Visible light assisted photocatalytic degradation of methyl orange using Ag/N–TiO₂ photocatalysts

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ABSTRACT

For the sake of efficient utilization of sunlight, Ag nanoparticles loaded N-doped TiO₂ photocatalysts (Ag/N–TiO₂) were successfully fabricated via a two-step method to make the best use of the respective advantages of noble metal loading and nonmetal doping. Ag/N–TiO₂ was characterized using XRD, XPS and UV–Vis DRS. Compared to TiO₂, the dramatic enhancement of the visible-light-induced photocatalytic degradation efficiency of Ag/N–TiO₂ obtained for the degradation of methyl orange should be attributed to the synergistic effect of N-doping and Ag-loading, including the good visible light absorption and the effective electron–hole separations. This demonstrates Ag/N–TiO₂ is a promising photocatalytic material for organic pollutant degradation under visible light irradiation.

Key words | Ag-loading, N-doping, plasmon resonance, titanium dioxide, visible light

INTRODUCTION

A large portion of industrial wastewater including resistant-biodegradable pollutants such as dyeing wastewater must be removed by physicochemical methods. In the past decades, advanced oxidation processes (AOPs) have emerged and been accepted as efficient ways for the degradation of bio-refractory organic pollutants (Ben Abdelmelek et al. 2011). Photocatalytic technology, as one of the advanced oxidation processes, has been widely used for wastewater treatment. Titanium dioxide (TiO₂), as a cheap, nontoxic, highly efficient, stable and ecological friendly photocatalyst, has been widely used and investigated for the photogradation of organic pollutants (Lu et al. 2011). However, owing to its wide band gap (3.2 eV for anatase), TiO₂ can only be excited under ultraviolet irradiation. For the sake of efficient utilization of sunlight, many routes have been developed to synthesize modified TiO₂ with visible light responsive activity. Substitutional or interstitial doping of non-metallic elements, such as C (Chen et al. 2009), N (Wu et al. 2010) and I (Hong et al. 2005) seems to be a very promising way to efficiently extend the optical response of TiO₂ from ultraviolet to visible light region. Especially, the synthesis of N-doped TiO₂ has been the focus of recent photocatalyst researches, where photocatalytic activity under visible light irradiation has been discussed by a great number of studies (Asahi et al. 2001; Wu et al. 2010).

In addition, to enhance charge separation in semiconductors and decrease electron–hole pairs recombination, noble metals have been used as surface modifiers, such as Au (Youn et al. 2010), Pt (Shiraishi et al. 2010) and Ag (Song et al. 2011). To make the best use of the respective advantages of noble metal loading and nonmetal doping, the combination of two methods might be useful for improving the visible-light-induced activity of TiO₂. Nitrogen-doped together with gold-deposited TiO₂ exhibited much higher visible-light photocatalytic activity compared with single N-doped or Au-loaded TiO₂ (Tian et al. 2009). Pt impregnation onto the N-doped TiO₂ considerably improved its photocatalytic H₂ production activity (Sreethawong et al. 2009) and increased the degradation rate of phenol under either solar or visible light irradiation (Zhang et al. 2009).

However, some noble metals such as Pt and Au are too expensive to be used in industrial scale. There is considerable interest in using Ag for this purpose because of its high efficiency and low cost compared to Pt and Au, and antimicrobial properties. Silver can trap the photoexcited electrons from TiO₂ and leave the holes for degrading organic species (He et al. 2011). At the same time, metal silver nanoparticles could strongly absorb visible light because of its plasmon resonance (Logar et al. 2010). Zhang et al. have successfully fabricated Ag nanoparticles loaded N-doped TiO₂ nanotube arrays with enhanced visible light photocatalytic performance by an electrodeposition method (Zhang et al. 2011). In this study, Ag loaded N-doped TiO₂ photocatalysts (Ag/N–TiO₂) were prepared by a simple method. The
photocatalytic activities of catalysts under visible light irradiation were evaluated by measuring the degradation of methyl orange (MO).

**EXPERIMENTAL**

**Preparation of the catalysts**

The catalysts of 0.5 wt% Ag/N–TiO₂ were prepared by two steps. Firstly, TiO₂ powders and urea (the mole ratio of N/Ti was 2:1) were calcined in a Schlenk tube under air at 400 °C for 2.0 h to get N–TiO₂ powders. Secondly, the Ag loading was successfully realized by a photoreduction treatment method. Briefly, a suspension was prepared by mixing N–TiO₂ powders and AgNO₃ aqueous solution with a small quantity of ethanol in a flat-bottom beaker. The suspension was then irradiated using a high pressure mercury lamp (100 W) for 0.5 h. Subsequently, the suspension was filtered and rinsed with deionized water for several times, and the powders were dried at 60 °C in a preheated oven. Finally, the obtained Ag/N–TiO₂ photocatalysts were stored in a glass desiccator.

**Materials characterization**

The structure and the morphology of Ag/N–TiO₂ photocatalysts were observed by Transmission Electron Microscope (TEM, JEM-100CX, JEOL, Japan). The crystallinity of the catalysts was characterized by X-ray diffraction (XRD, D/max-2200/PC, Rigaku Corporation, Japan) with Cu Kα radiation, operating at 40 kV and 30 mA, where λ = 0.15418 nm for the Cu Kα line. A diffuse reflectance UV–vis spectrophotometer (DRS, TU-1901) was used to obtain the absorption spectra of samples. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer), binding energies were calibrated by using the containment carbon (C 1s = 284.6 eV).

**Photocatalytic activity measurement**

The photocatalytic activity was evaluated through decomposition of methyl orange (MO) solution with a concentration of 10 mg/L. A 1,000 W halogen xenon lamp was used as the light source of the homemade photoreactor, surrounded with a water circulation facility at the outer wall through a quartz jacket. The short wavelength components (<400 nm) of the light were cut off using a glass optical filter. The distance between the lamp and the center of the beaker was 100 cm. For a typical photocatalytic experiment, a total of 0.05 g of catalyst powders was added to 50 ml of the above methyl orange solution in the beaker with stirring. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium. Samples were taken out at regular time intervals. The concentration of MO was monitored at 464 nm by spectrophotometry with a UNICO 7200 Spectrophotometer.

**RESULTS AND DISCUSSION**

**Crystal structure and morphology**

To determine the crystal phase composition of TiO₂, N–TiO₂ and Ag/N–TiO₂, X-ray diffraction (XRD) measurements were carried out over the diffraction angle (2θ) 20–70°, as shown in Figure 1. No obvious difference is observed among these samples, because all samples consist of anatase as the major crystalline phase. Unexpectedly, no XRD peaks corresponding to Ag can be distinguished for all Ag/N–TiO₂ samples, which might be due to the well dispersed nanocrystalline Ag particles in the TiO₂ matrix (Chang et al. 2008). According to Scherrer’s equation, 

\[
L_c = \frac{K \lambda}{\beta \cos \theta}
\]

where λ is the X-ray wavelength, β is the FWHM of the diffraction line, θ is the diffraction angle, and K is a constant, which has been assumed to be 0.9), and based on the full width at half maximum (FWHM) of the peak at 25.34°, an average particle diameter of about 10 nm can be calculated for N–TiO₂ and Ag/N–TiO₂, which is consistent with the measured value observed for HRTEM image (Figure 2). Unfortunately, small dark silver nanoparticles can be found, which may be ascribed to the metallic silver nanoparticles on the surface of Ag/N–TiO₂.

![Figure 1](https://iwaponline.com/wst/article-pdf/65/6/1027/442545/1027.pdf)
A highly dispersed state of silver nanoparticles benefits the separation of photogenerated electron–hole pairs.

**UV–vis absorption spectra**

The UV–vis absorption spectra of different samples are presented in Figure 3. Comparing DRS between TiO$_2$ and N–TiO$_2$, the results indicate that doping nitrogen by this method can give rise to a clear red-shift in the optical response of TiO$_2$ photocatalysts. Furthermore, N–TiO$_2$ shows higher visible absorbance. From the results, we can predict that N–TiO$_2$ should show high photocatalytic activity under visible light irradiation. Comparison of DRS between N–TiO$_2$ and Ag/N–TiO$_2$, Ag/N–TiO$_2$ absorbance plot shows a higher visible-light shift than that of N–TiO$_2$, and the Ag/N–TiO$_2$ has a stronger optical absorbance in the visible light region. The comparative data suggest that silver additive promotes visible light absorption of N–TiO$_2$ photocatalysts. This could be resulting from the surface plasmon absorption due to spatially confined electrons in Ag$^0$ particles (Li et al. 2009). It is also inferred that the Ag nanoparticles are highly dispersed on the N–TiO$_2$ synthesized by UV photoreduction process and this increase of metal nanoparticle dispersion results in increased interaction between Ag and N–TiO$_2$ particles leading to broadening of surface plasmon absorption (Ko et al. 2011).

**XPS spectra**

Ag/N–TiO$_2$ shows the stronger absorption in the visible light region (Figure 3), thereafter, the chemical states of the doped nitrogen and the loading Ag were investigated by XPS. Although there has been much work on the nitrogen doped TiO$_2$, the diverse chemical states of doping nitrogen species from different synthesis methods are still under discussion (Varley et al. 2011). It can be seen from Figure 4(a) that N 1s peak is found around 398.4 eV. We attribute the peak to the N/C anion incorporated in the TiO$_2$ as N–Ti–O structural feature, which is consistent with the characteristics in other literature (Xing et al. 2013). This is also further supported by the results of XPS spectra for the Ti$^{2+}$ region (Figure 4(b)). The Ti$^{2+}_{3/2}$ and Ti$^{2+}_{1/2}$ core levels of the N–TiO$_2$ appear at 457.9 and 463.7 eV, respectively. According to the XPS standard spectrum, the Ti$^{2+}_{3/2}$ peak of TiO$_2$ should be at 458.8 eV (Wang et al. 2008). The decrease of the binding energy of Ti$^{2+}_{3/2}$ after nitrogen doping shows that the electronic interaction of Ti with anions is considerably different from that of TiO$_2$. Because of the lower electronegativity of nitrogen compared to oxygen, partial electron transfer can occur from the N to the Ti. As a result, the electron density around the anion decreases, resulting in the increase in electron density around the cation (Sathish et al. 2005). This further testified that nitrogen incorporates into the lattice and substitutes for oxygen. In Figure 4(c), the Ag$^{3d}$ spectra of Ag–TiO$_2$ has two individual peaks at 373.3 and 367.7 eV, which can be attributed to Ag$^{3d}_{3/2}$ and Ag$^{3d}_{5/2}$ binding energies, respectively. It is important to note that the peak positions of Ag$^{3d}$ shift remarkably to the lower binding energy compared with that of bulk Ag (Ag$^{3d}_{3/2}$, 374.3 eV and Ag$^{3d}_{5/2}$, 368.5 eV) (Zheng et al. 2008). Thus, a strong interaction between metallic Ag and N–TiO$_2$ nanocrystals
can be inferred from the shift of the binding energy of metallic Ag.

**Photocatalytic activities**

The photocatalytic degradation curves of MO over TiO$_2$, N–TiO$_2$ and Ag/N–TiO$_2$ photocatalysts under visible light irradiation are shown in Figure 5. As a comparison, photocatalysis without anything was also performed under identical conditions, the change of MO concentration in 120 min was negligible. And TiO$_2$ could only degrade 8% of MO. Luckily, MO can be effectively degraded in the presence of N–TiO$_2$, and the degradation efficiency reaches up to about 37% in 120 min. Interestingly, Ag/N–TiO$_2$ is very effective at degrading MO, up to 54% of MO can be degraded in 120 min. The apparent rate constant ($k$) has been chosen as the basic kinetic parameter for the different photocatalysts, which was fitted by the equation $\ln(C/C_0) = -kt$, where $k$ is apparent rate constant, $C$ is the solution-phase concentration of organic pollutant (in this case, MO), and $C_0$ is the initial concentration of MO. Figure 6 reveals that the photodegradation of MO over photocatalysts follows first-order kinetics. The apparent rate constants of MO degradation under visible light irradiation are $7.34 \times 10^{-4}$, 0.0038, 0.0061 min$^{-1}$ for TiO$_2$, N–TiO$_2$, Ag/N–TiO$_2$, respectively. The photocatalytic efficiency of N–TiO$_2$ is estimated to be about five times higher than that of TiO$_2$. The stronger absorption of N–TiO$_2$ in the visible light region must be an important reason. Nitrogen doping would result in narrowing the banding energy of the sample, therefore N–TiO$_2$ can be excited under visible light irradiation, resulting in the formation of reactive oxygen species (including superoxide anion radicals, hydrogen peroxide and hydroxyl radicals) (Zhang et al. 2009), which can break down MO to smaller fragments that eventually completely decompose into simple inorganic minerals. By comparing the apparent rate constant of

![Figure 4](https://iwaponline.com/wst/article-pdf/65/6/1027/442545/1027.pdf)

**Figure 4** | X-ray photoelectron spectra of Ag/N–TiO$_2$: (a) N 1s, (b) Ti2p and (c) Ag3d.

![Figure 5](https://iwaponline.com/wst/article-pdf/65/6/1027/442545/1027.pdf)

**Figure 5** | Photocatalytic activity for decolorization of MO dye solutions under visible light irradiation by the photocatalyst respectively: (a) blank, (b) TiO$_2$, (c) N–TiO$_2$ and (d) Ag/N–TiO$_2$ nanoparticles.
Ag/N-TiO₂ with that of N-TiO₂, it is concluded that surface modification of N-TiO₂ with Ag nanoparticles improves the photocatalytic activity under visible light. The positive effect of noble metal deposits may be attributed to not only increase in visible light absorption resulting from the surface plasmon resonance (Li et al. 2009), but also enhancement of charge separation \( e^-/h^+ \) by trapping photoelectrons on silver nanoparticles. It has been known that when a metal and a semiconductor of different Fermi level position come into contact a Schottky barrier can be formed. In our experiment, contact between Ag and N-TiO₂ surface will lead to the formation of a Schottky barrier, resulting in the transfer of photogenerated electrons into Ag, which acts as electron trapping islands inhibiting \( e^-/h^+ \) recombination (Ko et al. 2011).

**Effect of Ag amount on the photocatalysis**

In order to investigate the effects of Ag amount on the photocatalytic activity, the amount of Ag was adjusted by controlling the volume of the AgNO₃ solution in the process of preparing Ag/N-TiO₂ photocatalyst. Observed from Figure 7, it is found that the 0.5 wt% Ag content was optimum to achieve the highest efficiency of the MO photodegradation for the N-TiO₂ nanocatalysts. The apparent rate constants of MO degradation under visible light irradiation are 0.0038, 0.0050, 0.0061, 0.0034 min⁻¹ for N-TiO₂, 0.2 wt% Ag/N-TiO₂, 0.5 wt% Ag/N-TiO₂, and 1.0 wt% Ag/N-TiO₂, respectively. By comparing the apparent rate constants, it is concluded that the photocatalytic activity of N-TiO₂ under visible light irradiation can be enhanced through loading the appropriate Ag content. However, excess amount of Ag is detrimental to the photocatalytic process. In this experiment, the apparent rate constants \( k \) of 1.0 wt% Ag/N-TiO₂ is even smaller than that of N-TiO₂. The adverse effect of excess Ag loadings on the photocatalytic activity of N-TiO₂, might be caused by the following two reasons. On the one hand, higher surface loadings may influence the penetration of visible light, leading to a decrease in the concentration of photogenerated charge carrier (Lu et al. 2008). On the other hand, at higher metal content than the optimum the over-accumulation of electrons on metal deposits could attract the photogenerated holes to the metal sites. This may encourage the recombination of charge carriers and the metal deposits behave in reverse as recombinant centers (Ren et al. 2009).

**CONCLUSIONS**

To modify the visible light absorption ability of TiO₂ photocatalyst, Ag nanoparticles loaded N-doped TiO₂ photocatalysts (Ag/N-TiO₂) were successfully fabricated via a two-step method to make the best use of the respective advantages of noble metal loading and nonmetal doping. Ag particles have little influence on the size and crystal phase of TiO₂ particles and the optimum Ag loading content is 0.5 wt%. The enhanced visible-light photocatalytic activity of Ag/N-TiO₂ should be ascribed to the synergistic effect of N-doping and Ag-loading, including the good visible light absorption and the effective electron-hole separations. This demonstrates Ag/N-TiO₂ to be a promising photocatalytic material for organic pollutant degradation under visible light irradiation.

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