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Enhanced Photocatalytic Activity of S-Doped TiO₂ Prepared *via* a Modified Sol-Gel Process

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S-Doped TiO₂ was prepared *via* modified sol-gel process. Transmission electron microscopy (TEM), N₂ adsorption, X-ray diffraction (XRD), UV-VIS spectroscopy and X-ray photoelectron spectroscopy (XPS) were conducted to characterize the prepared TiO₂ particles. It is shown that the prepared TiO₂ particles were around 10 nm with narrow particle size distribution. The addition of MCM-41 restricted the agglomeration and growth of TiO₂ particles, thus leading to the small particle size. The photocatalytic performance in the degradation of methylene blue indicated that S-doped TiO₂ showed much higher photocatalytic activity than pure TiO₂ under visible light. The sulfuration time and sulfuration temperature exhibited significant influence on the photocatalytic activity of prepared TiO₂ catalysts.

Key Words: TiO₂, Photocatalysis, Visible light, Sulfuration, Doping.

INTRODUCTION

Titanium dioxide is widely used for the mineralization of organic pollutants, because it exhibits strong oxidation activity under ultraviolet light[1]. Although TiO₂ has been widely investigated as a photocatalyst in the past decades, its low photo-quantum efficiency and low photocatalytic activity under visible light have limited its usage of solar energy. Therefore, modification of TiO₂ to extend its absorption edge toward the visible light region has been extensively pursued.

It is reported that TiO₂ doped with transition metals could absorb visible light and exhibited high photocatalytic activity under visible light irradiation[2]. However, the disadvantage of metal cation dopants is that they can serve as recombination centers for photogenerated electron-hole pairs, leading to a decreased activity[3]. Another effective modification method is non-metal doping. Asahi *et al.*[4], reported that the band gap of N-doped TiO₂ was narrowed by mixing N 2p and O 2p states, leading to enhanced activity in the decomposition of acetone and methylene blue under visible irradiation. Since then, various non-metal elements, such as N[4], S[5], I[6], P[7], B[8] and C[9], were used to modify TiO₂. Umebayashi *et al.*[5], reported that the gap band of TiO₂ had been narrowed by introducing sulfur into TiO₂. Recently, many methods, including oxidative heating[10], sol-gel[11], catalyzed hydrolysis[12], hydrothermal synthesis[13], ion implantation[14] and atomic layer deposition[15], have been reported to synthesize S-doped TiO₂. Among them, sol-gel method is one of the most widely used. Generally speaking, the TiO₂ prepared by sol-gel process is amorphous which need

the calcination procedure to form crystal TiO₂ and then used as photocatalyst. However, high temperature calcination generally gives rise to particle agglomeration and collapse of pore structure, leading to remarkable surface area reduction. The properties mentioned above are significantly important to the photocatalytic performance[1]. To resolve this problem, we report a modified sol-gel method to prepare S^{6+} doped TiO₂ using MCM-41 as hard template to inhibit the particles aggregation in this paper. The prepared S^{6+} doped TiO₂ catalysts were tested in the photocatalytic degradation of methylene blue under visible light. A possible mechanism for the photocatalysis was proposed.

EXPERIMENTAL

Siliceous MCM-41 was synthesized with the use of sodium silicate hydrate as the SiO₂ source and cetyltrimethyl-ammonium bromide as the template, following a procedure reported elsewhere[16]. The synthesized siliceous MCM-41 had a specific surface area of 1028 m² g⁻¹, a pore volume of 0.90 cm³ g⁻¹ and a BJH average pore size of 3.4 nm. 5 g tetrabutyl titanate was dissolved in 25 mL ethanol. 2 g MCM-41 was added into above solution under stirring. The formed suspension was stirred to form the gel. The gel was dried at 100 ºC for 2 h to obtain the precursor. The precursor was kept in H₂S flow (40 mL min⁻¹) for x h at different temperature (10 ºC/min). The obtained solid was added into 30 mL 10 % HF solution and stirred for 0.5 h to remove the MCM-41. The resulting product was washed with deionized water, separated by centrifugation and dried at 100 ºC for 8 h. The obtained

TiO_2 powder was denoted as MTS(x)-y, in which, x stands for the nitridation time (h), y stands for the sulfuration temperature. For comparison, two more samples MT(1)-500 and TS(1)-500 were prepared by the same procedure above but in the absence of sulfuration and MCM-41, respectively.

XRD patterns of the prepared TiO_2 samples were recorded on a Rigaku D/max-2400 instrument using CuK_α radiation (λ = 1.54 Å). TEM images were measured using a Philips Tecnai G220 model microscope. UV-VIS spectroscopy measurement was carried out on a JASCO V-550 model UV-VIS spectrophotometer, using $BaSO_4$ as the reflectance sample. Nitrogen adsorption was measured at -196 ºC on a Micromeritics 2010 analyzer. All the samples were degassed at 393 K before the measurement. BET surface area was calculated according to the adsorption isotherm. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al K_α radiation as the exciting source. The binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect.

Methylene blue (MB) was selected as model compound to evaluate the photocatalytic performance of the prepared TiO_2 particles in an aqueous solution under visible light irradiation. 0.1 g TiO_2 powders were dispersed in 100 mL aqueous solution of methylene blue (50 ppm) in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor and stirred for 0.5 h in darkness to achieve the adsorption equilibrium. In the photoreaction under visible light irradiation, the suspension was exposed to a 110 W high-pressure sodium lamp with main emission in the range of 400-800 nm and air was bubbled at 130 mL/min through the solution. The UV light portion of sodium lamp was filtered by 0.5 M $NaNO_2$ solution. All runs were conducted at ambient pressure and 30 ºC. At given time intervals, 4 mL suspension was taken and immediately centrifuged to separate the liquid samples from the solid catalyst. The concentrations of methylene blue before and after reaction were measured by means of a UV-VIS spectrophotometer at a wavelength of 665 nm. The percentage of degradation D % was determined as follows:

$$D\,(\%) = \frac{A_0 - A}{A_0} \times 100\,\%$$

(1)

where A_0 and A are the absorbances of the liquid sample before and after degradation, respectively. Commercial Degussa P25 TiO_2 (anatase/rutile = 75/25) with a specific surface area of 50 m^2/g was used for comparison.

RESULTS AND DISCUSSION

It is reported that the phase composition and particle size of TiO_2 have significant influence on its photocatalytic activity[1]. The XRD patterns of the P25 and MTS(1)-y (Fig. 1) indicated that all TiO_2 samples were pure anatase phase. The particle sizes of the catalysts were calculated by their XRD patterns according to the Debye-Scherrer equation[17]. The results indicated that the particle sizes increased with increasing the sulfuration temperature.

Fig. 2 shows the TEM and HRTEM micrographs of the MTS(1)-500 and TEM of TS(1)-500. It is shown that MTS(1)-500 own almost the same particle size around 10 nm. Moreover,
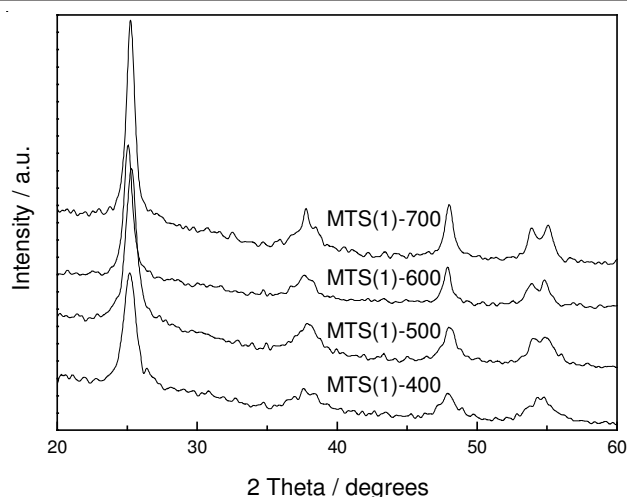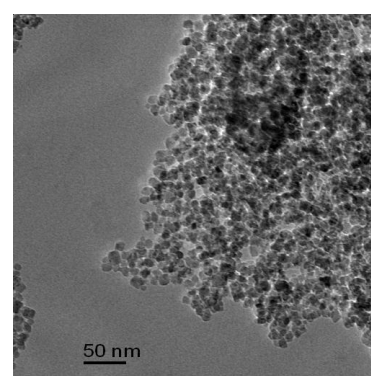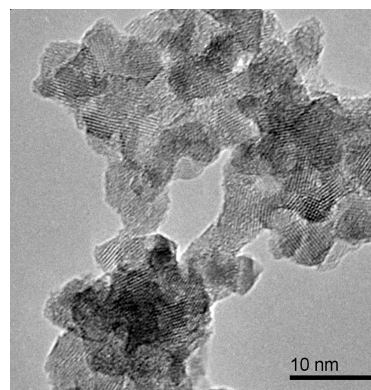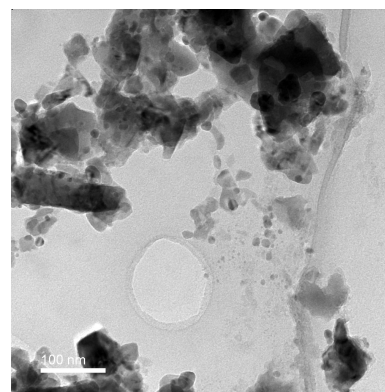

Fig. 1. XRD patterns of the prepared MTS(1)-y

(a)

(b)

(c)

Fig. 2. TEM (a) and HRTEM (b) of MTS(1)-500 and TEM (c) of TS(1)-500

MTS(1)-500 also exhibit narrow particle size distribution. The HRTEM micrograph shows that MTS(1)-500 particles had a good crystalline structure. However, in the absence of MCM-41, the obtained TS(1)-500 exhibited a much larger particle size than that of MTS(1)-500. This indicated that the addition of MCM-41 restricted the agglomeration and growth of TiO_2 particles, thus leading to the small particle size.

The UV-VIS diffuse reflectance spectra of prepared samples are shown in Fig. 3. MT(1)-500 showed no absorption in the visible light region. However, after sulfuration treatment, MTS(x)-500 exhibited obvious shifts of the absorption band into the visible light region. This shift to the visible light region is possibly due to the incorporation of sulfur into TiO_2 framework, leading to a slight alteration of crystal and electronic structures. TiO_2 is an indirect gap semiconductor. The band gap can be estimated from the tangent lines in the plots of the square root of the Kubelka-Munk functions against the photon energy[18]. The band gap energies of prepared samples were estimated to be 3.0 and 2.8 eV for MT(1)-500 and MTS(x)-500, respectively. Umebayashi *et al.*[5], calculated the density of states (DOS) of the valence band and conduction band for S-doped TiO_2, which showed that S 3p state contributed to the formation of the valence band with O 2p and Ti 3d states, resulting in a narrowing in the band gap energy. Therefore, it is proposed that the red shift of the absorption of TiO_2 by the sulfuration treatment might be ascribed to the narrowing of the band gap.
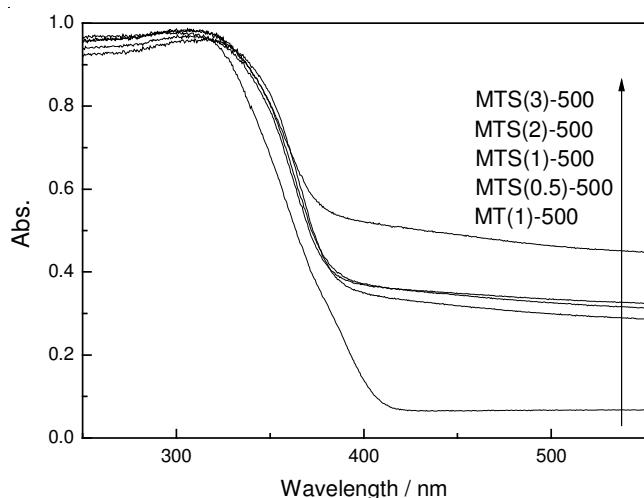

Fig. 3. UV-VIS diffuse reflectance spectra of prepared samples

Fig. 4 shows the XP spectra of prepared samples in the region of S 2p (a) and Ti 2p (b). In the spectrum of S 2p region, the peak around 168.2 eV which attributed to S^{6+} was observed for MTS(1)-500. This indicated that the sulfur atoms were incorporated into TiO_2 framework. In the region of Ti 2p, an obvious shift to lower binding energy was observed for MTS(1)-500 compared with MT(1)-500. The shifts of binding energy for Ti^{4+} species may be associated with the formation of S-Ti-O structure in MTS(1)-500 after sulfuration treatment. Due to the higher electronegativity of oxygen, partial electrons of S might be transferred from S to Ti, leading to the increased electron density of Ti. This increased electron density led to the decreased binding energy of MTS(1)-500.
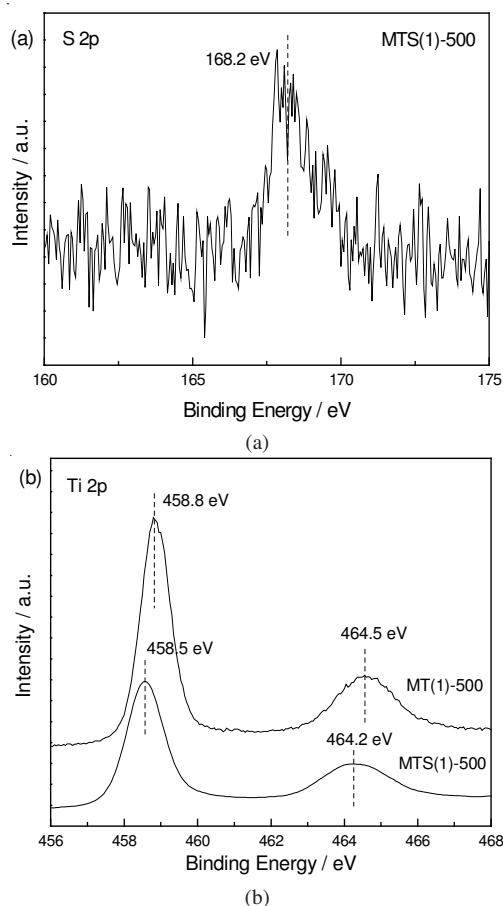

Fig. 4. XP spectra of prepared samples in the region of S 2p (a) and Ti 2p (b)

The photocatalytic activities of MTS(1)-y under visible light are shown in Fig. 5. It is shown that the activity of prepared samples increased firstly and then decreased when the temperature beyond 500 ºC. More than 80 % methylene blue were degraded after 4 h in the presence of MTS(1)-500. This may be attributed to the increased particle size with increasing the sulfuration temperature. The number of surface active sites will decrease with the increase in the particle size, leading to the decrease in the surface charge carrier transfer rate in photocatalysis process and thus to the increase in the electron-hole recombination[1].
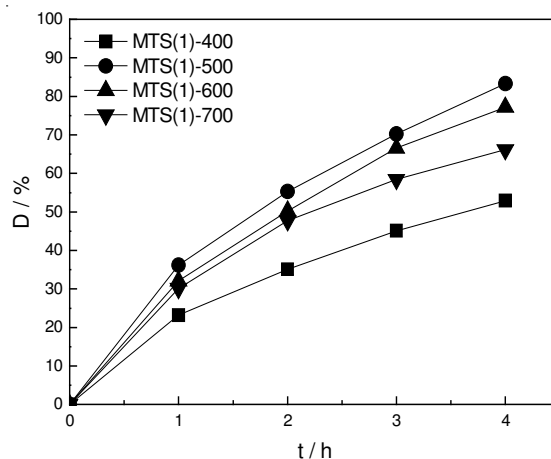

Fig. 5. Photocatalytic activities of MTS(1)-y under visible light

The photocatalytic activities of MTS(x)-500 and TS(1)-500 under visible light are shown in Fig. 6. MTS(x)-500 showed much higher photocatalytic activity than that of TS(1)-500. Among them, MTS(1)-500 showed the highest photocatalytic activity, indicating that there existed an optimal doping content. The enhanced photocatalytic activity after sulfuration treatment must result from the doping of sulfur on TiO_2, which gave rise to the narrowed band gap and thus to the enhanced absorption in the visible region. When the doping content beyond the optimal value, the particle sizes increased sharply, leading to the decreased activity.
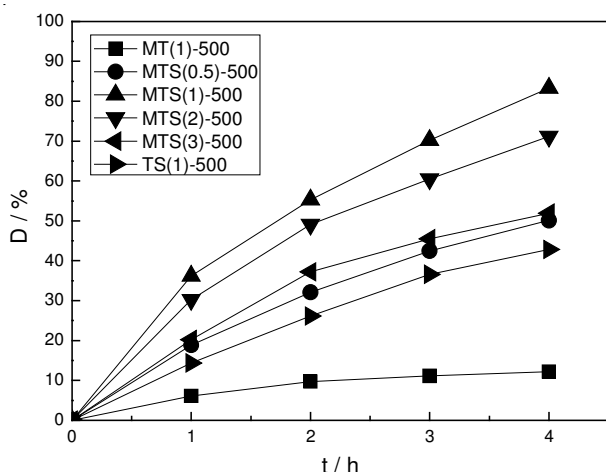

Fig. 6. Photocatalytic activities of MTS(x)-500 and TS(1)-500 under visible light

Conclusion

S-Doped TiO_2 was prepared *via* modified sol-gel process. The prepared TiO_2 particles were around 10 nm with narrow particle size distribution. The addition of MCM-41 restricted the agglomeration and growth of TiO_2 particles, thus leading to the small particle size. The photocatalytic performance in the degradation of methylene blue indicated that S-doped TiO_2 showed much higher photocatalytic activity than pure TiO_2 under visible light. The sulfuration time and sulfuration tempe-rature exhibited significant influence on the photocatalytic activity of prepared TiO_2 catalysts. The optimal sulfuration time and sulfuration temperature are 1 h and 500 ºC.

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