Enhancing the photocatalytic activity of Ag-TiO$_2$/SiO$_2$ and its potential application in water treatment

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Abstract Ag-doped TiO$_2$/SiO$_2$ with visible light response was prepared by a simple sol-gel method using titanium $n$-butoxide (TNB), tetraethoxysilane (TEOS) as precursors, and silver nitrate (AgNO$_3$). The synthesized Ag-TiO$_2$/SiO$_2$ were characterized by SEM, XRD, PL (photoluminescence) emission and UV-Vis absorption spectroscopy. Their photocatalytic activities were evaluated by treating aqueous solutions of phenol under simulated visible light illumination. The role of silver doped was investigated in the range 1% – 5% (molar ratio), resulting in the best bandgap value of 2.93 eV for Ag(3%)-TiO$_2$/SiO$_2$ compared to 3.18 eV for the un-doped TiO$_2$/SiO$_2$. Consequently, the best phenol treating yield – about 97% after 4 hours – was obtained using Ag(3%)-TiO$_2$/SiO$_2$. So the synthesized Ag(3%)-TiO$_2$/SiO$_2$ might serve as a potential photocatalyst for water treatment using visible lights.

Keywords: doped TiO$_2$/SiO$_2$, sol-gel, photocatalysis, water treatment, phenol residues

1. Introduction
Titanium dioxide TiO$_2$ is recognized as the most efficient and environmentally benign photocatalyst, which is capable to treat various water pollutants. However, TiO$_2$ application in this field is limited by its wide energy bandgap (3.2 eV), its relatively low specific surface area and ease electron-hole recombination [1, 2]. Hence, many attempts to improve the photocatalytic characteristics of TiO$_2$ modifying its microstructure with various elements and/or compounds have been reported [3, 4]. Among others, Silicon dioxide SiO$_2$ appeared very suitable macro-component due to its positive effects on the resulting TiO$_2$/SiO$_2$ composites [3]. The presence of SiO$_2$ retarded the growth of TiO$_2$ particles as well as the anatase-rutile phase conversion. Consequently, the particle sizes of resulting SiO$_2$/TiO$_2$ composites decreases and the specific surface areas increases comparing to those of the pure TiO$_2$ [2, 5-7]. Moreover, the combination SiO$_2$/TiO$_2$ is believed to delay the photoelectron–hole recombination and therefore to increase the photocatalytic activity of the resulting composites, too [8]. The last effects could be achieved doping TiO$_2$ with noble metals. Among them, silver Ag is considered more relevant for industrial applications due to its non-toxicity, special oxygen adsorption behavior, and relatively acceptable cost [9].
Moreover, doping Ag would form Ag-rich clusters overlapping with TiO$_2$ particles which results in plasmon resonance at the interfaces. The overlapping Ag-clusters/TiO$_2$ also promotes the interfacial charge transfer process, therefore lowers the recombination rates [10].

In this paper, efforts to prepare various Ag doped SiO$_2$/TiO$_2$ composites to enhance their photocatalytic activity under illuminating visible lights are described and discussed.

2. Experiment

2.1. Preparation of Ag-TiO$_2$/SiO$_2$ composites

Titanium n-butoxide Ti(OCH$_2$CH$_3$CH$_2$CH$_3$)$_4$ – TNB (99%) and tetraethyl orthosilicate Si(OC$_2$H$_5$)$_4$ – TEOS (99%) were purchased from Sigma-Aldrich. Silver nitrate AgNO$_3$ (99 %) was purchased from Xilong, China. Acetyl acetone CH$_3$COCH$_2$COCH$_3$ – ACAC (99 %), polyethylene glycol – PEG (av. MW 20,000), and ethanol – EtOH (99.5%) were purchased from Merck. Other chemicals of reagent grade and double distilled water were used throughout this work.

Ag-doped TiO$_2$/SiO$_2$ and the reference un-doped TiO$_2$/SiO$_2$ composites as well as pure TiO$_2$ were prepared through a typical sol-gel method. For preparing Ag-doped TiO$_2$/SiO$_2$ composites, solution A containing TNB, ACAC and HNO$_3$ (molar ratio 1: 1: 1), AgNO$_3$ (1, 3 and 5 moles % relating to TiO$_2$) and EtOH was vigorously stirred at 90$^\circ$C for 1 hour, then cooled to room temperature for 30 min. Solution B containing TEOS, HNO$_3$, PEG, H$_2$O (mass ratio 2: 11: 3: 35) and EtOH was vigorously stirred for 1 hour. Solution A was then dropwise added to solution B under stirring at room temperature to create mixtures with the Ti/Si molar ratio 95:5, then aged at ambient temperature for 40 hrs., dried at 100$^\circ$C for 3 hrs. and calcined in air at 500$^\circ$C for 2 hrs. The above mentioned solution A did not contain AgNO$_3$, respectively solution B was not necessary when the reference un-doped composites and pure TiO$_2$ were prepared.

2.2. Characterization of prepared composites

All prepared composites were characterized with X-ray diffraction (XRD) using a D2 Phaser (Bruker) with Cu K$_{α}$ radiation ($λ = 0.154$ nm) for crystallinity. Their surface morphology was investigated using JSM-6500F JEOL Scanning Electron Microscope (SEM). Their bandgap energy was estimated from diffuse reflectance spectra (DRS) ranging from 850 to 220 nm, at the rate of 400 nm/min using a Solid UV–Vis JASCO V-550 Spectrophotometer. Their photoluminescence (PL) emission spectra were obtained using an iHR 550 spectrophotometer at room temperature.

2.3. Determination of photocatalytic activity

The photocatalytic activity of all prepared materials was evaluated monitoring phenol decomposition in model aqueous samples using a laboratory-scale photoreactor. In each experiment, 200 mg prepared material was dispersed in 200 mL phenol solution (10 mg/L). During the photocatalytic process at room temperature, this dispersion was constantly stirred and illuminated by a compact lamp (Natural light PT 2191-ExoTerra) emitting in the wavelength range 390–640 nm, with the strongest intensity at ca. 540 nm. The dispersions were stirred in the dark for 60 min to ensure the establishment of the adsorption-desorption equilibrium before turning on the lamp. After certain time intervals, 5 mL samples were taken from the dispersion, their aqueous phase separated, and phenol concentration determined according to a standard procedure [11] adding 4-amino antipyrine and potassium ferric cyanide at pH 10 and monitoring their absorption peak at 510 nm by a Hitachi UV-Vis spectrometer.

3. Result and discussion

3.1. Characteristics of prepared composites

The XRD patterns of prepared TiO$_2$, TiO$_2$/SiO$_2$, Ag(1%)-TiO$_2$/SiO$_2$, Ag(3%)-TiO$_2$/SiO$_2$ and Ag(5%)-TiO$_2$/SiO$_2$ are summarized in Fig.1. All patterns show the typical peaks of TiO$_2$ anatase phase (JCPDS 21-1272), e.g. those at diffraction angles $2θ = 25.2^\circ$ (101), 36.9$^\circ$ (004), 48.24$^\circ$ (200), 54.86$^\circ$ (211) and
63.01° (213). No typical peaks of TiO$_2$ rutile phase can be observed on the XRD patterns of the composites while SiO$_2$ presence inhibits the anatase to rutile phase transition. In addition, no typical peaks of SiO$_2$ were observed, indicating that SiO$_2$ exists in composites in amorphous state. Moreover, peak intensities in the XRD patterns of composites are slightly affected, indicating that Si substitution in the TiO$_2$ lattice should be taken into account, too. It is worth to note that no XRD patterns of the composites exhibit any peaks indicating impurity phases such as Ag metal or its oxides, even at the highest applied content (5 mol. % Ag). This could be interpreted positively as the TiO$_2$ anatase phase was not disturbed upon Ag doping. On the other side, however, the content of doped Ag might be too low to be registered on the XRD patterns. Unfortunately, an additional ICP-MS analysis to prove the Ag content in composites has not been performed.

**Figure 1:** X-ray patterns of prepared TiO$_2$, un-doped and Ag-doped TiO$_2$/SiO$_2$ composites

The crystallite size of prepared composites was determined based on the XRD spectrum according to the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D is the average crystallite size (nm), K is the particle shape factor – taken as 0.89, $\lambda$ is the X-ray wavelength corresponding to the Cu-K$_\alpha$ irradiation, $\beta$ is the full width at half maximum (FWHM) and $\theta$ is the angle of diffraction peak [12, 13]. Based on the main diffraction peak of the anatase phase (101), the crystallite sizes of prepared composites are evaluated and summarized in Table 1. It is worth to note the crystallite size sharply decreased from 14.55 nm in TiO$_2$ to 5.57 nm in TiO$_2$/SiO$_2$. Effects of doped Ag onto the crystallite sizes in prepared composites are not very strong.

**Table 1.** Crystallite size of TiO$_2$, TiO$_2$/SiO$_2$, Ag(1%)-TiO$_2$/SiO$_2$, Ag(3%)-TiO$_2$/SiO$_2$ and Ag(5%)-TiO$_2$/SiO$_2$ composites.

| Sample               | Crystallite size (nm) |
|----------------------|------------------------|
| TiO$_2$              | 14.55                  |
| TiO$_2$/SiO$_2$      | 5.57                   |
| Ag(1%)-TiO$_2$/SiO$_2$| 5.24                   |
| Ag(3%)-TiO$_2$/SiO$_2$| 5.35                   |
| Ag(5%)-TiO$_2$/SiO$_2$| 5.09                   |

The morphology of prepared TiO$_2$, TiO$_2$/SiO$_2$ and Ag(3%)-TiO$_2$/SiO$_2$ are summarized in Fig.2. It is clearly shown the prepared nanoparticles are spherical with aggregations of tiny crystals. Among all prepared products, the pure TiO$_2$ exhibits the largest crystallite size, the composites TiO$_2$/SiO$_2$ and Ag(3%)-TiO$_2$/SiO$_2$ exhibit similar crystallite sizes, smaller than those of pure TiO$_2$. 

Figure 2: SEM images of (a) TiO$_2$; (b) TiO$_2$/SiO$_2$; (c) Ag(3%)-TiO$_2$/SiO$_2$

Figure 3 shows the relationships between $(a\nu v)^2$ and $\nu v$ (in eV), whereby the bandgaps of TiO$_2$, TiO$_2$/SiO$_2$, Ag(1%)-TiO$_2$/SiO$_2$, Ag(3%)-TiO$_2$/SiO$_2$, Ag(5%)-TiO$_2$/SiO$_2$ were determined as 3.15, 3.18, 3.17, 2.93 and 2.89 eV, respectively. The resulting values for band gap energy of prepared pure TiO$_2$ and TiO$_2$/SiO$_2$ composites only slightly differ from each other. So the main role of SiO$_2$ in prepared composites is rather delaying the photoelectron-hole recombination than lowering the bandgap.

Figure 3: Band-gap energy of prepared TiO$_2$, un-doped and Ag-doped TiO$_2$/SiO$_2$ composites

The role of doped Ag in prepared composites, besides the plasmon resonance effect mentioned above, is evidently shown as the bandgap energy decreases with increasing the percentage of doped Ag from 1% to 5%, so the photocatalytic activity under visible light illumination would be enhanced [13].

Figure 4: Photoluminescence spectra of TiO$_2$/SiO$_2$ and Ag(3%)-TiO$_2$/SiO$_2$
Photoluminescence spectroscopy (PL) is an effective technique for discovering the electronic structure, transmission and recombination rate of electron-hole pairs in semiconductors [14, 15]. The PL spectra of the TiO$_2$/SiO$_2$ and Ag(3\%)-TiO$_2$/SiO$_2$ sample are shown in Fig.4. It can be observed that the emission peak of TiO$_2$/SiO$_2$ is almost similar to that of Ag(3\%)-TiO$_2$/SiO$_2$, but the PL intensity of the Ag(3\%)-TiO$_2$/SiO$_2$ is lower than that of TiO$_2$/SiO$_2$. The intensity of the PL spectrum is lively related to the recombination for photo-generated electrons. Lower PL intensity indicates a delay in recombination rate, which also implies that a large number of photogenic electrons and holes are involved in the photochemical transformation. So the photocatalytic activity of Ag(3\%)-TiO$_2$/SiO$_2$ is improved comparing with other composites [14].

3.2. Photocatalytic activity of prepared composites

Fig.5 compares the photocatalytic activity of prepared composites at the same dosage 1.0 g/L to 10 mg/L phenol solution under the same illuminating conditions for 4 hrs. After 4 illumination hours, the phenol removing efficiency sharply increased from 38.5 \% to 91.5\% changing the pure TiO$_2$ to the un-doped TiO$_2$/SiO$_2$ composite, respectively. The later was further slightly increased to 97.4\% applying the Ag(3\%)-TiO$_2$/SiO$_2$ composite. What is more interesting, both the lower (1\%) and higher (5\%) contents of doped Ag resulted lower phenol removing efficiency, 82.6 \% and 41.4 \% respectively. Table 2 also summarizes values for the observed phenol removing rate constant and their confidence level which were calculated by the least squared method and therefore less prone to the experimental errors.

![Figure 5](image)

**Figure 5:** Photocatalytic efficiency of the prepared composites in phenol degradation

**Table 2.** Phenol degradation efficiency and observed reaction rate constants using prepared composites

| Catalyst          | Phenol Degradation (%) | Rate Constant $k$ (min$^{-1}$) | $R^2$ |
|-------------------|------------------------|-------------------------------|-------|
| TiO$_2$           | 38.5                   | 0.0020                        | 0.961 |
| TiO$_2$/SiO$_2$   | 91.5                   | 0.0082                        | 0.993 |
| Ag(1\%)-TiO$_2$/SiO$_2$ | 82.6               | 0.0069                        | 0.988 |
| Ag(3\%)-TiO$_2$/SiO$_2$ | 97.4               | 0.0114                        | 0.990 |
| Ag(5\%)-TiO$_2$/SiO$_2$ | 41.4               | 0.0023                        | 0.988 |

Based on the results obtained, it is evident that under the conditions investigated, retarding respectively delaying the photoelectron–hole recombination played a much more important role than decreasing the
bandgap. The un-doped TiO$_2$/SiO$_2$ composite exhibits the same respectively a slightly higher bandgap, its photocatalytic efficiency in phenol removing is substantially higher compared to the pure TiO$_2$. Doping Ag into TiO$_2$/SiO$_2$ composites evidently decreased the bandgap values. On the other side doping Ag apparently facilitates the photoelectron–hole recombination. Therefore, Ag(1%)-TiO$_2$/SiO$_2$ exhibits slightly lower efficiency and removing rate constant comparing to those of un-doped TiO$_2$/SiO$_2$. This effect certainly increases with increasing the content of Ag doped and becomes predominant at 5% Ag, when Ag(5%)-TiO$_2$/SiO$_2$ exhibits practically the same photocatalytic efficiency as the pure TiO$_2$, i.e. the opposite effects of “doped” SiO$_2$ and Ag in this composite balance each other. The best efficiency obtained with Ag(3%)-TiO$_2$/SiO$_2$ could only be attributed to its enhanced photonic efficiency [14]. The plasmon resonance at interfaces seems to have better conditions in Ag(3%)-TiO$_2$/SiO$_2$ comparing to Ag(1%)-TiO$_2$/SiO$_2$, so the photoelectron–hole recombination is overridden. However, additional experiments should be performed to verify these arguments, e.g. preparing composites with another contents of doped Ag as well as verifying their real chemical composition by ICP-MS.

Figure 6: Effect of the dosage of Ag(3%)-TiO$_2$/SiO$_2$ on phenol (10ppm) degradation

Fig.6 shows effects of applied Ag(3%)-TiO$_2$/SiO$_2$ dosage on the phenol degradation efficiency. As expected and in accordance with observations described in the literatures, phenol degradation efficiency and rate increased with increasing the dosage of Ag(3%)-TiO$_2$/SiO$_2$ to ca. 3.0 g/L, when almost complete phenol degradation was registered after 3.5 hours illumination. Further increasing this dosage, e.g. to 4.0 g/L, slightly decreases the phenol degradation efficiency due to shielding effects of dense suspensions against the illumination [16-18].

Figure 7: Effects of the initial phenol concentration onto its degradation efficiency
Fig. 7 demonstrates effects of the initial phenol concentration on its degradation efficiency. For the first glance the phenol degradation efficiency decreases with increasing the initial phenol concentration. Similar results were reported using another (photo-)catalysts, too. It is due to the fixed number of active adsorption/catalytic sites on the catalysts’ surface which limits the reaction rates and consequently the treatment efficiency at certain time intervals [19]. In order to reach the required efficiency, either increasing the catalyst’s dosage or prolonging the treatment time should be taken into account, depending on the actual situation.

4. Conclusions

Several Ag-doped TiO$_2$/SiO$_2$ composites preparing by a sol-gel method exhibit their crystallite sizes of ca. 5.2 nm, the spherical shape of particles in aggregates, their prevailing anatase phase in microstructure, lower bandgaps values and PL intensities, and enhanced photocatalytic activity under visible light illumination. From their applicability viewpoint, the Ag(3%)-TiO$_2$/SiO$_2$ or even the un-doped TiO$_2$/SiO$_2$ (molar ratio Ti/Si = 95/5) proved to be suitable for treating phenol and possibly other organic residues in water. However, further investigation should be performed to clear up the roles of doped Ag and SiO$_2$ in lowering both the bandgap and the photoelectron–hole recombination rate.

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References

[1] Cui L, Song Y, Wang F, Sheng Y and Zou H 2019 Appl. Surf. Sci. 488 284-92.
[2] Feng H, Xu H, Feng H, Gao Y and Jin X 2019 Chem. Phys. Lett. 733 136676
[3] Guo N, Liang Y, Lan S, Liu L, Ji G, Gan S, Zou H and Xu X 2014 Appl. Surf. Sci. 305 562-74.
[4] Tahir M 2018 J. Clean. Prod. 170 242-50.
[5] Sun R, Chen Z, Yang Y, Peng J and Zheng T 2019 Mater. Res. Express 6 046409
[6] Cheng Y, Luo F, Jiang Y, Li F and Wei C 2018 Colloids Surf. A: Physicochem. Eng. Aspects 554 81-5.
[7] Wu L, Yan H, Xiao J, Li X and Wang X 2017 Ceram. Int. 43 9377-81.
[8] Dong R, Na C, Wang X, Zhang H, Li Z, Chen Z and Jin C 2016 Mater. Chem. Phys. 174 81-90.
[9] Elsellami L, Dappozze F, Houas A and Guillard C 2017 Superlattice. Microst. 109 511-8.
[10] Vargas Hernández J, Coste S, García Murillo A, Carrillo Romo F and Kassiba A 2017 J. Alloy. Compd. 710 355-63.
[11] Medjor W, Wepuaka C and Godwill S 2015 Int. Res. J. Pure Appl. Chem. 7 150–6.
[12] Tabasishde S, Maleki A, Shahmoradi B, Gahremanei E and McKay G 2017 Sepn. Purif. Technol. 189 186-92.
[13] Fan M, Fan G, Zhang G and Zheng S 2019 Res. Chem. Intermed. 46 1127-39.
[14] Ali T, Ahmed A, Alam U, Uddin I, Tripathi P and Muneer M 2018 Mater. Chem. Phys. 212 325-35.
[15] Chen X, Sun H, Zhang J, Guo Y and Kuo D-H 2019 J. Mole. Liquids 273 50-7.
[16] Chiou C H and Juang R S 2007 J. Hazard. Mater. 149 1-7.
[17] Rabhi S, Belkacemi H, Bououdina M, Kerrami A, Ait Brahem L and Sakher E 2019 Mater. Lett. 236 640-3.
[18] MirzaHedayat B, Noorisepehr M, Dehghanifard E, Esrafili A and Norozi R 2018 J. Mole. Liquids 264 571-8.
[19] Singh N and Balomajumder C 2016 Appl. Water Sci. 7 3241-55.
[20] Hemmati Borji S, Nasseri S, Mahvi A H, Nabizadeh R and Javadi A H 2014 J. Environ. Health Sci. Eng. 12 101.