for organic molecules to interact. Figure 6b presents kinetic curve plots for experimental data of the pseudo-first-order model as a function of visible irradiation time. The linear regression method using the slope was employed to estimate the rate constant ($k$) of the fitting kinetic model. As summarized in Table 3, the kinetic rate constants for all WO$_3$/CeO$_2$ nanocomposites showed higher values compared to those of blank photocatalysts. The 0.5 wt % WO$_3$/CeO$_2$ sample revealed the highest kinetic rate constants at about 0.0353 min$^{-1}$, which were about 4 and 5 times greater than blank CeO$_2$ (0.0082 min$^{-1}$) and WO$_3$ (0.0069 min$^{-1}$), respectively. The observed increase in kinetic rate constants of nanocomposite samples can be ascribed to the ability for separating photoinduced electron–hole pairs in the heterojunction structure of CeO$_2$ and WO$_3$, in which the higher values of the rate constant represent more efficient photocatalytic performance.

The results obtained for IC photodegradation enable the proposal of a possible mechanism for visible-light excitation of WO$_3$/CeO$_2$ photocatalysts, as shown in Figure 7. To draw a schematic for the proposed energy level of the WO$_3$/CeO$_2$ nanocomposite, the values of the conduction band ($E_{CB}$) and the valence band ($E_{VB}$) edge position can be calculated from eqs 6 and 7:

$$E_{VB} = 0.5E_g - E^C + \chi$$

$$E_{CB} = -E_g + E_{VB}$$

where $\chi$ is the absolute electronegativity of the semiconductor ($\chi$ is 6.59 and 5.56 eV for WO$_3$ and CeO$_2$, respectively), $E^C$ is the energy of free electrons on the NHE scale (ca. 4.5 eV), and $E_g$ is the calculated band gap of the prepared photocatalyst. According to the equations mentioned above, band edge positions of CB and VB of CeO$_2$ were found to be 2.66 and $-0.54$ eV, respectively. For WO$_3$, the VB and CB edge potentials were determined as 3.37 and 0.82 eV, respectively.

According to the proposed energy level of the WO$_3$/CeO$_2$ nanocomposites, irradiation of the photocatalyst initiates the photogenerated electrons and holes. Since the CB band edge potential of CeO$_2$ ($-0.54$ eV) has a lower value than that of WO$_3$ ($+0.82$ eV), the excited electrons in the CB of CeO$_2$ migrate to the CB of WO$_3$. The localized electrons can readily follow the reduction reactions on the CB of WO$_3$, subsequently reacting with the absorbed O$_2$ molecules to produce O$_2$•$^-$ (superoxide radicals) and OH$^*$ (hydroxyl radical), which then react with the adsorbed IC dye molecules to CO$_2$ and less-toxic small fragments. Simultaneously, the photogenerated holes in the VB of WO$_3$ move to the VB of CeO$_2$ since the VB edge of CeO$_2$ (+2.66 eV) is less positive than that of WO$_3$ (+3.37 eV) for oxidation reactions. In such a position, active oxidizing species such as OH$^*$ can be used in the VB of CeO$_2$ by the reaction of holes and OH$^-$, which then react with the IC dye molecules.

This system can be classified into type II band alignment of a heterojunction (staggered gap), which is preferred and suitable for charge carrier separation. Predictably, the recombination of photogenerated electron–hole pairs could be inhibited under light irradiation during the photocatalytic process. Hence, the photogenerated charge carriers have more time to react with adsorbed dye molecules on the photocatalyst surface, resulting in higher photocatalytic degradation.
4. CONCLUSIONS

In summary, this study successfully prepared blank CeO₂ nanoparticles, rod-shaped WO₃, and WO₃/CeO₂ nanocomposites with different contents of WO₃. Among the various nanocomposites, 0.5 wt % WO₃/CeO₂ nanocomposites showed the highest photocatalytic activity after 2 h of visible-light irradiation. The enhancement of nanocomposite photocatalysts can be attributed to:

- Interfacial charges transfer at the heterojunction interface of WO₃/CeO₂ nanocomposites, which leads to the efficient separation of electron–hole pairs.
- An increase in the specific surface area of CeO₂ after adding WO₃ in the nanocomposite sample, which enables the provision of more active sites for the adsorption of the dye molecules over the photocatalyst surface for further degradation under light-on.

Based on the modification method, the experimental results reported in this study may be useful for the development of other photocatalysts for the photocatalytic degradation of organic pollutants in water.

AUTHOR INFORMATION

Corresponding Author

Auppatham Nakaruk – Centre of Excellence for Innovation and Technology for Water Treatment and Department of Industrial Engineering, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand; orcid.org/0000-0002-7399-5016; Email: auppathamn@nu.ac.th

Authors

Duangdao Channei – Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand; Centre of Excellence for Innovation and Technology for Water Treatment, Naresuan University, Phitsanulok 65000, Thailand

Kantapat Chansaenpak – National Nanotechnology Center, National Science and Technology Development Agency, Pathum Thani 12120, Thailand

Sukon Phanicphont – Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Panada Jannoey – Department of Biochemistry, Faculty of Medical Science, Naresuan University, Phitsanulok 65000, Thailand

Wilawan Khanitchaidecha – Centre of Excellence for Innovation and Technology for Water Treatment and Department of Civil Engineering, Faculty of Engineering, Naresuan University, Phitsanulok 65000, Thailand

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02453

Notes

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