Fabrication of nano-sized Ag2CO3/RGO photocatalyst with enhanced visible-light photocatalytic activity and stability

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Fabrication of nano-sized Ag$_2$CO$_3$/reduced graphene oxide photocatalyst with enhanced visible-light photocatalytic activity and stability

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Nano-sized Ag$_2$CO$_3$ and reduced graphene oxide (RGO) composites were fabricated by a facile chemical precipitation approach in N,N-dimethylformamide (DMF) solvent. The as-prepared Ag$_2$CO$_3$/RGO nanocomposites were characterized by X-ray diffraction pattern (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and ultraviolet-visible (UV-vis) diffuse reflectance spectroscopy (DRS). The photocatalytic activity of the samples was evaluated by photocatalytic degradation of methyl orange (MO) under visible light irradiation. The results showed that the nano-sized Ag$_2$CO$_3$ particles are deposited on the surfaces of RGO. The Ag$_2$CO$_3$/RGO nanocomposites exhibited much higher photocatalytic activity than the pure nano-sized Ag$_2$CO$_3$ due to the improved separation efficiency of photogenerated carriers, and Ag$_2$CO$_3$/2 wt% RGO displayed the highest photocatalytic degradation efficiency. Furthermore, the photocatalytic and structural stability of Ag$_2$CO$_3$ is greatly enhanced due to the good electron transfer of RGO.

1. Introduction

Photocatalytic degradation of organic pollutants by using semiconductor photocatalysts is of growing interest for water purification. Among these materials, titanium dioxide (TiO$_2$) is the most widely used photocatalyst because of its large availability, low cost, nontoxicity, and relatively high chemical stability. However, due to the large band gap (3.2 eV), TiO$_2$ is mainly catalytically active under UV light irradiation, which merely accounts for ca. 4.5% of solar energy. Considering energy saving and utilization, sunlight or visible-light (which accounts for ca. 45% of solar energy), is the most promising energy source for the operation of the photocatalysts. Therefore, it is desirable to develop novel photocatalysts that can utilize visible light under sunlight irradiation. Recently, silver-containing compounds have been demonstrated to be efficient photocatalytic materials under visible-light irradiation. For example, Hu and co-workers reported fabrication of monoclinic structural Ag$_5$VO$_4$ and its visible-light photocatalytic activity for the decolorization of azo dye acid red B. Singh et al. reported synthesis of illmenite AgSbO$_3$ by ion-exchange reaction of NaSbO$_3$ with silver nitrate, which showed visible-light photocatalytic activity for the decomposition of methylene blue, rhodamine B, and 4-chlorophenol. Huang and co-workers reported that silver halides exhibit high visible-light photocatalytic activity and photostability due to the plasmon resonance of Ag nanoparticles formed on the surface of silver halide particles. Ye et al. reported that the Ag$_5$PO$_4$ photocatalyst exhibits extremely high photocatalytic capabilities in the oxidation of water and in the photodecomposition of organic contaminants in aqueous solution under visible-light irradiation. Wang and co-workers found that crystalline Ag$_2$O particles can be used as an efficient photocatalyst for the decomposition of methyl orange (MO) under visible-light irradiation. Tang et al. reported the synthesis of novel AgFIO$_4$ semiconductor, which shows much higher activity than Ag$_2$PO$_4$ or Ag$_2$AsO$_4$. Very recently, it was reported that Ag$_2$CO$_3$ crystal exhibited universal high-efficient photodegradation performance for (rhodamine B, methylene blue, MO) and phenol. However, Ag$_2$CO$_3$ is unstable. The transformation of Ag into Ag usually takes place due to the combination of the photo-induced electron and interstitial Ag during the photocatalytic process, which results in the photocorrosion of Ag$_2$CO$_3$ in the absence of electron acceptors. Reduced graphene oxide (RGO), as a two-dimensional single-layer carbon sheet, has attracted great interest for photocatalytic applications because of its unique properties, such as a large theoretical specific surface area, superior mobility of charge carriers, and good chemical stability. The ability of graphene to transfer electrons can lengthen the lifetime of photoexcited electrons, which can suppress the recombination of photoexcited electrons and holes. For the moment, Ag$_2$CO$_3$/Graphene oxide (GO) composites have been synthesized to improve the structural stability and photocatalytic activity of Ag$_2$CO$_3$. It is reported that the electrical conductivity was improved after GO was reduced, and the high electrical conductivity is beneficial to transferring of the photogenerated electrons. However, there has no work focusing on preparing Ag$_2$CO$_3$/RGO composites for degrading organic pollutants under the visible light. Moreover, the particle size of Ag$_2$CO$_3$ remains relatively large, hindering its performance in photocatalytic applications.
processes. It is widely accepted that a large surface area of the catalyst enhances the photocatalytic activity of the photocatalyst because a high surface area increases the number and density of redox reaction sites. Considering the remarkable properties of RGO, the limitations of the Ag$_2$CO$_3$ photocatalytic system and the higher surface area of nanoparticles than microparticles, the combination of RGO and nano-sized Ag$_2$CO$_3$ could be regarded as an ideal strategy to construct stable and efficient composite photocatalyst.

In this work, we, for the first time, synthesized Ag$_2$CO$_3$/RGO nanocomposites by a chemical precipitation method. It is found that the obtained nano-sized Ag$_2$CO$_3$/RGO photocatalysts showed remarkably enhanced photocatalytic activities toward degradation of MO in comparison with pure nano-sized Ag$_2$CO$_3$ under visible light. More importantly, the addition of RGO could enhance the photocatalytic stability of Ag$_2$CO$_3$.

2. Experimental

2.1. Sample preparation

All reagents used in this study were of analytical grade and were purchased from Shanghai Chemical Reagent Factory of China without further purification. Graphene oxide (GO) was prepared by a modified Hummers method and reduced graphene oxide (RGO) was obtained by a chemical reduction of GO using sodium borohydride. Typically, 100 mg of GO was exfoliated in 200 mL of distilled water by ultra-sonication for 3 h to form a homogeneous brown GO colloidal dispersion with a concentration. Subsequently, 1.135 g of NaBH$_4$ was added into the above GO solution under vigorous stirring. After the mixture was stirred for 3 h at 80 °C, the obtained precipitates were separated by centrifuge followed by washing with distilled water for several times. The product was then dried in a vacuum oven at 40 °C.

For synthesis of nano-sized Ag$_2$CO$_3$/RGO composite, a certain amount of the RGO was dispersed into 30 mL of N,N-dimethylformamide (DMF) with sonicating for 2 h to form the dispersion of RGO. Subsequently, 3 mmol of AgNO$_3$ was added into the dispersion of RGO under vigorous stirring. After stirring for 10 min, 3 mmol of K$_2$CO$_3$ dissolved in 15 mL of mixed solution of ethanol and water (volume ratio, 1:1) was then added dropwise into the above dispersion under magnetically stirring. The mixture was stirred for 20 min. The obtained precipitates were then washed with distilled water and ethanol for several times, respectively. Finally, powdered sample was obtained after drying in a vacuum oven at 60 °C. The contents of adding RGO are 2, 4, 8, and 12 mg, and the obtained samples are labeled as Ag$_2$CO$_3$/0.5 wt% RGO, Ag$_2$CO$_3$/1 wt% RGO, Ag$_2$CO$_3$/2 wt% RGO, and Ag$_2$CO$_3$/3 wt% RGO, respectively. For comparison purpose, pure Ag$_2$CO$_3$ nanoparticles were synthesized without the addition of RGO. Micro-sized Ag$_2$CO$_3$ and N-doped TiO$_2$ were synthesized by previously reported methods, respectively.

2.2 Characterization

X-ray diffraction (XRD) patterns were obtained on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation at a scan rate (2θ) of 0.05° s$^{-1}$. Scanning electron microscopy (SEM) were performed in an S-4800 Field Emission SEM (FESEM, Hitachi, Japan) at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) analyses were conducted with a JEM-2100F electron microscope (JEOL, Japan) operating at 200 kV. Raman spectra were acquired on a Reflex Raman Microprobe (Renishaw inVia, England). X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MKII XPS system with an Mg Ka source and a charge neutralizer. The UV-visible diffuse reflectance spectra were obtained using a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). Fine BaSO$_4$ powder was used as a standard.

3. Results and discussion

3.1. Structures and morphology

![Fig. 1 XRD patterns of micro-sized Ag$_2$CO$_3$ (a), nano-sized Ag$_2$CO$_3$ (b), Ag$_2$CO$_3$/0.5 wt% RGO (c), Ag$_2$CO$_3$/1 wt% RGO (d), and Ag$_2$CO$_3$/3 wt% RGO (e) composites.](image)

Fig. 1 XRD patterns of micro-sized Ag$_2$CO$_3$ (a), nano-sized Ag$_2$CO$_3$ (b), Ag$_2$CO$_3$/0.5 wt% RGO (c), Ag$_2$CO$_3$/1 wt% RGO (d), and Ag$_2$CO$_3$/3 wt% RGO (e) composites.

XRD analysis (Fig. 1) shows that all the diffraction peaks of the as-prepared samples were in good agreement with those of the monoclinic structure of Ag$_2$CO$_3$ (JCPDS file No. 26-0339). The XRD peak intensities of the nano-sized Ag$_2$CO$_3$ are weaker than that of the micro-sized Ag$_2$CO$_3$, and the width of all diffraction peaks is broader than that of the micro-sized Ag$_2$CO$_3$ sample, suggesting the formation of smaller Ag$_2$CO$_3$ crystallites in nano-sized Ag$_2$CO$_3$. This was attributed to the synergic performance of DMF and ethanol. In DMF solvent, the Ag$^+$ ions and DMF could form the weakly bound [Ag(amide)]$^-$ complex. When the CO$_3^{2-}$ ions in ethanol and water were added into the above DMF
solvent, strong chemical combination occurred between the Ag$^+$ ions in the [Ag(amide)]$^-$ complex and CO$_3^{2-}$ ions, resulting in the formation of Ag$_2$CO$_3$ particles. The bound DMF in [Ag(amide)]$^-$ complex and ethanol, which was acted as a capping agent, can hinder the growth of Ag$_2$CO$_3$ crystal, leads to the formation of Ag$_2$CO$_3$ nanoparticles. Fig. S1 shows that peak of RGO at around 2θ = 10.2° corresponds to the (001) reflection. However, no peak attributed to RGO was observed in the XRD pattern, which may be attributed to the destruction of the regular stacking of graphene sheets by the loading of Ag$_2$CO$_3$ nanoparticles.$^{31,32}$

The presence of RGO and Ag$_2$CO$_3$ are further supported by Raman spectroscopy. As is shown in Fig.2, two characteristic peaks of RGO can be observed, the G-band, which is due to the $E_{2g}$ vibrational mode of sp$^2$ bonded carbon and is observed at 1580 cm$^{-1}$, and the D-band at 1350 cm$^{-1}$ is due to the A$_{1g}$ mode breathing vibrations of six-membered sp$^2$ carbon rings. The Raman spectra of Ag$_2$CO$_3$ display four characteristic peaks located at approximately 959 cm$^{-1}$, 1102 cm$^{-1}$, 1120 cm$^{-1}$, 1170 cm$^{-1}$. Besides the bands attributed to the Ag$_2$CO$_3$ vibrations, two characteristic peaks for the graphitized structures are observed in the Raman spectrum of Ag$_2$CO$_3$/RGO composite, suggesting the existence of RGO in the Ag$_2$CO$_3$/RGO composite.

Fig. S3 shows the whole XPS spectrum of the Ag$_2$CO$_3$/2 wt% RGO composite. In the high-resolution XPS spectrum of Ag 3d, two individual peaks at about 368.1 and 374.0 eV can be assigned to Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ binding energies, respectively, which is characteristic of Ag$^+$ in Ag$_2$CO$_3$. The peaks centered at 284.8, 286.2, 288, and 289.1 eV in Fig. S3c can be attributed to C–C, C–O, C=O and O=C–O groups, respectively. The peaks at 531.5, 532.6, and 533.3 eV in Fig. S3d consist with the characteristic peaks of oxygen in Ag$_2$CO$_3$, O=C, and O=C=O, respectively.

Fig. 2 Raman spectra of RGO (a) pure Ag$_2$CO$_3$ (b) and Ag$_2$CO$_3$/2 wt% RGO (c) composite.

The morphology of the as-prepared samples was investigated using SEM. RGO exhibits flaky foam-like structures (Fig. S2). Fig. 3 shows the SEM images of the micro-sized, nano-sized Ag$_2$CO$_3$ and Ag$_2$CO$_3$/RGO samples. In contrast to the micro-sized Ag$_2$CO$_3$ particles with an average size of ca. 2-4 μm (Fig. 3a), the particle size of the nano-sized Ag$_2$CO$_3$ (Fig. 3b) and Ag$_2$CO$_3$/1 wt% RGO (Fig. 3c) samples decreases sharply, indicating that the DMF and ethanol play dominant roles in the formation of nano-sized Ag$_2$CO$_3$. This is in a good agreement with the above XRD results. The particle size of the nano-sized Ag$_2$CO$_3$ and Ag$_2$CO$_3$/RGO samples is ca. 100 nm. A further observation indicates that Ag$_2$CO$_3$ nanoparticles were attached on the surface of RGO in the Ag$_2$CO$_3}$/RGO sample. It is reported that the hydrophobic RGO can be well dispersed in DMF, and RGO has large specific surface area, which facilitates the absorption of Ag$^+$ ions by the oxygen-containing functional groups (COOH, C–OH, and C–O–C) on the surface of RGO. When CO$_3^{2-}$ ions were added into the dispersion, Ag$_2$CO$_3$ nanoparticles could grow on the surface of RGO and the desired Ag$_2$CO$_3$/RGO nanocomposite were obtained. The TEM image (Fig. 3d and 3e) show that RGO exhibits a large size and flat structure and the well-dispersed Ag$_2$CO$_3$ nanoparticles adhere to the surface of RGO closely. The results are in good agreement with the SEM images.
3.2. Optical properties

The light-absorbance property of nano-sized Ag$_2$CO$_3$ and Ag$_2$CO$_3$/RGO composites was probed with UV–vis absorption spectra, as shown in Fig. 4. Pure Ag$_2$CO$_3$ shows a sharp fundamental absorption edge at about 480 nm. Compared with the spectrum of Ag$_2$CO$_3$, there is an obvious enhanced absorbance in the visible-light region when Ag$_2$CO$_3$ was incorporated with RGO, and the absorption increases with the increase of RGO content in the Ag$_2$CO$_3$/RGO composites.

![Fig. 4 UV–Vis absorption spectra of nano-sized Ag$_2$CO$_3$ (a), Ag$_2$CO$_3$/0.5 wt% RGO (b), Ag$_2$CO$_3$/1 wt% RGO (c) Ag$_2$CO$_3$/2 wt% RGO (d) and Ag$_2$CO$_3$/3 wt% RGO (e) composites.](image)

3.3. Photocatalytic activity

Fig. 5 shows a comparison of photocatalytic activities of the Ag$_2$CO$_3$/RGO composites. After 60 min of irradiation, the photocatalytic decomposition of MO by micro-sized and nano-sized Ag$_2$CO$_3$ was up to 51% and 66%, respectively; however, only a little MO was decomposed by N-doped TiO$_2$ under the same condition. Nano-sized Ag$_2$CO$_3$ exhibits a higher visible-light photocatalytic activity than micro-sized Ag$_2$CO$_3$ due to the higher specific surface area of nanoparticles than microparticles. Further observation shows that the RGO content has a great effect on the photocatalytic activity of Ag$_2$CO$_3$. The pure Ag$_2$CO$_3$ sample shows a poor photocatalytic activity compared with that of Ag$_2$CO$_3$/RGO composites. A small amount of RGO could lead to a sharp increase of MO decomposition from 9% to 25%. Ag$_2$CO$_3$/2 wt% RGO nanocomposite shows the best photocatalytic degradation ability among these Ag$_2$CO$_3$/RGO composites with various RGOs contents. About 91% MO was decomposed by Ag$_2$CO$_3$/2 wt% RGO after 60 min of irradiation. The photocatalytic activity of Ag$_2$CO$_3$/2 wt% RGO composite is also higher than the corresponding Ag$_2$CO$_3$/2 wt% GO sample.

The higher activity may be attributed to the high electrical conductivity of RGO, which is beneficial to transferring of the photogenerated electrons, and then improving the separation of photoinduced carriers.

![Fig. 5 Photocatalytic degradation curves of MO over N-TiO$_2$ (a), Micro-sized Ag$_2$CO$_3$ (b) nano-sized Ag$_2$CO$_3$ (c), Ag$_2$CO$_3$/0.5 wt% RGO (d), Ag$_2$CO$_3$/2 wt% RGO (f), Ag$_2$CO$_3$/3 wt% RGO (g) and Ag$_2$CO$_3$/1 wt% GO (h) composites under visible light irradiation.](image)

![Fig. 6 (A) Repeated photocatalytic degradation of MO solution under visible light irradiation (square: nano-sized Ag$_2$CO$_3$; circle: Ag$_2$CO$_3$/2 wt% RGO composite); (B) XRD patterns of Ag$_2$CO$_3$/2 wt% RGO composite after the first and third cycle experiments.](image)
experiments, respectively. As shown in Fig. 6A, the photocatalytic activity of Ag$_2$CO$_3$/2 wt% RGO is decreased slowly in three successive experimental runs. However, the rate of MO degradation for pure Ag$_2$CO$_3$ decreases more significantly in three successive experimental runs under the same conditions. This result indicates that the Ag$_2$CO$_3$/RGO nanocomposites are more stable than the pure Ag$_2$CO$_3$ nanoparticles. The used Ag$_2$CO$_3$/2 wt% RGO was further collected after three cycle times and characterized by XRD. It was also showed that the photocatalyst treatment after the recycling experiment had no significant effect on the structure of the Ag$_2$CO$_3$/2 wt% RGO sample (Fig. 6B). The results further confirm the enhanced stability of Ag$_2$CO$_3$/RGO nanocomposites.

The enhanced photocatalytic activity and stability of Ag$_2$CO$_3$/RGO composite could be ascribed to the ability of RGO to separate and transfer electron–hole pairs efficiently. As shown in Fig. 7, under visible light irradiation, electrons (e$^-$) in the valence band (VB) of Ag$_2$CO$_3$ can be excited to its conduction band (CB), causing the generation of holes (h$^+$) in the VB of Ag$_2$CO$_3$ simultaneously. Because of the presence of conductive RGO, it can serve as an effective acceptor of the photoexcited electrons; hence, the photogenerated CB electrons of Ag$_2$CO$_3$ can be transferred to RGO in the Ag$_2$CO$_3$/RGO composites. The transportation and mobility of electrons on RGO are very rapid in the specific π-conjugated structure; thus the efficient electron transfer from Ag$_2$CO$_3$ to RGO keeps electrons away from the Ag$_2$CO$_3$ nanoparticles. The used Ag$_2$CO$_3$/RGO nanocomposites are stable and directly produced via a facile chemical precipitation approach in DMF solvent. The Ag$_2$CO$_3$/RGO nanocomposites exhibited a higher photocatalytic activity and stability than that of the pure nano-sized Ag$_2$CO$_3$ for the degradation of MO, and Ag$_2$CO$_3$/2 wt% RGO exhibited the highest photocatalytic degradation efficiency. The enhanced photocatalytic activity and stability can be mainly attributed to the existence of RGO, which can accelerate the charge separation, transportation and transfer.

**4. Conclusions**

The nano-sized Ag$_2$CO$_3$/RGO composites have been successfully and directly produced via a facile chemical precipitation approach in DMF solvent. The Ag$_2$CO$_3$/RGO nanocomposites exhibited a higher photocatalytic activity and stability than that of the pure nano-sized Ag$_2$CO$_3$ for the degradation of MO, and Ag$_2$CO$_3$/2 wt% RGO exhibited the highest photocatalytic degradation efficiency. The enhanced photocatalytic activity and stability can be mainly attributed to the existence of RGO, which can accelerate the charge separation, transportation and transfer.

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**Notes and references**

‡ Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.


Graphical abstract

Nano-sized Ag$_2$CO$_3$/RGO photocatalysts were fabricated by a facile chemical precipitation approach in DMF solvent. The Ag$_2$CO$_3$/RGO nanocomposites exhibited higher photocatalytic activity and stability than the pure nano-sized Ag$_2$CO$_3$. 