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Article

Low-cost and efficient visible-light-driven $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres fabricated *via* an ion exchange route

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ABSTRACT

$\text{CaMg}(\text{CO}_3)_2$ microspheres were prepared and used as hard templates to fabricate a series of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composite microspheres *via* a fast and low-cost ion exchange process. The effects of ion exchange time and temperature on the physicochemical properties and photocatalytic activities of the composite microspheres were studied through photocatalytic degradation of Acid Orange II under xenon lamp irradiation. The obtained samples were analyzed by X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, UV-vis diffuse reflectance spectroscopy, N_2 physical adsorption, and photocurrent tests. The $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ sample with the highest activity was obtained with an ion exchange time of 4 h and temperature of 40 °C. The degradation rate of Acid Orange II by this sample reached 83.3% after 15 min of light irradiation, and the sample also performed well in phenol degradation. The $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ produced under these ion exchange conditions showed a well-ordered hierarchical morphology with small particle sizes, which was beneficial to light absorption and the transfer of photoelectrons (e^-) and holes (h^+) to the catalyst surface. Moreover, the separation of photogenerated carriers over the composites was greatly improved relative to bare $\text{CaMg}(\text{CO}_3)_2$. Despite the very low content of Ag_2CO_3 (2.56%), excellent photocatalytic performance was obtained over the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres.

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1. Introduction

Photocatalysis is attracting intensive attention in the field of pollutant degradation as a green chemistry technology [1–8]. Photocatalysis is deemed a particularly effective and sustainable technology in water purification [9–12]. Many photocatalysts have the powerful ability to decompose organic pollutants

in water. The development of visible-light-driven photocatalysts is particularly desired, as these allow the utilization of natural solar light for both environmental remediation and energy generation [13–20].

In recent years, silver-based semiconductors, such as Ag_2O [21], AgX ($X = \text{Cl}, \text{Br}, \text{I}$) [22–25], Ag_2WO_4 [26], Ag_3PO_4 [27], Ag_3VO_4 [28], and Ag_3AsO_4 [29] have aroused great research

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interest because of their considerable visible-light response. Ag_2CO_3 is another typical silver-based semiconductor, which can decompose various organic dyes under visible light irradiation [30–32]. However, its application is greatly limited by its high operational cost and serious susceptibility to photocorrosion, the latter of which causes very poor stability and recyclability [33]. Various strategies have been proposed to improve the stability of Ag_2CO_3 against photocorrosion. For example, the design of heterojunctions, e.g. $\text{TiO}_2/\text{Ag}_2\text{CO}_3$ [20,33], $\text{Ag}_2\text{CO}_3/\text{ZnO}$ [34], $\text{Ag}_2\text{O}/\text{Ag}_2\text{CO}_3$, and $\text{AgI}/\text{Ag}_2\text{CO}_3$ [35,36], can effectively restrain the photocorrosion and enhance the stability of Ag_2CO_3 . A well-defined heterojunction can suppress the recombination of photogenerated electrons (e^-) and holes (h^+) and thereby improve the photocatalytic performance [3,37]. Photochemical corrosion can also be efficiently inhibited by adding AgNO_3 into the photocatalytic reaction system [38]. Deposition of silver nanoparticles (NPs) to form a plasmonic photocatalyst is another effective means to improve the photocatalytic stability and activity [39,40]. Because silver is a noble metal, the cost of fabrication of Ag_2CO_3 is relatively high. Bare Ag_2CO_3 cannot be reused, which further increases its operational cost. Moreover, the practical application of Ag_2CO_3 as a photocatalyst requires the addition of AgNO_3 as well as the deposition of noble metal NPs, thus further limiting its viability as a result of increased cost. On the other hand, photocatalytic performance is closely related to the morphological structures of catalysts [41,42]. Recent investigations have indicated that microsphere photocatalysts can display remarkably improved aqueous photocatalytic performance because of their efficient light-harvesting and carrier separation ability, high surface area, ease of settling and delivery, and high surface permeability [43–47].

In this work, $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composite microspheres were successfully prepared by a simple ion exchange route using $\text{CaMg}(\text{CO}_3)_2$ microspheres as the hard template. The relationships between the photocatalytic activity and preparation conditions for the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres were discussed. The results showed that under the optimum conditions, i.e., an ion exchange time of 4 h and reaction temperature of 40 °C, a high degree of ion exchange took place. The produced $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres showed a unique hierarchical morphology and high photocatalytic performance. More importantly, the fabrication cost of the Ag_2CO_3 photocatalyst was greatly reduced because of the low content of Ag_2CO_3 in $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$.

2. Experimental

2.1. Preparation of $\text{CaMg}(\text{CO}_3)_2$ microsphere template

All chemicals were of analytical grade and used without further purification. The $\text{CaMg}(\text{CO}_3)_2$ microsphere template was synthesized according to the literature [48]. Typically, 0.01 mol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL distilled (deionized, DI) water, and then 0.01 mol $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was added to the above solution. After stirring for 10 min, the mixture became a clear solution. Then, 20 mL of 0.02 mol Na_2CO_3 solution

was added dropwise into the above clear solution under continuous stirring and a white emulsion precipitate appeared. The suspension was vigorously stirred for 30 min at room temperature. Then, the suspension was heated at 60 °C for 24 h. The product was washed with DI water several times and dried at 100 °C for 6 h to obtain the $\text{CaMg}(\text{CO}_3)_2$ template.

2.2. Preparation of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composite microspheres at different conditions

The Ag_2CO_3 composite microspheres were prepared via an ion exchange route. In this procedure, the as-prepared $\text{CaMg}(\text{CO}_3)_2$ template powder was dispersed ultrasonically in DI water (30 mL) for 10 min. Then, 15 mL AgNO_3 aqueous solution with stoichiometric AgNO_3 (CO_3^{2-} in $\text{CaMg}(\text{CO}_3)_2$) was added dropwise to the above mixture at 40 °C and the reaction time was variously controlled as 2, 4, 6, 12, and 24 h. The resulting products were obtained by vacuum filtration, washed with DI water and ethanol, then collected after drying at 60 °C for 6 h. With a fixed 4 h reaction time, the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres were also fabricated at different temperatures. The controlled reaction temperatures were 30, 40, 50, and 60 °C. The product was obtained by vacuum filtration, washed with DI water and ethanol, and then collected after drying at 60 °C for 6 h.

2.3. Characterization

The crystal properties of the fabricated products were characterized by powder X-ray diffraction (XRD) on a Bruker D8-Advance X-ray diffractometer at 40 kV and 40 mA using monochromatized $\text{Cu } K_\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The morphology of the samples was observed by a Philips XL30 scanning electron microscope (SEM). The UV-vis diffuse reflectance spectra (DRS) were recorded on a UV-vis spectrophotometer (UV-2550, Shimadzu). The absorption spectra were referenced to BaSO_4 . Fourier transform infrared (FT-IR) spectra were collected on a Nicolet-470 Frontier. Samples were pressed into KBr disks using a disk preparation apparatus. The Brunauer-Emmett-Teller (BET) surface areas of the samples were analyzed from N_2 adsorption-desorption isotherms determined at liquid nitrogen temperature (−196 °C) on an automatic analyzer (ASAP 2020). Photocurrent measurements were performed on a CHI 660E electrochemical workstation (Chenhua Instruments, China) in a conventional three-electrode configuration with a Pt foil as the counter electrode and a Ag/AgCl (saturated KCl) as the reference electrode. A 300-W xenon lamp (PLS-SXE 300) served as the light source. The electrolyte was a Na_2SO_4 aqueous solution (0.1 mol/L). The working electrodes were prepared as follows: 15 mg photocatalyst and 0.5 mL Nafion dispersing reagent were added to 5 mL absolute ethanol, and sonicated for 30 min. The slurry was then spread on a 1.0 cm × 1.0 cm indium-tin oxide (ITO) glass substrate and dried in air. The photoresponses of the samples, with light on and light off, were measured at 0.3 V.

2.4. Photocatalytic test

Under xenon lamp irradiation, the photocatalytic activities of the fabricated samples were examined by photodegradation of Acid Orange II in aqueous solution. In a typical photodegradation process, 50 mg of photocatalysts was added into 80 mL of Acid Orange II solution (20 mg/L). Prior to irradiation, the suspensions were magnetically stirred in the dark for 40 min to ensure the adsorption-desorption equilibrium of Acid Orange II on the surface of the photocatalysts. Using a 500-W xenon lamp (solar 500N) as the light source, the above suspension was vigorously stirred during the photocatalytic reaction process at room temperature. The reaction mixture was sampled at given time intervals during light illumination. After centrifugation, the Acid Orange II concentration was measured on a UV-vis spectrophotometer (Agilent, HP 8453). To investigate the photocatalytic activity of the samples against typical organic phenolic contaminants, activity tests were carried out with 10 ppm of phenol as the target contaminant.

3. Results and discussion

3.1. Ag_2CO_3 content in $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composites

The $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composites were obtained via the following ion exchange reaction: $4 \text{Ag}^+ + \text{CaMg}(\text{CO}_3)_2 \rightarrow 2 \text{Ag}_2\text{CO}_3 + \text{Ca}^{2+} + \text{Mg}^{2+}$. The reaction degree of the photocatalysts prepared by this method was obtained by analyzing the mass fraction of the generated Ag_2CO_3 as a percentage of the total mass, which was estimated by measuring the concentration of Ag^+ ions by inductively coupled plasma emission spectroscopy (ICP). The process was as follows. First, 20 mg sample was dissolved in 20 mL dilute HNO_3 solution and the obtained solution was diluted 100 times. The concentration of Ag^+ ions in the obtained solution was measured by ICP. The mass fraction of Ag_2CO_3 in the composite was calculated using the molar concentration of Ag^+ . Table 1 gives the calculated Ag_2CO_3 contents in the produced composites. The mass fraction of Ag_2CO_3 in the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples ranged from 1.40% to 2.56%. The solubility of Ag_2CO_3 (8.45×10^{-12} mol/L) is much smaller than that of CaCO_3 (3.32×10^{-9} mol/L) and MgCO_3 (6.82×10^{-6} mol/L). Therefore, we can infer that Ag^+ was able to replace Mg^{2+} and Ca^{2+} in the $\text{CaMg}(\text{CO}_3)_2$. Moreover, the ion exchange reaction first took place on the outer layer of the $\text{CaMg}(\text{CO}_3)_2$

Table 1

Ag_2CO_3 content in $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ determined by ICP.

Ion exchange conditions	ICP result (ppm)	Ag_2CO_3 mass percent (%)
2 h, 40 °C	0.1086	1.40
4 h, 40 °C	0.1981	2.56
6 h, 40 °C	0.1431	1.85
12 h, 40 °C	0.1335	1.72
24 h, 40 °C	0.1140	1.47
4 h, 30 °C	0.1764	2.28
4 h, 40 °C	0.1981	2.56
4 h, 50 °C	0.1365	1.76
4 h, 60 °C	0.1158	1.49

crystals, after which the Ag_2CO_3 phase gradually replaced the core of $\text{CaMg}(\text{CO}_3)_2$. We can thus infer that the obtained $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples were core-shell-like composites. The $\text{CaMg}(\text{CO}_3)_2$ template partly remained as the shrinking core. Therefore, the fabrication cost of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ photocatalyst was greatly reduced because of the low content of Ag_2CO_3 in these composites.

3.2. XRD and surface area analysis

XRD was used to investigate the phase composition of the catalysts synthesized via ion exchange at different ion exchange temperatures and times. Fig. 1 shows the XRD patterns of the obtained samples. For the pure template sample, a clear diffraction peak at 30.6° appeared, which was indexed to the (104) plane of the rhombohedral phase of $\text{CaMg}(\text{CO}_3)_2$ (JCPDS No. 73-2444). For the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composites, all the samples exhibited sharp and intense diffraction peaks at 2θ of 18.6° , 20.5° , 32.5° , 33.7° , 37.0° , and 39.7° . These peaks were attributed to the monoclinic phase of Ag_2CO_3 (JCPDS No. 07-2184). In contrast, no characteristic peaks for $\text{CaMg}(\text{CO}_3)_2$ could be clearly detected in the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composites, possibly because of either the weakness of the diffraction peaks of $\text{CaMg}(\text{CO}_3)_2$, or interference from the coated Ag_2CO_3 phase. Fig. 1(c) shows the XRD patterns of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ (4 h, 40 °C) before and after reaction. It can be found that no obvious phase variation was observed.

The Scherrer equation was used to estimate the average crystallite sizes of the Ag_2CO_3 phase in the composites, as fol-

Fig. 1. XRD patterns of the samples. (a) $\text{CaMg}(\text{CO}_3)_2$ template and $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composites obtained at 40 °C for different ion exchange times; (b) $\text{CaMg}(\text{CO}_3)_2$ template and $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composites obtained after ion exchange time of 4 h at different temperatures; (c) The $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ sample (40 °C, 4 h) before and after reaction.

lows: $D = 0.89\lambda/(\beta\cos\theta)$, where λ is the wavelength of the X-rays, β is the width in radian of the XRD peak at half the peak height for the (130) plane, and θ is the measured diffraction angle. The results are shown in Tables 2 and 3. From Table 2, it can be seen that the average crystallite size of the Ag_2CO_3 phase decreases with the increase of reaction time. Table 3 indicates that the average crystallite size of the Ag_2CO_3 phase in the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples prepared at 40 °C is larger than that of the other samples.

The influence of different preparation conditions on the surface area of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ was further investigated by N_2 physical adsorption-desorption. These results are also presented in Tables 2 and 3. We can see that all the catalysts exhibit small specific surface areas (0.03–1.27 m^2/g), and the preparation conditions have little effect on the specific surface areas of the samples.

3.3. Morphological analysis

The morphology of typical samples of each product was characterized by SEM. From Fig. 2(a), we can see that the $\text{CaMg}(\text{CO}_3)_2$ template is composed of microspheres with diameters of $\sim 10\ \mu\text{m}$ and very smooth surfaces. From Fig. 2(b) to (e) it can be seen, to our surprise, that the morphologies are considerably altered after the ion exchange reaction, and the smooth surfaces have disappeared. Although the products still maintain their spherical morphology, the microspheres are transformed into stacked aggregations of small crystal particles, and the size of these spherical aggregations is not uniform. From the previous XRD analysis, we can infer that the small crystal particles are mainly composed of Ag_2CO_3 crystals. The variation in temperature (30 to 60 °C) exerted only minor influence on the morphology. The $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples prepared at 50 or 60 °C for 4 h display irregular spherical morphologies. Fig. 2(f) shows that, in contrast to the other

Fig. 2. SEM images of typical fabricated samples. (a) $\text{CaMg}(\text{CO}_3)_2$; (b) $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared at 30 °C for 4 h; (c) $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared at 40 °C for 4 h; (d) $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared at 50 °C for 4 h; (e) $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared at 60 °C for 4 h; (f) $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared at 40 °C for 8 h; (g) and (h) $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ (40 °C, 4 h) after the reaction.

Table 2

Average crystallite sizes and specific surface areas of the prepared $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples obtained at 40 °C for different ion exchange times.

Ion exchange time (h)	Average crystallite size (nm)	Specific surface area (m^2/g)
2	81.1	0.20
4	54.9	0.17
6	54.1	0.14
12	35.0	0.05
24	28.5	0.03

Table 3

Average crystallite sizes and specific surface areas of the prepared $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples obtained after ion exchange time of 4 h at different temperatures.

Ion exchange temperature (°C)	Average crystallite size (nm)	Specific surface area (m^2/g)
30	37.7	0.19
40	54.9	0.17
50	31.9	0.18
60	26.4	1.27

samples, the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared at 40 °C for 8 h shows no microsphere morphology. From the SEM analysis, we can see that the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ fabricated at 40 °C for 4 h shows the most regular microsphere morphology. These $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres are hierarchical composite nanostructures constructed of very small and irregular nanocrystals. The SEM images of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ (40 °C, 4 h) sample after the reaction are shown in Fig. 2(g) and (h). It's obvious that this sample still has the regular spherical morphology, which suggests the good stability of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$.

3.4. Light absorption analysis

The optical properties of the as-prepared catalysts were measured by UV-vis DRS, as shown in Fig. 3. The pure $\text{CaMg}(\text{CO}_3)_2$ microspheres show no light absorption in the visi-

Fig. 3. UV-vis absorption spectra of the prepared Ag_2CO_3 samples: (a) different preparation times; (b) different preparation temperatures.

ble light range. After the ion exchange reaction, despite their low Ag_2CO_3 content, the obtained $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composites display wide and intense absorption in the visible light range, which is essential for significant photocatalytic activity [49]. In Fig. 3(a), we also find that at the fixed temperature of 40 °C, the ion exchange reaction time slightly influences the light absorption ability. Among the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples prepared at 40 °C, the sample prepared for 4 h exhibits the strongest light absorption, which could be related to the nanostructures of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres or the overall Ag_2CO_3 content. Fig. 3(b) indicates that the temperature of ion exchange also slightly affects the light absorption ability. However, the variation in light absorption ability with the change of temperature does not follow a regular trend. But all of samples show better light absorption than the bare Ag_2CO_3 prepared by precipitation method. The band gap energy (E_g) for $\text{CaMg}(\text{CO}_3)_2$ and Ag_2CO_3 was determined by $E_g = 1240/\lambda_g$ (eV), where λ_g is the absorption edge of the samples and λ_g was obtained from the intercept between the tangent of the absorption curve and the abscissa [8]. The calculated band gap energies for $\text{CaMg}(\text{CO}_3)_2$ and Ag_2CO_3 are 4.92 eV and 2.52 eV, respectively. We can see that Ag_2CO_3 is the active phase because the band gap of $\text{CaMg}(\text{CO}_3)_2$ is very large and is almost the insulator.

3.5. FT-IR properties

The FT-IR spectra of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples are presented in Fig. 4. All of the samples showed three main absorption bands. The broad peak at 3000–3500 cm^{-1} was ascribed to the O–H stretching vibrations of physically adsorbed water [4]. The broad peak at 3200 cm^{-1} was considered to be the stretching vibration of surface O–H groups on the catalyst. Surface O–H groups can trap photogenerated holes (h^+) to form hydroxyl radicals ($\cdot\text{OH}$), which are powerful oxidizing agents. Therefore, the increased surface hydroxyl groups on the catalyst can be expected to accelerate the degradation of dye molecules. The peaks at 1640 cm^{-1} originate from the H–O–H bending vibration of the adsorbed water. The peaks at around 1350 and 1450 cm^{-1} were attributed to the characteristic absorption of the carbonate ion (CO_3^{2-}). Careful comparison of the spectra suggested that the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared at 40 °C for 4 h shows the strongest intensity of O–H groups, which would be expected to promote the photocatalytic degradation reaction, as mentioned above. The FT-IR of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ sample (40 °C, 4 h) before and after reaction are shown in Fig. 4(c). We can still find the obvious peaks in 1350 cm^{-1} and 1450 cm^{-1} which belong to CO_3^{2-} . The peaks of $\cdot\text{OH}$ and the bending vibration of H–O–H of the adsorbed water molecules are rela-

Fig. 4. FT-IR spectra of the prepared $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples. (a) Prepared at 40 °C for different times; (b) Prepared for ion exchange time of 4 h at different temperatures; (c) the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ sample (40 °C, 4 h) before and after reaction.

tively enhanced, which could be due to the humidity of the sample.

3.6. Photocurrent test

We carried out photocurrent tests to explore the influence of different preparation temperatures and reaction times on the separation efficiency of the photogenerated electron and holes in $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ [50]. When the electrodes were illuminated under a xenon lamp light, clear photocurrent responses were observed [51]. It can be seen from Fig. 5(a) that the intensity of the photocurrents of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples prepared for different ion exchange times follows the order $4 > 6 > 2 > 24 > 12$ h. All the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples produce larger photocurrents than that of bare Ag_2CO_3 prepared by precipitation. At the fixed temperature of 40 °C, the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ sample obtained for an ion exchange time of 4 h displays the strongest photocurrent. Fig. 5(b) shows the influence of fabrication temperature on the photocurrent response. Clearly, $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ synthesized at 40 °C shows a much higher photocurrent than the samples fabricated at other temperatures. Furthermore, the distinct photocurrent responses of all the samples of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ are again stronger than that of bare Ag_2CO_3 . According to the literature [50,52], a high photocurrent response suggests a high separation efficiency of the photogenerated electrons and holes. The photocurrent test results thus demonstrated that an ion exchange reaction temperature of 40 °C and reaction time of 4 h were the optimal conditions for synthesizing $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$, producing a sample with high photocatalytic performance because of the enhanced separation efficiency of charge carriers.

3.7. EIS test

Electrochemical impedance spectroscopy (EIS) is a well-established approach to analyze the charge transfer resistance and separation efficiency of the photogenerated electrons and holes of photocatalysts. As shown in Fig. 6, in the EIS tests, the sample of Ag_2CO_3 prepared by precipitation produced

Fig. 6. Electrochemical impedance spectroscopy of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ and Ag_2CO_3 samples.

a larger arc radius than that of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ prepared by ion exchange at 40 °C for 4 h. The smaller the radius, the smaller the migration resistance of the carriers [53], and the higher the separation efficiency of photogenerated electrons and holes. Hence, the results indicate that the existence of $\text{CaMg}(\text{CO}_3)_2$ reduced the migration resistance of carriers in Ag_2CO_3 to improve its photocatalytic performance.

3.8. Photocatalytic performance

Under xenon lamp irradiation, the photocatalytic activities of the as-prepared samples were evaluated by photodegradation of a dye, Acid Orange II. Fig. 7 shows the photocatalytic performance test over $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples. Firstly, from Fig. 7(a) and (b), we can see that the adsorption capacity of all the as-prepared catalysts to acid orange was weak in the degradation process, indicating that the reaction temperature and time had little effect on the adsorption performance of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$, which could be due to their small specific surface area. Fig. 7(a) indicates that the $\text{CaMg}(\text{CO}_3)_2$ template exhibits no photocatalytic activity, while all the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples display clearly perceptible activity in dye degradation. Evidently, the ion exchange time and

Fig. 5. Photocurrent densities produced under simulated solar light irradiation (xenon lamp) by different $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ samples. (a) Prepared at 40 °C for different times; (b) Prepared for ion exchange time of 4 h at different temperatures.

Fig. 7. The photocatalytic performance test over $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ samples: (a) At 40 °C for different time; (b) At 4 h for different temperature; (c) The photocatalytic performance test of degradation phenol.

temperature greatly influenced the activity. At the fixed temperature of 40 °C, the ion exchange time of 4 h produced the $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ sample with the highest activity. Further increases in reaction time exerted an adverse effect on the activity, and a decrease in photocatalytic performance was observed. After light irradiation for 15 min, the degradation rates of Acid Orange II were 77%, 84%, 69%, 72%, and 61% over $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ prepared for ion exchange times of 2, 4, 6, 12, and 24 h, respectively. Compared with pure Ag_2CO_3 prepared by the precipitation method, all the $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ samples show better photocatalytic performance.

Fig. 7(b) shows the influence of preparation temperature on the photocatalytic activity. After light irradiation for 15 min, the degradation rates of Acid Orange II were 66%, 82%, 78%, and 41% over $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ prepared at 30 °C, 40 °C, 50 °C, and 60 °C, respectively. Once again, therefore, the sample prepared at 40 °C for 4 h displays the highest catalytic activity.

Activity tests were also carried out for degradation of another typical organic contaminant, phenol. As shown in Fig. 7(c), bare Ag_2CO_3 exhibited low degradation activity. In contrast, excellent photocatalytic performance was obtained over the $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ composite microspheres, which further confirms the superior properties of these core-shell-structured microspheres.

$\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ and Ag_2CO_3 were also subjected to stability tests. Fig. 8 compares the activity of the two catalysts during repeated cycling, suggesting that despite the low con-

Fig. 8. Stability test of $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ and Ag_2CO_3 for degradation of Acid Orange II.

tent of Ag_2CO_3 in the composite microspheres, the stability of $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ was significantly higher than pure Ag_2CO_3 . The active phase of $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ is Ag_2CO_3 , so it still suffers photocorrosion; however, the photocorrosion rate is much lower than that of bare Ag_2CO_3 . Therefore, the existence of the $\text{CaMg}(\text{CO}_3)_2$ core not only brings about a large increase in activity but also in stability.

3.8. Discussions

To explore the radicals involved in the photodegradation process over $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$. We used electron spin resonance (ESR) to test the active species. 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as a capture agent and the results are shown in Fig. 9. In this figure, before irradiation, it can be found that there is no ESR signal for the sample. After illumination, the sample has a weak ESR signal of $\text{DMPO}\cdot\text{O}_2^-$, indicating that O_2^- is an active species in the process of photocatalytic reaction. Moreover, we can see the significant ESR characteristic signals of $\text{DMPO}\cdot\text{OH}$ in the field of about 3488 to 3516 (G). Therefore, it can be concluded that $\cdot\text{OH}$ plays an important role in the photodegradation process.

To account for the superior photocatalytic performance of the $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ microspheres prepared under various

Fig. 9. ESR signals of $\text{DMPO}\cdot\text{OH}$ and $\text{DMPO}\cdot\text{O}_2^-$ of $\text{CaMg}(\text{CO}_3)_2@Ag_2CO_3$ (40 °C, 4 h).

Fig. 10. Schema of $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres' preparation and photocatalytic degradation reaction.

conditions, we must first understand the formation mechanism of the core-shell composite microspheres. Fig. 10 illustrates the preparation procedure and the photodegradation reaction. After ion exchange reaction of Ag^+ for Ca^{2+} and Mg^{2+} , the compact $\text{CaMg}(\text{CO}_3)_2$ microspheres transform into more loosely structured, hierarchical $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres. The outer layers of the microspheres contain nano-sized Ag_2CO_3 crystals. Under irradiation by visible light, Ag_2CO_3 produces photogenerated electrons and holes. The holes migrate to the surface to generate hydroxyl radicals ($\cdot\text{OH}$), which oxidize the dye molecules to CO_2 and H_2O . Meanwhile, the adsorbed O_2 can capture individual photogenerated e^- to generate photocatalytically active $\text{O}_2^{\cdot-}$ radicals [6]. XRD and ICP analysis indicate that the obtained samples underwent a relatively large degree of ion exchange. The UV-vis absorption spectra indicate that the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres absorbed much more strongly in the visible region than did the bare Ag_2CO_3 prepared by the precipitation method. Moreover, the results of the photocurrent test for $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ implied that the photogeneration of electrons and holes was enhanced over the composites. The intimate interfacial contact between $\text{CaMg}(\text{CO}_3)_2$ and Ag_2CO_3 improved the separation efficiency of charge carriers. In addition, the small particle size and hierarchical structure of the Ag_2CO_3 phase deposited on the outer layer of the microspheres benefitted the harvesting of light and adsorption of dye molecules.

4. Conclusions

Core-shell-like $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composite microspheres with low content of Ag_2CO_3 were prepared via a facile ion exchange route. The influences of ion exchange time and temperature on the morphology and structure of the composite microspheres and photocatalytic performance of the photocatalysts were investigated. The ICP test for decomposition of Acid Orange II demonstrated that the content of Ag_2CO_3 is 2.56% in $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ microspheres produced by ion exchange (of Ag^+ for Ca^{2+} and Mg^{2+}) for 4 h at 40 °C. These composite microspheres possess a hierarchical structure and

enhanced visible light absorption. Moreover, the existence of the $\text{CaMg}(\text{CO}_3)_2$ core promotes the separation of photogenerated electrons and holes. Compared with bare Ag_2CO_3 , the cost for the fabrication and operation of the $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composite microspheres was greatly decreased, and superior photocatalytic performance was obtained over the microspheres. We believe these low-cost $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ composite microspheres have potential applications as photocatalysts in environmental remediation.

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Graphical Abstract

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**Low-cost and efficient visible-light-driven
CaMg(CO₃)₂@Ag₂CO₃ microspheres fabricated via an ion
exchange route**

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Core-shell like CaMg(CO₃)₂@Ag₂CO₃ composite microspheres with low content of Ag₂CO₃ were prepared via a facile ion exchange route, the existence of CaMg(CO₃)₂ cores could largely promote the separation of photogenerated electrons and holes, leading to high photocatalytic activity and stability.

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离子交换法制备廉价而高效的可见光驱动CaMg(CO₃)₂@Ag₂CO₃微球光催化剂

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摘要: Ag₂CO₃是一种典型的银基半导体, 可在可见光照射下降解各种有机染料, 但制备成本高, 光腐蚀严重, 稳定性差, 难以循环利用等, 因而限制了它的实际应用. 针对这些问题, 目前多数的改进措施是构建异质结, 有效的分离光生电子与空穴来提高Ag₂CO₃的光催化性能. 比如典型的异质结光催化剂有TiO₂/Ag₂CO₃, Ag₂CO₃/ZnO, Ag₂O/Ag₂CO₃和AgX/Ag₂CO₃等. 也有在表面化学沉积, 光化学还原Ag等贵金属形成等离子体等方式提高其光催化性能, 但是很少通过特殊形貌控制以

提高 Ag_2CO_3 的光催化性能。最近的研究表明, 由于多尺度微球结构催化剂具有高效的光捕能力, 同时具有比表面积大、易沉降, 良好的物质传输能力和表面的渗透性, 因而在液相光催化反应中具有明显的优势。因此, 我们期望制备出一个多尺度微球结构 Ag_2CO_3 光催化剂。 $\text{CaMg}(\text{CO}_3)_2$ 是一种具有微球结构的半导体, 它与 Ag_2CO_3 有相同的阴离子结构, 但是两者在水溶液中的溶解度相差较大, 利用这个特性理论上可以将两个不同的半导体结合在一起, 得到一种新型的复合微球。

本文以 $\text{CaMg}(\text{CO}_3)_2$ 微球为硬模板, 通过简单的离子交换成功制备了粒径约为 $10\ \mu\text{m}$ 的 $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ 微球。利用X射线衍射、 N_2 物理吸附、扫描电镜、傅里叶变换红外光谱和紫外-可见漫反射吸收光谱、光电流等手段对在不同反应时间与温度下制得的 $\text{CaMg}(\text{CO}_3)_2$ 与 Ag_2CO_3 的复合物进行了表征。结果表明, 在 $40\ ^\circ\text{C}$ 下 Ag^+ 与 Ca^{2+} 、 Mg^{2+} 离子交换4 h后, 得到了一种多尺度 $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ 复合微球。此时, 微球中 Ag_2CO_3 的含量约为2.56%。结果表明, 这种具有多尺度结构的复合微球能够增强可见光的吸收。电化学阻抗测试和光电流测试表明, $\text{CaMg}(\text{CO}_3)_2$ 核的存在可以降低光生载流子的迁移阻力, 进而促进光生电子与空穴的分离。在光降解酸性橙II的测试中, 核壳结构的 $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ 复合微球表现出了更高的催化活性, 而且具有更好的循环使用性能。同时, 相对于纯 Ag_2CO_3 光催化剂来说, $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ 复合微球制备的成本大幅度降低。ESR测试证明了 $\cdot\text{OH}$ 为 $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ 复合微球光催化过程中的主要活性物质。

关键词: 硬模板; 离子交换; $\text{CaMg}(\text{CO}_3)_2@ \text{Ag}_2\text{CO}_3$ 复合微球; 光催化性能

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