Materials Research Express

PAPER

Exceptional photocatalytic activity for Ag, Cr-SrTiO₃ activated by H₂O₂ for removal of organic pollutants

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Keywords: Ag, Cr-decorated, H₂O₂, photocatalysis, SrTiO₃

Abstract

Ag, Cr-SrTiO₃ nanocomposite was successfully prepared through the one-pot situ solvothermal method by using butyl titanate, CrCl₃·6H₂O and Sr(NO₃)₂ as raw materials. The obtained nanocomposites were characterized by x-ray diffraction, scanning electron microscopy and x-ray photoelectron spectroscopy. UV-visible diffuse reflectance spectroscopy was used to investigate the optical properties and the results demonstrated the extension of spectral response from ultraviolet to visible light region. Compared with pure SrTiO₃, Ag, Cr-SrTiO₃ exhibited remarkable enhancement in adsorption and photocatalytic ability. More importantly, samples activated by H₂O₂ revealed extraordinary photocatalytic activity, which could remove 98.8% of MO within 60 min with 0.4 wt% Ag, Cr-SrTiO₃. This work not only indicates that Ag, Cr-SrTiO₃ is a desired photocatalytic material to degrade of organic pollutants under enlarging response range of solar light, but also shows that the addition of H₂O₂ can promote the photodegradation reaction.

1. Introduction

Fenton catalytic system is an effective method for photodegrading pollutions, through the Fenton mechanism involving reactive oxygen species (ROS), which have been successfully employed in dye wastewater, medical wastewater, organic wastewater and landfill leachate etc. The Fenton reaction is an efficient advanced oxidation process for organic compounds treatment [1]. In the system of the traditional Fenton homogeneous catalytic reaction, Fe²⁺/Fe³⁺ ions and H₂O₂ are the essential ingredient, Fenton technique will consume a lot of H₂O₂ and at the same time produce a mass of iron sludge that needs further treatment. Nevertheless, because of its wide band gap (3.2–3.4 eV), it responded to UV region only and it is necessary to extend its absorption into visible region [11, 12]. In addition, previous studies have proved that the doping of metallic elements into these wide band gap semiconductors is a feasible method to extend their light absorption into the visible region, which further improves their performance in organic pollution degradation [11]. For example, Yang used the Ag/AgCl surface plasma to improve the photocatalytic efficiency of SrTiO₃ [12]. Guo designed a heterojunction Ag₃PO₄/Cr-SrTiO₃ to eliminate the gaseous pollutants isopropyl alcohol [13]. Although these experiments have achieved relatively ideal experimental results, the system of the degradation experiments was different and the preparation of the catalyst required two or even three steps. The process of photocatalyst preparation is complicated.

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In this work, Ag,Cr-SrTiO₃ nanoparticles were synthesized by the one-pot situ solvothermal method and the nanoparticles were homogeneous. The photocatalytic performance of degrading acidic methylene blue (MO) was investigated using SrTiO₃ modified with Ag and Cr as catalyst, and the doping amounts, the solvothermal reaction temperature and surfactant were optimized. In degradation experiment, the introduction of H₂O₂ led to the formation of free radicals such as -OH, which accelerated the oxidation of organic matter on the gas-liquid surface. The results demonstrated a unique and simple way to improve the photocatalytic properties of SrTiO₃. Ag,Cr-SrTiO₃ could be easily separated from the solution and recycled. In this reaction system, it does not need to consume a lot of Fe²⁺/Fe³⁺ ions, and at the same time the nanoparticles can be used repeatedly.

2. Experimental

2.1. Reagents and materials

All chemical reagents in this experiment were of analytical grade and were used without further purification.

2.2. Preparation of Cr-SrTiO₃ and Ag/Cr-SrTiO₃

Firstly, 8.1 ml of butyl titanate, 0.02 g CrCl₃·6H₂O, 3 ml oleic acid and 5.079 g Sr(NO₃)₂ were dropped slowly into 18 ml of isopropyl alcohol solution under continuous stirring. Then, a mixture of 30 ml of methanol, 3 ml of distilled water and 3.78 g of KOH was added dropwise into the above solution, and the reaction system was stirred for about 30 min. After that, a certain amount of 0.1 mol l⁻¹ AgNO₃ was added under stirring. The mixed solution was transferred into a 100 ml Teflon autoclave and heated at 160 °C for 24 h. Lastly, the precipitate was separated by centrifugation, alternately washed 3 times with deionized water and ethanol, and dried at 60 °C for 12 h. For comparison, samples without addition of silver and chromium were prepared at the same time. The synthesized samples were labeled as SrTiO₃, Cr-SrTiO₃, Ag-SrTiO₃ and Ag,Cr-SrTiO₃.

2.3. Characterization of photocatalysts

The crystal structures of the composites were determined by x-ray diffraction. The x-ray photoelectron spectroscopy (XPS) spectra were collected on a PHIS6000X of PerkinElmer from USA. The morphologies of the as-prepared samples were examined by emission scanning microscopy and field emission transmission electron microscopy. Elemental mapping images were obtained using an energy dispersive x-ray spectrometer (EDX). The Brunauer–Emmett–Teller (BET) surface area test was performed on a ASAP2020 surface area analyzer. The UV-Vis spectra of the catalysts were obtained on a LambdaBio40 UV-Vis spectrometer. The photoluminescence (PL) spectra were obtained on a fluorescence spectrophotometer.

2.4. Photocatalytic performance test

The photocatalytic tests were fulfilled in the quartz cuvette for containing 5 ml of solution. The experiment was carried out at ambient temperature. The synthesized sample (0.075 g) was poured into a 75 ml 20 mg l⁻¹ MO solution, and the pH was adjusted to 2.0. Then 0.75 ml H₂O₂ were added. The mixed solution was stirred for 30 min in dark to achieve absorption/desorption equilibrium. The reaction system was illuminated with a 500W xenon lamp at continuous magnetic stirring. The MO solution was analyzed by the UV–vis spectra at wavelength of 507 nm at a 15 min periods. The photocatalytic performance test repeated 3 times to avoid experimental errors.

3. Results and discussion

3.1. Structure characterization

Figure 1 shows the XRD patterns of the samples. The average particle sizes of these samples were about 33.8 nm, 42.6 nm, 18.7 nm and 18.7 nm for SrTiO₃, Cr-SrTiO₃, 4wt% Ag-SrTiO₃ and 4 wt% Ag,Cr-SrTiO₃ as estimated from the half-peak width of the (110) diffraction peak. For pure SrTiO₃, the characteristic diffraction peaks were observed at 2θ of 32.4°, 39.9°, 46.5°, 57.8°, 67.8° and 77.2°, these were readily indexed to the cubic crystal (110), (111), (200), (211), (220) and (310) planes, respectively. All the diffraction peaks could be assigned to the perovskite type of SrTiO₃ (JCPDS No.35-0734). Compared with SrTiO₃, the major diffraction peaks of Cr-SrTiO₃ nanoparticle had a tiny displacement, and its crystal structure maintained even it was doped with Cr, indicating that Cr³⁺ ions could easily incorporate into the crystal lattice without changing the position of the diffraction peak [14]. The reason may be that the ionic radius of Cr³⁺ (61.5 pm) is similar to Ti⁴⁺ (60.5 pm) and less than that of Sr²⁺ (1.26 Å), it can replace some of the lattice titanium and have no influence on its structure. The tiny displacement of 2θ was about 0.06°. For Ag,Cr-SrTiO₃, several new diffraction peaks at 2θ of 38.1°, 44.3°, 64.4° and 77.5° appeared, corresponding to the (111), (200), (220) and (311) planes of cubic phase Ag.
(JCPDS No.04-0783), which indicated that Ag,Cr-SrTiO₃ could be obtained by the one-pot situ solvothermal reaction.

As shown in figure 1(b), with the increase of the doping amount of Ag, the diffraction peaks of the samples strengthen gradually. Meanwhile, the characteristic peaks of the SrTiO₃ crystal decrease and widen, indicating that the crystallinity and particle size of the samples decrease as the increasing of incorporated Ag amount. The average particle sizes were 37.9, 29.5, 19.2, 20.5, 18.7, 17.3 and 14.2 nm for 0.1, 1, 2, 3, 4, 5 and 8 wt% Ag,Cr-SrTiO₃ according to the Scherrer formula. The results show that the higher the doping amount is, the smaller the crystallinity and crystal size of the sample is. As we all know, low crystallite means large surface area and benefits for the subsequent reaction. Conversely, the decrease of crystallinity is unfavorable to photocatalytic reaction.

Figure 2 shows the XPS spectra of Ag,Cr-SrTiO₃. As shown in figure 2(a), all the peaks assigned to Sr, Ti, O, Ag and Cr elements were detected in the XPS spectrum. The high resolution spectra of each element is shown as figures 2(b)–(f). In figure 2(b), Sr 3d binding energy peaks at 132.8 eV and 134.7 eV were observed, which could be assigned to Sr 3d₅/₂ and Sr 3d₇/₂ [15]. Figure 2(c) depicted the Ag 3d XPS spectra with two peaks centered at 367 eV and 373 eV, corresponding to the electric states of Ag 3d₅/₂ and Ag 3d₇/₂, which indicated that Ag species existed in the form of Ag⁺ and a bit of Ag⁰ [16, 17]. From figure 2(d), the two peaks at about 576.2 eV and 585.5 eV could be ascribed to Cr³⁺ 2p₃/₂ and Cr³⁺ 2p₁/₂, confirming that Cr doped into the crystal of SrTiO₃ and it existed mainly as the form of trivalent oxide [14].

On the basis of Tian [18], he pointed out that Cr³⁺ could replace the lattice position of Ti⁴⁺ with charge compensation by oxygen vacancies at the nearest neighbor site. In this way, the doping Cr³⁺ ions can bring ‘free’ excess negative charge, which could create vacancies or interstitial titanium ions.

The binding energy of Ti 2p is shown in figure 2(e), with two binding energy of 458.5 eV and 463.9 eV, which corresponds to Ti⁴⁺ of Ti 2p₃/₂ and Ti 2p₁/₂ for SrTiO₃ [19–21]. The peak of Ti 2p₁/₂ for Ag,Cr-SrTiO₃ shits to 463.1 eV, which means existing Ti³⁺ in the lattice and these Ti³⁺ species result from the doping of Ag and Cr. As exhibited in figure 2(f), there were two peaks of O 1s at 530.07 eV and 531.2 eV for SrTiO₃, which could be attributed to oxygen in the oxide lattice and surface hydroxyl groups [22]. The peaks of O 1s for Ag,Cr-SrTiO₃ migrated to 528.7 eV and 530.9 eV, which meant an increase in surface hydroxyl groups. The surface OH group, through reaction with photoinduced holes, would be favorable to generate -OH radicals for oxidizing organic pollutants.

The morphology of the composite samples is investigated by SEM and EDX (inset) in figure 3. SrTiO₃ and Cr-SrTiO₃ were well-crystallized with irregular particles presented in figures 3(a) and (b). There were no significant differences in the size and morphology of the nanoparticles, which were nanospheres with a size of ca. 32 nm and 30 nm for SrTiO₃ and Cr-SrTiO₃. The size of the nanoparticles seem to change slightly after Cr doping. The EDX of Cr-SrTiO₃ as shown in the inset clearly indicated the presence of Cr, Sr, Ti and O elements. Figure 3(c) shows the EDX of Ag,Cr-SrTiO₃, the atomic ratio of O:Ti = 2.21:1, which was slightly smaller than the composition of SrTiO₃. The phenomenon suggested the existence of oxygen vacancy in the lattice, which could introduce electrons into the structure. In addition, the contents of Sr, Ag and Cr were 2.7%, 0.4% and 0.6%, respectively. On the surface of Ag,Cr-SrTiO₃ nanospheres, the roughness increased after doping of metal ion, which could improve the adsorption surface area and was also beneficial to increase the photocatalytic activity. Combining the EDX and XPS analysis, there are oxygen vacancy and Ti³⁺ species in the sample of Ag,Cr-SrTiO₃, these oxygen vacancies can suppress the recombination of electrons and holes thus enhancing the photocatalytic activity [23]. Figures 3(d), (e) shows the representative TEM and HRTEM images of
Ag, Cr–SrTiO₃. The uniform nanospheres with a particle size of ca. 30 nm can be observed from the TEM. The crystal lattice of 0.28 nm should be due to the (110) plane of SrTiO₃, and corresponding the fringe lines with 0.24 nm spacing due to the Ag (111) planes.

3.2. Optical absorption properties
Figure 4 shows the UV–vis absorption spectra of all the as-synthesized samples. The light absorbance edges of pure SrTiO₃ was around 390 nm, while it was as 419, 400 and 466 nm for Cr–SrTiO₃, Ag–SrTiO₃ and Ag, Cr–SrTiO₃, respectively. Accordingly, the bandgap was 3.18, 2.96, 3.1 and 2.66 eV. Compared to pure SrTiO₃, sample of Cr–SrTiO₃ presented significantly red-shifted to visible region, which displayed obvious visible light absorbance. While Ag and Cr were co-doped into SrTiO₃, the light absorption intensity was the highest in all these samples. The absorption edge at about 466 nm indicated that Ag, Cr–SrTiO₃ could response to visible light [24], and this phenomenon might be due to plasma effect of silver. Further, the surface plasmon resonance effect of Ag is also important. The plasmon resonance effect can broaden the photoresponse range of the photocatalyst to the visible region, and increase the utilization of visible light. In figure 4(b), as the increase of doping Ag, the region of absorbance light increased and the bandgap energy of them were 2.7 (0.5 wt% Ag, Cr–SrTiO₃), 2.78 (1 wt% Ag, Cr–SrTiO₃), 3.2 (2 wt% Ag, Cr–SrTiO₃), 3.25 (3 wt% Ag, Cr–SrTiO₃), 2.66 (4 wt% Ag, Cr–SrTiO₃).
Figure 3. SEM and EDX spectrum of SrTiO₃ (a), Cr-SrTiO₃ (b), Ag,Cr-SrTiO₃ (c), and TEM (d), HRTEM (e) images of Ag,Cr-SrTiO₃.

Figure 4. UV-vis DRS of different samples (a) and Ag,Cr-SrTiO₃ with different Ag amount (b).
Ag, Cr–SrTiO₃, 2.66 (5 wt% Ag, Cr–SrTiO₃) and 3.2 eV (8 wt% Ag, Cr–SrTiO₃), respectively. When the nominal amount of Ag doping reached 4 wt% and the actual amount 0.4%, the sample showed a relatively ideal absorbance in the visible region, meaning a high photocatalytic activity in degradation of pollutants.

3.3. Textural properties

Figure 5 shows the N₂ adsorption-desorption isotherms curves and the average pore diameter of the samples. As shown in figure 5, the obtained isotherm curves of Ag, Cr–SrTiO₃ is the type IV according to IUPAC classification, indicating the formation of mesopores nanostructure. The BET specific surface area of SrTiO₃, Cr–SrTiO₃ and Ag–SrTiO₃ was 38.2, 57.7 and 45.3 m²·g⁻¹, respectively. Conversely, it can be observed that the BET surface area of Ag, Cr–SrTiO₃ obtained by solvothermal method is about 84.3 m²·g⁻¹ and the average pore diameter is about 6 nm (figure 5 inset).

3.4. Photocatalytic activity

Figure 6 shows the photocatalytic degradation MO under visible light (λ > 400 nm) and the corresponding kinetic curve. In these experiments, H₂O₂ was added to activate the photocatalyst to improve the effect of degrading pollutants. Figure 6(a) shows that, compared with different samples, Ag, Cr–SrTiO₃ has the ideal reactive activity. To decrease the measuring error, three parallel experiments were carried out for each experiment, and the curve was plotted with the average value. The degradation rate is 98.8% for Ag, Cr–SrTiO₃, which is higher than SrTiO₃ after 60 min light illumination. As illustrated in figures 6(b), (c), Ag, Cr–SrTiO₃ degradation of MO belongs to the first order kinetics and 4 wt% Ag, Cr–SrTiO₃ has the highest degradation rate in all these samples, which is 1.38 times of SrTiO₃. This result also corresponded to UV-visible diffuse reflection spectrum. The linear relationship of Ln(C₀/C) versus irradiation time for degradation of MO with Ag, Cr–SrTiO₃ is plotted in figure 6(c). It was obvious that 4 wt% Ag, Cr–SrTiO₃ had the highest k value of 0.067, which suggested the best photocatalytic ability and the fastest reaction rate among all these samples. The MO degradation under different condition with 4 wt% Ag, Cr–SrTiO₃ is illustrated in figure 6(d). In these experiments, we explored that the photocatalytic properties were quite different under different reactive condition. It could be clearly seen that the degradation rate was about 12.4% in the absence of H₂O₂, while it reached to 21.1% in the presence of H₂O₂ and pH 2. Then, adding the sample of Ag, Cr–SrTiO₃ made the degradation rate increase dramatically to 98.8% and it was almost 5 times. The addition of H₂O₂ can increase the amount of ·OH and at the same time promote the conversion of superoxide radicals to ·OH, which could accelerate the oxidation of MO.

3.5. Photoluminescence and photoelectronchemical properties

Figure 7 shows the photoluminescence emission spectroscopy of Ag, Cr–SrTiO₃ and transient photocurrent responses. The PL spectra have been verified to be an efficient approach to study the separation rate of electron–hole pairs, which could greatly affect photocatalytic activity [25, 26]. Generally, low fluorescence
intensity means high separation efficiency of electron–hole pairs. It was clearly observed that 4 wt% Ag,Cr-SrTiO$_3$ had a lower peak intensity compared to 0.5 wt% Ag,Cr-SrTiO$_3$, implying that incorporation of Ag could effectively suppress the charge carrier recombination at the interface and decrease the intensity of the emission spectrum. The interface charge carrier transfer and separation efficiency could be further evaluated by the photoelectron chemical technique [27]. The transient photocurrent responses (TPR) of 4 wt% Ag,Cr-SrTiO$_3$, Cr-SrTiO$_3$, and SrTiO$_3$ under the irradiation of visible light were also measured to confirm the promoted separation efficiency of photo-generated carriers. As shown in figure 7(b), loading of Ag and Cr on SrTiO$_3$ nanoparticles improved the photocurrent density effectively. It showed that Ag,Cr-SrTiO$_3$ had lower electron-hole recombination rate and more efficient charge separation than SrTiO$_3$.

Figure 6. Photocatalytic degradation of MO (a, b), the corresponding linear relationship curves (c) and MO degradation under different condition with 4 wt% Ag,Cr-SrTiO$_3$ (d).

Figure 7. PL spectra of Ag,Cr-SrTiO$_3$ under an excitation wavelength of 325 nm (a) and transient photocurrent responses (b).
3.6. Photocatalytic mechanism

The mechanism of degradation reaction by this composite could be explained on the basis of literature [28]. Illumination of photon with appropriate wavelength resulted in molecular excitation which led to generation of electron–hole ($e^-/h^+$) pairs. The photogenerated $e^-$ in conduction band (CB) moved towards the surface of Ag, Cr-SrTiO$_3$ NPs to produce hydroxyl radical ($\cdot$OH) finally. Holes ($h^+$) in valence band (VB) reacted with H$_2$O/ OH$^-$ as well as to produce active species such as $\cdot$OH under H$_2$O$_2$. Highly oxidative species including superoxide radical anion ($O_2^-$) and $\cdot$OH produced when the holes ($h^+$) were absorbed by water molecules (H$_2$O) or hydroxyl (OH$^-$), and the electrons on CB of SrTiO$_3$ were captured by surface-adsorbed oxygen molecules (O$_2$). The following steps could be possible in MO degradation reaction:

\[
\begin{align*}
\text{Ag, Cr} & \rightarrow \text{SrTiO}_3 + \text{hv} \rightarrow h^+ + e^- \\
h^+ + \text{H}_2\text{O} & \rightarrow \cdot\text{OH} + H^+ \\
\text{H}_2\text{O}_2 + \text{hv} & \rightarrow 2 \cdot \text{OH} \\
h^+ + \text{OH}^- & \rightarrow \cdot\text{OH} \\
\cdot\text{O}_2^- + \text{H}_2\text{O}_2 & \rightarrow \cdot\text{OH} \\
\text{O}_2 + e^- & \rightarrow \cdot\text{O}_2^- \\
\text{H}^+ + \cdot\text{O}_2^- & \rightarrow \cdot\text{OH} \\
\text{MO} + \cdot\text{OH} & \rightarrow \text{Products}
\end{align*}
\]

Figure 8 shows the possible mechanism of responsive photocatalysis by Ag, Cr-SrTiO$_3$. Generally, $\cdot$OH is generated from electron transfer between H$_2$O$_2$ and Ag, Cr-SrTiO$_3$ sites. In this reaction, the catalyst was the key step in generation of $\cdot$OH. As a Lewis base, H$_2$O$_2$ tends to adsorb onto the Lewis acid sites. Hydrogen peroxide is an ideal oxidant, which can produce hydroxyl free radicals in the reaction process without new pollutants.

4. Conclusions

In summary, co-doping Ag and Cr on SrTiO$_3$ was studied and the composite material of Ag, Cr-SrTiO$_3$ was obtained under the optimum conditions of 160 $^\circ$C, oleic acid as a surfactant and the actual doping amount of Ag 0.4 wt%. The doping Ag existed in the form of Ag$^+$ and a bit of Ag$^0$, and Cr was existing mainly in the form of trivalent oxidation state. Doping of Ag and Cr was conducive to surface OH group, oxygen vacancies and Ti$^{3+}$. The Cr$^{3+}$ could replace the lattice position of Ti$^{4+}$ with charge compensation by oxygen vacancies at the nearest neighbor site. In addition, Ti$^{3+}$ species are created due to the doping of Ag and Cr. The oxygen vacancies and Ti$^{3+}$ could promote the degrade of pollution. The absorption range of the nanoparticles extended to visible region revealed that the red shift occurred because of Ag and Cr doping. Furthermore, the degradation efficiency of MO catalyzed by Ag, Cr-SrTiO$_3$ reached up to 98.8% after visible light illumination for 60 min under H$_2$O$_2$, which was far higher than that of without H$_2$O$_2$. Exceptional photocatalytic activity for Ag, Cr-SrTiO$_3$ activated by H$_2$O$_2$ for removal of organic pollutant was realized and OH$^-$ was the main active specie.
Acknowledgments

This work was partly supported by the National Natural Science Foundation of China (Grant no. 21605111), the Nature Science Foundation of Shanxi (Grant no. 201601D011079), and also partly supported by the JSPS KAKENHI Grant Number JP16H06439 (Grant-in-Aid for Scientific Research on Innovative Areas), the Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials, the Cooperative Research Program of ‘Network Joint Research Center for Materials and Devices’, TAGEN project.

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