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ARTICLE

Fabrication of $Ag_2CO_3/SrCO_3$ Rods with Highly Efficient Visible-light Photocatalytic Activity

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Abstract: $Ag_2CO_3/SrCO_3$ rods were prepared by a facile precipitation method using $AgNO_3$, $Sr(NO_3)_2$, and Na_2CO_3 as precursors. The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherms, and UV-visible (UV-vis) diffuse reflectance spectroscopy. The photocatalytic activity was evaluated by photodegradation of methyl orange (MO) aqueous solutions under visible-light irradiation (λ > 420 nm). The results indicate that the $Ag_2CO_3/SrCO_3$ rods become thinner and shorter with the decrease of $Ag_2CO_3/SrCO_3$ molar ratio. The as-prepared $Ag_2CO_3/SrCO_3$ rods show excellent visible-light photocatalytic activity. Moreover, $Ag_2CO_3/SrCO_3$ composites exhibit an enhanced photocatalytic activity compared with the monocomponent Ag_2CO_3 and $SrCO_3$. $Ag_2CO_3/SrCO_3$ rods with the $Ag_2CO_3/SrCO_3$ molar ratio of 1:5 exhibit the highest activity due to the synergetic effects of the large surface area and the heterostructure.

Key words: $Ag_2CO_3/SrCO_3$ rod; visible light; photocatalytic; heterostructure

In order to make full use of solar energy, the design and preparation of new photocatalysts with a high activity under visible light irradiation has become one of the research hotpots in recent years[1-5]. Among various photocatalysts, Ag-based compounds with strong visible-light activity have attracted much attention. Photoactive Ag_3PO_4[6-10], Ag*X* (*X* = Cl[11], Br[12], I[13]), and Ag_3VO_4[14] have been well studied for photodegradation of organic pollutants. Very recently, it has been reported that Ag_2CO_3 possesses excellent photocatalytic properties for decomposition of organic pollutants under visible-light irradiation[15-17].

Semiconductor composite, which constructs a heterojunction interface between two types of semiconductors, can facilitate the separation of photoinduced charges and improve the photocatalytic activity. The hybridization of silver-containing photocatalysts with other semiconductors, such as Ag_3PO_4/graphene[18], AgBr/WO_3[19], Ag_3VO_4/TiO_2[20] and Ag*X*/Ag_3PO_4 (*X* = Cl, Br, I)[21] has been confirmed to be an effective way to enhance the performance of Ag-based compounds.

Herein, we synthesized $Ag_2CO_3/SrCO_3$ rods with enhanced visible-light photocatalytic performance for the photodecomposition of methyl orange (MO). The effects of different molar ratios of $Ag_2CO_3/SrCO_3$ on photocatalytic activity were investigated.

1 Experiment

All chemicals used in this study were of analytical-grade and were purchased from Shanghai Chemical Regent Factory of China without further purification. Distilled water was used in all experiments. $Ag_2CO_3/SrCO_3$ was synthesized by a simple precipitation process. In a typical procedure, 0.1 g $AgNO_3$ was added to 20 mL of distilled water under constant stirring. Then ammonia aqueous solution (0.3 mol/L) was dropped into the above solution to form a clear solution. Afterwards, 0.22 g of $Sr(NO_3)_2$ was added into the solution with the $Ag_2CO_3/SrCO_3$ molar ratio of 1:5. The mixed solution was stirred for 20 min, followed

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by addition of 2 g of Na_2CO_3 to ensure full precipitation of Ag_2CO_3 and $SrCO_3$. The obtained yellow precipitates were washed with distilled water and dried in vacuum at 60 °C. For comparison, $Ag_2CO_3/SrCO_3$ composites with different $Ag_2CO_3/SrCO_3$ molar ratios were also prepared under the same experimental conditions.

The photocatalytic performance of the as-prepared samples was characterized by decomposing MO under visible light irradiation at room temperature. Briefly, 0.1 g of $Ag_2CO_3/SrCO_3$ composite powders were dispersed into 20 mL of MO solution (4×10^{-5} mol/L) in a disk with a diameter of ca. 6 cm. The solution was allowed to reach an adsorption-desorption equilibrium among the photocatalyst, MO, and water before visible light irradiation. A 200 W Xe arc lamp equipped with a UV- cutoff filter (λ = 420 nm) was used as a visible-light source. The concentration of MO was determined by an UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). After irradiation for 5 min, the reaction solution was centrifuged to measure the concentration change of MO. The photocatalytic activity of Nitrogen doped-TiO_2 was also measured as a reference.

2 Results and Discussion

Fig.1 shows the XRD patterns of the $Ag_2CO_3/SrCO_3$ composites with different $Ag_2CO_3/SrCO_3$ molar ratios. All the peaks of the pure $SrCO_3$ sample (Fig.1a) coincide with the orthorhombic $SrCO_3$ phase (JCPDS No. 05-0418). With the increase of Ag_2CO_3 content, the peak intensities of monoclinic structure of Ag_2CO_3 (JCPDS file No. 26-0339) increase.

Fig.2 shows SEM morphologies of $Ag_2CO_3/SrCO_3$ samples with different $Ag_2CO_3/SrCO_3$ molar ratios. The pure $SrCO_3$ is constructed by many small and loose nanoparticles (Fig.2a). Contrarily, pure Ag_2CO_3 product consists of microrods (Fig.2d). The surface of pure Ag_2CO_3 rods is smooth and the average particle size of Ag_2CO_3 is 2~10 μm. In the case of $Ag_2CO_3/SrCO_3$ samples (Fig.2b and 2c), Ag_2CO_3 rods coated with many $SrCO_3$ nanoparticles is observed. In addition, with the decrease of $Ag_2CO_3/SrCO_3$ molar ratio, the $Ag_2CO_3/SrCO_3$ rods become thinner and shorter, indicating that the growth of Ag_2CO_3 is suppressed by the coating of $SrCO_3$.

It is widely accepted that photocatalysts with higher specific surface area and porous structures are beneficial to the enhancement of photocatalytic performance, due to more surface active sites for the adsorption of reactants molecules, ease transportation of reactant molecules and products through the interconnected porous networks, and enhanced harvesting of exciting light by multiple scattering within the porous framework[22]. Fig.3 shows the nitrogen adsorption-desorption isotherms at 77 K for the $Ag_2CO_3/SrCO_3$ samples. It can be seen that all the samples show the type IV isotherms with type H3 hysteresis loops according to brunauer-deming-deming-teller (BDDT) calssification[23], indicating the presence of mesopores (2~50 nm). Moreover, the observed hysteresis loops of the both samples approach P/P_0 = 1, suggesting the presence of macropores (>50 nm)[23,24]. The presence of $SrCO_3$ in the synthesis mixture has a significant influence on the nitrogen adsorption-desorption isotherms. With the increasing $SrCO_3$ amount, the surface area increase greatly due to the decrease of the Ag_2CO_3 particle size. The BET surface areas of $Ag_2CO_3/SrCO_3$ with the molar ratio 0:1, 1:5, 1:1 and 1:0 are 0.23, 2.69, 10.02 and 16.09 m^2/g, respectively.

The UV-vis DRS of the different samples are shown in Fig.4a. $SrCO_3$ shows a weak light absorption in the wide visible-light range, while Ag_2CO_3 displays strong capability of light absorption in both UV and visible light region with

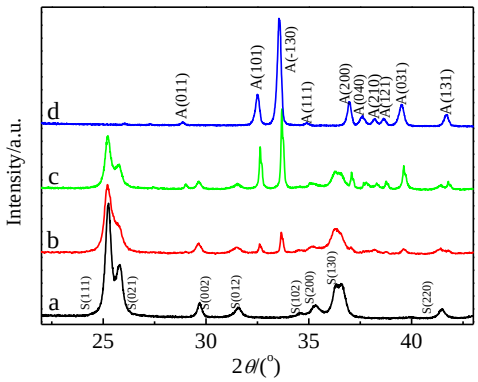

Fig.1 XRD patterns of $Ag_2CO_3/SrCO_3$ samples with different $Ag_2CO_3/SrCO_3$ molar ratios (a-0:1, b-1:5, c-1:1, d-1:0)

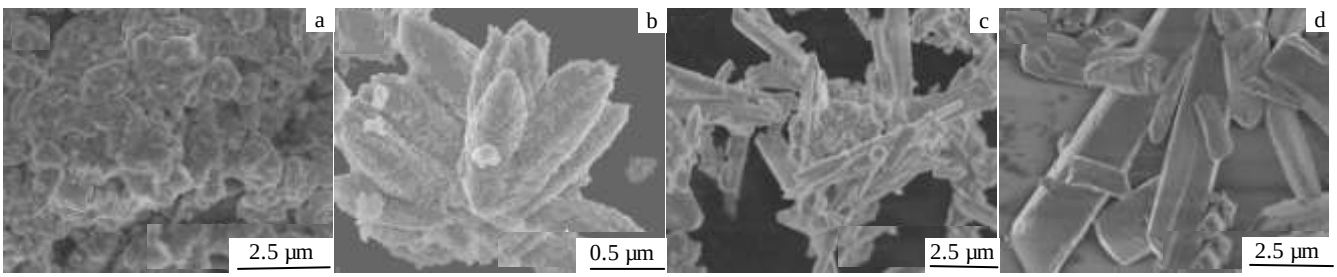

Fig.2 SEM images of $Ag_2CO_3/SrCO_3$ samples with different $Ag_2CO_3/SrCO_3$ molar ratios: (a) 0:1, (b) 1:5, (c) 1:1, (d) 1:0

an absorption edge of 480 nm. The UV-vis spectra of $Ag_2CO_3/SrCO_3$ samples also exhibit an enhanced absorption in the visible light range of 400~480 nm, and the light absorption in the visible light range increases with the increasing Ag_2CO_3 content in the composite. Assuming $SrCO_3$ is an indirect semiconductor, the band gap energy can be estimated from the intercept of the tangents to the plots of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$). The band gap energy of $SrCO_3$ estimated from the intercept (Fig.4b) is 2.64 eV.

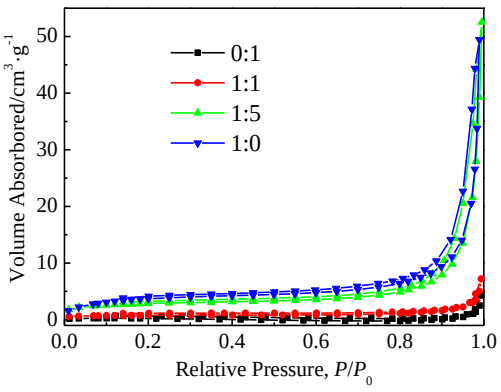

Fig.3 Nitrogen adsorption-desorption isotherms of $Ag_2CO_3/SrCO_3$ samples with different $Ag_2CO_3/SrCO_3$ molar ratios

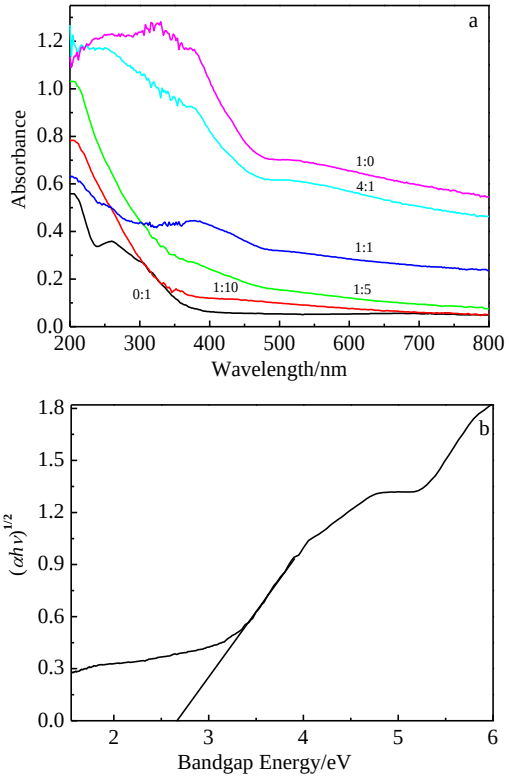

Fig.4 UV-vis diffuse reflectance spectra of $Ag_2CO_3/SrCO_3$ samples with different $Ag_2CO_3/SrCO_3$ molar ratios (a); band gap energy of pure $SrCO_3$ (b)

The photocatalytic activity of the prepared samples was evaluated by photocatalytic decolorization of MO aqueous solution under visible light. MO is a kind of dye pollutants which is chemically stable and difficult to be decomposed. Under dark conditions (no light irradiation), the concentration of MO does not change for measurements on the $Ag_2CO_3/SrCO_3$ samples studied. Also, irradiation in the absence of photocatalysts does not result in the photocatalytic decolorization of MO. Therefore, the presence of both irradiation and $Ag_2CO_3/SrCO_3$ sample is necessary for the efficient degradation of MO. These results suggest that the decomposition of MO aqueous solutions is caused by photocatalytic reactions on the $Ag_2CO_3/SrCO_3$ surface under the visible light irradiation. Fig.5a exhibits the photocatalytic activities of different samples. The $SrCO_3$ and N-TiO_2 exhibit neglectable visible-light photocatalytic activities. However, the photocatalytic activities of $Ag_2CO_3/SrCO_3$ samples are remarkably enhanced and the MO removals over $Ag_2CO_3/SrCO_3$ samples reach 52.5%~90.9% after 50 min of irradiation. Obviously, Ag_2CO_3 in the composites plays a crucial rule in enhancing the photocatalytic activity and a small amount of Ag_2CO_3 ($Ag_2CO_3/SrCO_3$ molar ratio = 1:10) could lead to a sharp increase of MO decomposition from 9% to 79%. As the $Ag_2CO_3/SrCO_3$ molar ratio increases to 1:5, the best photocatalytic activity is achieved, at which 90.9% of MO dye molecules are decomposed. However, the photocatalytic activity decreases at higher Ag_2CO_3 concentration, suggesting that the optimal $Ag_2CO_3/SrCO_3$ molar ratio is 1:5.

The stability of a photocatalyst is one of the important parameters for its practical applications. Ag_2CO_3 suffers from stability issues because it will photochemically decompose apart from the presence of a sacrificial reagent[15]. Partial Ag_2CO_3 is reduced into metallic silver when it is used for photocatalytic degradation of rhodamine B, resulting in the sharp decrease of its photocatalytic stabilities. To compare the photocatalytic stability of the pure Ag_2CO_3 and $Ag_2CO_3/SrCO_3$ composite, the used pure Ag_2CO_3 and $Ag_2CO_3/SrCO_3$composite were collected and reused in three successive MO degradation experiments. As shown in Fig.5b, the photocatalytic activity of $Ag_2CO_3/SrCO_3$ with the molar ratio of 1:5 is more stable than that of Ag_2CO_3 for photocatalytic degradation of MO solutions. Although some photocatalytic activity losses are observed for the $Ag_2CO_3/SrCO_3$ after three times of cycle experiment, the rate of MO degradation over pure Ag_2CO_3 decreases more significantly after the third degradation cycle under the same conditions. This result indicates that the $Ag_2CO_3/SrCO_3$ composite is more stable than the Ag_2CO_3.

According to the above results, the enhanced photocatalytic activity and stability of $Ag_2CO_3/SrCO_3$ can

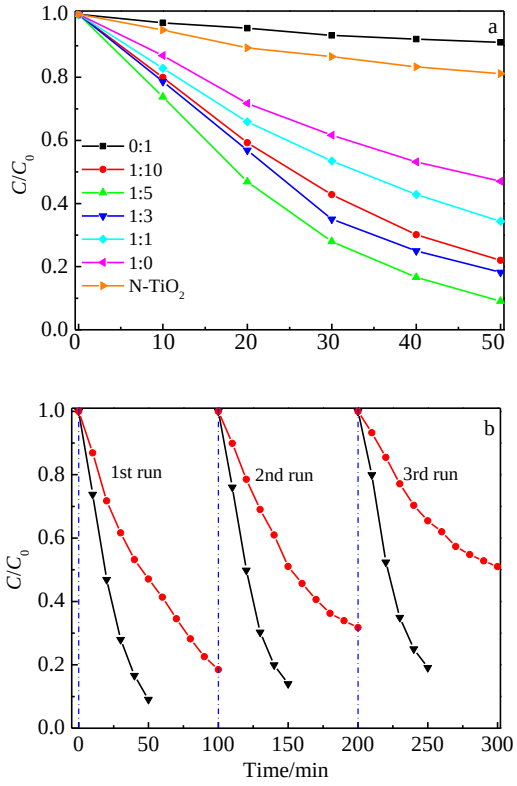

Fig.5 Photodegradation of MO using N-TiO_2 and Ag_2CO_3/$SrCO_3$ samples with different Ag_2CO_3/$SrCO_3$ molar ratios (a); repeated photocatalytic degradation of MO under visible light irradiation (photocatalyst: Ag_2CO_3/$SrCO_3$ (molar ratio = 1:5) (triangles), Ag_2CO_3 (circles), (b)

be attributed to the synergetic effects of the high surface area and heterostructure. Firstly, with the decrease of Ag_2CO_3/$SrCO_3$ molar ratio, the Ag_2CO_3/$SrCO_3$ rods become thin and short, thus increasing the surface area of Ag_2CO_3/$SrCO_3$ rods. The larger surface area resulted from the rough surface of the composites can provide more reaction sites for the photocatalytic degradation of MO. Secondly, the heterostructured photocatalyst can realize the vectorial transfer of photogenerated carriers from one to the other, thus increasing the photocatalytic efficiency[25]. The charge separation in the Ag_2CO_3/$SrCO_3$ heterostructure under visible light irradiation is elucidated schematically in Fig.6. The photoinduced electrons on conduction band (CB) of Ag_2CO_3 can migrate to the CB of $SrCO_3$, and the photoinduced holes on the valence band (VB) of $SrCO_3$ can transfer to Ag_2CO_3. In such a way, the recombination of the photoinduced electrons and holes is largely reduced and more effective electrons and holes take part in the photodegradation process. Therefore, the Ag_2CO_3/$SrCO_3$ rods exhibit much higher photocatalytic performances than the single Ag_2CO_3 or $SrCO_3$. At the same time, the efficient electron transfer from Ag_2CO_3 to $SrCO_3$ keeps electrons

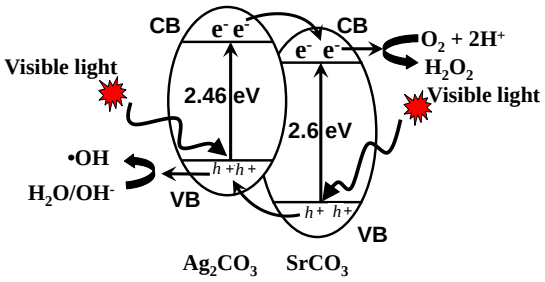

Fig. 6 Scheme diagram of the band levels of Ag_2CO_3/$SrCO_3$ rods and the possible reaction mechanism of the photocatalytic procedure

away from the $SrCO_3$, preventing the formation of silver atoms by the combination of the photoinduced electrons and the interstitial silver ion, reducing the decomposition rates of Ag^+ to metallic Ag and improving the stability of Ag_2CO_3/$SrCO_3$ composites in the photocatalytic process.

3 Conclusions

1) The Ag_2CO_3/$SrCO_3$ rods by a facile precipitation process at low temperature exhibit enhanced visible-light photocatalytic activities against methyl orange in comparison with pure Ag_2CO_3 and $SrCO_3$.

2) The Ag_2CO_3 in the Ag_2CO_3/$SrCO_3$ rods plays a decisive role in the photocatalytic activity and the optimized Ag_2CO_3/$SrCO_3$ molar ratio is 1:5.

3) The remarkable enhancement in the visible-light photocatalytic activity of Ag_2CO_3/$SrCO_3$ rods can be attributed to combined effects of two factors, including the large surface and the heterostructure reducing the recombination of photogenerated electrons and holes.

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棒状 $Ag_2CO_3/SrCO_3$ 的制备与高可见光光催化活性

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摘 要：以$AgNO_3$, $Sr(NO_3)_2$和Na_2CO_3为前驱体，通过简单的沉淀法制备了棒状$Ag_2CO_3/SrCO_3$复合物。用X射线衍射，扫描电镜，氮吸附-脱附等温曲线表征了所制备的样品。通过在可见光下降解甲基橙来检测光催化活性。结果表明，随着$Ag_2CO_3/SrCO_3$摩尔比的减小，$Ag_2CO_3/SrCO_3$棒逐渐变细变短。棒状$Ag_2CO_3/SrCO_3$显示了极好的可见光光催化活性，与单一的Ag_2CO_3和$SrCO_3$比较，$Ag_2CO_3/SrCO_3$复合物的活性增强，摩尔比为1:5的$Ag_2CO_3/SrCO_3$棒活性最高。棒状$Ag_2CO_3/SrCO_3$的高活性是由于其高比表面积和它们之间形成了异质结协同作用的结果。

关键词：棒状 $Ag_2CO_3/SrCO_3$；可见光；光催化；异质结

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