Facile Preparation of Ag-TiO₂ Nanocomposite with Enhanced Photocatalytic Properties

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Abstract. For decades, photocatalytic semiconductor materials were regretfully limited to low-yield preparation method and poor catalytic efficiency although it has dramatically captured attention in sewage treatment applications. To expand this slim range of semiconductor catalysts, the nanocrystalline silver embedded in titanium dioxide (Ag-TiO₂) heterojunction was prepared by means of facile mechanical milling technique capable of large-scale production, in terms of optimum Ag content. The as-obtained Ag-TiO₂ nanocomposite particles were systematically characterized by means of X-ray diffraction technique, Raman spectra, X-ray photoelectron spectroscopy, transmission electron microscopy analysis, and UV-vis spectrophotometry. Results suggest that in comparison with pure TiO₂ catalyst, Ag-TiO₂ nanocomposite catalyst significantly enhanced photocatalytic activity for the degradation of methylene blue (MB), whereas its band gap decreased in view of the red-shift phenomenon. In terms of the experimental results, a mechanism was proposed to explain the enhancement of photocatalytic activity. Our findings offer a promising route towards the large-scale preparation of high-efficiency photocatalysts for commercial applications.

1. Introduction
Semiconductor photocatalysis is one of the most straightforward and efficient approaches for treating environmental water pollution. Semiconductor materials in photocatalytic technology have the advantages of high efficiency, stable chemical properties, and processing pollutant degradation at room temperature in sewage rehabilitation engineering.¹ As early as in 1972, Fujishima and Honda presented a hydrogen generation effect of TiO₂ based on electrochemical decomposition of water, which motivated intensive efforts devoting to the TiO₂ based catalyst study in the past decades.² TiO₂ is a versatile and technologically important material with abundant photocatalytic activity, which has been intensively investigated in the field of decomposition of organic pollution thanks to their low-cost and good environmental stability in nature.

However, the available experimental results about this TiO₂ based photocatalysis are unfortunately limited to two key points in preparing suitable samples for studying the photocatalytic effect as follows: (i) wide band gap and high electron-hole recombination rate restrict the photocatalytic efficiency,³ and (ii) current reports on TiO₂ photocatalysis are limited to small-scale laboratory production due to the confinement of preparation method of photocatalyst, preventing the practical commercial applications. For improving the photocatalytic efficiency of TiO₂, many approaches have
been carried out to overcome this scientific issues through several technique such as introducing metal nanoparticles, coupling of semiconductor, and synthesis of titania with high surface area (thin films, nanosheets, etc.). Among them, introducing metal nanoparticles is the most extensive and feasible method, which is highly effective for enhancing photocatalytic activity. The role of metal nanoparticles can not only promote the separation of photoinduced charge carriers but also provided an alternative reaction pathway to the reaction products with a lower activation energy, subsequently enhancing the photocatalytic activity. Also, the sterilization effect for metal nanoparticles (i.e. Ag) is beneficial so that the metal-semiconductor heterojunction structure can be a promising application for biological wastewater treatment of enriched bacteria. To expand the slim range of small-scale preparation is also the key issue for realizing degradation of organic pollution in large-area commercial applications. Previous methods preparing photocatalysts are mainly to focus on chemical solution method. This method is considerably limited compared to mass production and industrialization in treating large-area sewage owing to that it needs strict reaction conditions, complex steps, and after-treatment. Recently, mechanical milling for preparation of photocatalysts has become an interesting research hot due to its characteristics via a simple and feasible technique for processing advanced materials. In particular, this method allows us to develop a large-scale preparation of semiconductor photocatalysts for wastewater treatment.

Herein, we prepared the Ag-TiO2 nanocomposite photocatalyst via a facile mechanical milling, and then characterized their crystal structure, particle size, surface morphology, band gap, and chemical bonding states. We also investigated the photocatalytic properties of the Ag-TiO2 nanocomposite. In addition, the photocatalytic mechanism of the Ag-TiO2 nanocomposite has been discussed in detail.

2. Experiment Section

2.1. Synthesis
Commercial silver (purity 99.95%) and titanium oxide (purity 99.99%) powders were used as raw materials, the nanosized Ag-TiO2 heterojunction catalyst was prepared by milling small-amount Ag and high-amount TiO2 particles in terms of the optimum ratio (i.e. 2 wt.%), which occurred in a WC vial with WC balls under air atmosphere by means of a Fritsch P4 planetary ball mill. The mixed raw powders (Ag and TiO2 particles) were milled at 250 rpm for 4 h complying with ball-to-powder weight ration of 50:1, then the ball-milled samples were thermally treated in air ambient at 400 °C for 1 h. Two types of catalyst, pure TiO2 (control group) and 2% Ag-TiO2 nanocomposite were synthesized for comparative study.

2.2. Characterization and Measurements
The crystal structure of the catalysts was detected by means of a X-ray diffraction technique(XRD: Rigaku D/Max-2400 X-ray diffractometer) measurements with Kα radiation of copper target. The average grain sizes of silver and titanium oxide nanoparticles were estimated by using the Scherrer equation according to the line broadening of the XRD diffraction peaks. The Raman spectra (Horiba Jobin Yvon LABRAM H800) was recorded with a laser wavelength of 532 nm. The chemical states of the catalysts were examined by a X-ray photoelectron spectroscopy analysis (XPS: PHI-5702) with Al Kα radiation. Observation based on transmission electron microscopy (TEM: FEI Tecnai G² F30) characterization was carried out with a beam energy of 300 KeV. The morphology of the catalysts was observed. Light absorption measurements were implemented by using UV-Vis spectrophotometer (CSHI-MADZU, UV-3101) to analyze the absorption range and band gap of the catalysts. Photocatalytic performance was tested on a UV-2401 spectrophotometer. Lamp source of 500 W monitored ultraviolet by using a mercury lamp with a wavelength focused on 365 nm. In the experiment, the as-prepared photocatalyst samples of 20 mg were added into the MB solution of starting concentration 20 mg/L about 10 mL. Before the irradiation treatment, the suspension was magnetically stirred under dark conditions for 0.5 h in order to obtain the establishment of the adsorption/desorption equilibrium of the MB solution onto the surface of photocatalysts. Then, light irradiation was added into the mixture of MB solution and photocatalysts.
3. Results and Discussion

Figure 1a illustrates the typical XRD pattern of Ag-TiO₂ nanocomposite particles. Partially indexed diffraction peaks can be assigned to those of the tetragonal TiO₂ phase (JCPDS No. 21-1272), being anatase structure. In addition to TiO₂ matrix diffraction peaks, four obvious diffraction peaks were indexed to the (111), (200), (220), and (311) planes in the standard spectrum of metallic silver (JCPDS No. 04-0783). No impurity phase such as Ag₂O was examined in the XRD patterns. According to the Scherrer equation, the average grain sizes of metallic Ag and TiO₂ phase were estimated to be ~25 nm and ~40 nm, respectively, which confirmed nanocrystalline in nature.

![Figure 1](image)

Figure 1. (a) XRD pattern and (b) Raman spectra of Ag-TiO₂ nanocomposite photocatalyst. (c) XPS spectra of Ag-TiO₂ nanocomposite photocatalyst for Ag 3d region.

Raman spectroscopy is one of the powerful methods to further investigate the structural characteristics of Ag-TiO₂ nanocomposite photocatalyst (figure 1b). The Raman vibration peaks of 400, 518.2, and 640.9 cm⁻¹ can be assigned to the vibration modes of B₁g, B₂g, and Eₕ of anatase TiO₂ phase, respectively, which is in accordance with the Raman analysis of ~30 nm anatase TiO₂ reported by Choi et al. and further confirmed the nanocrystalline in nature.

The chemical state of embedded Ag was further studied by XPS technique, as displayed in figure 1c. It was observed that two obvious energy binding peaks appear at 367.9 eV and 373.9 eV, which corresponds to Ag 3d₅/₂ and Ag 3d₃/₂ peaks in Ag-TiO₂ nanocomposite, respectively. This result suggested that Ag exists in the metallic state (Ag⁰), agreed well with the XRD analysis.

Figure 2 illustrates TEM observations of the synthesized Ag-TiO₂ nanocomposite particles. These particles can be clearly distinguished in the bright field image (figure 2a) though agglomerated particles occurred. The crystal structure of Ag phase was investigated by means of the selected area electron diffraction (SAED) pattern which could be marked by the red circles, as shown in figure 2b. The diffraction spots of the SAED image were successfully indexed by comparing XRD JCPDS cards (No. 04-0783), which further confirmed the XRD and XPS results. Figure 2c depicts the high-angle annular dark field (HAADF) image recorded with a scanning transmission electron microscope (STEM) for Ag-TiO₂ nanocomposite particles, where the bright field contrast is from embedded Ag nanoparticles due to that image formation in HAADF-STEM is sensitive to the difference of elemental atomic number. A magnified STEM image for further analysis, as shown in figure 2d, in which the diameter of the Ag nanoparticles was estimated to be about 18-27 nm, the same as the particle size found from XRD measurements.

The light absorption characteristics versus wavelength range curves of pure TiO₂ sample and Ag-TiO₂ nanocomposite sample were investigated and are displayed in figure 3. The band gap energy, calculated from the intercept of the tangents (Eg= 1240/λ) of the plots, is 3.25 eV and 3.13 eV for the pure TiO₂ and Ag-TiO₂ nanocomposite particles, respectively. The UV-Vis spectra of the prepared Ag-TiO₂ nanocomposite indicated an obvious red-shift phenomenon in comparison with the pure TiO₂ particles, which should be ascribed to the size effect of the band gap energy. For the milled Ag-TiO₂ nanocomposite, the Femi level between the conduction band (CB) and valence band (VB) shifts down, accompanying with that the electrons in VB is easy to be excited by lower energy light and then migrate to CB. Nanocrystalline Ag-TiO₂ heterojunction structure materials exhibited a larger absorption range in the 200-400 nm region, which is effective to enhance the photo-quantum efficiency and photocatalytic activity.
Figure 2. TEM images of Ag-TiO2 nanocomposite particles: (a) bright field, (b) SAED pattern, (c) STEM image, and (d) a magnified STEM image.

Figure 3. UV-visible absorption spectra of pure TiO2 and Ag-TiO2 nanocomposite particles. Figure 4a illustrates the photo-degradation rate of MB in different photocatalysts under UV irradiation (wavelength peak at 365 nm). Prior to photocatalytic treatment, MB dye solutions with catalysts were continuously stirred under dark environment for 30 min in order to achieve a stable equilibrium condition. Experimental results indicated that the adsorption of MB molecules on catalysts is almost negligible due to the nearly unchanged C/C0 value. After light irradiation for 60 min, the maximum of MB degradation efficiency has achieved to be 85% in Ag-TiO2 nanocomposite catalyst, whereas only 41% of MB dye molecules can be decomposed by the pure TiO2 catalyst. As shown in figure 4b, the resultant degradation process of MB is in well agreement with the first-order kinetics model according to Langmuir-Hinshelwood expression, and their kinetics can be expressed as follows:

\[ \ln \left( \frac{C_0}{C} \right) = kt \]  

Where \( C_0 \) denotes the initial concentration of aqueous MB, \( C \) denotes the concentration of aqueous MB at the react time \( t \), and \( k \) is the apparent reaction rate. The determined \( k \) value was shown as linear slope, and the determined reaction rate constants \( (k) \) were \( 8.21 \times 10^{-3} \) min\(^{-1}\) and \( 32.01 \times 10^{-3} \) min\(^{-1}\) for the pure TiO2 and Ag-TiO2 nanocomposite catalysts, respectively.
Figure 4. (a) Photo-degradation rate of MB dye by different photocatalysts, (b) The fitting linearly of $-\ln \left( \frac{C}{C_0} \right)$ versus the irradiation time.

On the basis of the experimental results and analysis, the probably photocatalytic reaction mechanism was proposed to explain the enhancement of photocatalytic activity, as shown in figure 5. A tentative pathway of charge transfer in the photocatalytic process was revealed. We know that light irradiation is helpful to generate photoinduced electrons ($e^-$) and hole ($h^+$) (Eqs. 2). The electrons of the TiO$_2$ conduction band is easy to access reducing ability, then reacting with O$_2$ that is dissolved in the aqueous solution to create superoxide radical ($\cdot$O$_2^-$) (Eqs. 3). Whereas, hydroxy (OH$^-$) in the adsorbed water can be oxidized to hydroxyl radical ($\cdot$OH) by photo-induced holes (Eqs. 4–5). Finally, these resultant free radicals will act as the reactive species to generate oxidation of organic MB dyes (Eqs. 6–7). The possible photocatalytic reactions as follows: 

\[
\begin{align*}
\text{Ag-TiO}_2 + \text{hv} & \rightarrow \text{Ag-TiO}_2 (e^- + h^+) \quad (2) \\
\text{O}_2 + e^- & \rightarrow \cdot\text{O}_2^- \quad (3) \\
\text{H}_2\text{O} & \leftrightarrow \text{H}^+ + \text{OH}^- \quad (4) \\
\text{OH}^- + h^+ & \rightarrow \cdot\text{OH} \quad (5) \\
\cdot\text{O}_2^- + \text{MB} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (6) \\
\cdot\text{OH} + \text{MB} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (7)
\end{align*}
\]

In terms of the Ag-TiO$_2$ nanocomposite based photocatalytic effect, the charge transfer from the excited conduction band of TiO$_2$ to Ag is feasible. The tight attachment of Ag and TiO$_2$ is conducive to the enhancement of photocatalytic performance due to preventing the recombination effect of the electron-hole pairs. On the other side, MB molecules, adsorbed in the surface of Ag nanoparticles, can be directly oxidized by means of the positive charges of Ag nanoparticles, which also provides an approach to degrade the MB molecules.
4. Conclusion
In summary, silver embedded in titania nanocomposite photocatalyst was prepared by means of a facile mechanical milling. The Ag-TiO\textsubscript{2} nanocomposite catalyst exhibited enhancement of photocatalytic activity such as a photocatalytic efficiency as high as 85\% for the degradation of MB after 1 h irradiation, which is superior to that of the pure TiO\textsubscript{2} catalyst (only ~41\% with photocatalytic efficiency). Additionally, a narrowed band gap (3.13 eV) in Ag-TiO\textsubscript{2} nanocomposite was inspected by UV-visible absorption spectra as compared to pure TiO\textsubscript{2} catalyst (3.25 eV). The photocatalytic results are in accordance with the first-order kinetics equation. This enhancement with photocatalytic activity can be ascribed to that the Ag nanoparticles embedded in the TiO\textsubscript{2} surfaces can efficiently collect the free electrons. This study serves as a feasible, promising, and high-yield approach for the large-scale catalysis of waste water in practical applications.

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