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Boosting the photocatalytic performance of Ag_2CO_3 crystals in phenol degradation *via* coupling with trace N-CQDs

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ABSTRACT

A series of N-CQDs/ Ag_2CO_3 composite crystals (where N-CQDs = Nitrogen doped carbon quantum dots) were prepared by adding different volumes of a solution of N-CQDs during Ag_2CO_3 crystal growth. Under irradiation from a 350-W Xe lamp light (with optical filter, $\lambda \geq 420$ nm), the performance of N-CQDs/ Ag_2CO_3 in photocatalytic degradation of phenol was evaluated. The as-prepared samples were analyzed by XRD, SEM, TEM, BET, element mapping, UV-vis DRS, FT-IR, XPS, transient photocurrent response and EIS testing. The results showed that after coupling with trace amounts of N-CQDs, both the photocatalytic activity and stability of Ag_2CO_3 were greatly boosted. The addition of N-CQDs solution influenced the crystallization of Ag_2CO_3 , resulting in a distinct decrease in Ag_2CO_3 crystal size and an obvious increase in surface area. Moreover, the charge transfer resistance was greatly reduced, and the separation efficiency of photogenerated electrons and holes was strongly promoted. The presence of NCQDs on the surface of the catalysts facilitates the transfer of photogenerated electrons, slowing the photocorrosion rate of Ag_2CO_3 , and then resulting in higher stability than bare Ag_2CO_3 in degradation. The synergistic effect of the improvement of morphology and charge transfer rate thus accounted for the superior photocatalytic performance of N-CQDs/ Ag_2CO_3 .

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1. Introduction

Semiconductor photocatalytic technology is used to remediate various organic pollutants in waste water and transform solar energy into chemical energy in the form of clean and renewable hydrogen fuel under mild conditions [1–6]. The key to the application of photocatalytic technology is the design and fabrication of a clean, non-toxic and environmentally friendly

photocatalyst [7–10]. Efficient photocatalysts have the powerful ability to decompose a range of organic contaminants in aqueous solution, such as dyes [11–15], antibiotics/drugs [16,17], aromatic compounds [18–20] and other synthesized organic compounds [21–23].

Recent studies reveal that Ag-based semiconductors exhibit prominent visible-light-driven catalytic activity because of their narrow band gap energy [24]. At present, significant research is

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focused on improving the activity and stability of Ag-based photocatalysts [15,25–30]. One of the most important Ag-based semiconductors is Ag_2CO_3 , which has the distinct advantage of being driven by visible light absorption. However, it suffers serious photocorrosion in the process of photocatalysis. Therefore, various strategies have been proposed to improve its activity and stability. One effective method is to design and construct a suitable heterojunction composite containing Ag_2CO_3 to enhance the separation of photogenerated electron-hole pairs [31]. For example, in our previous investigation, an effective $\text{Ag}_2\text{O}/\text{Ag}_2\text{CO}_3$ photocatalyst was synthesized by phase transformation during the thermal decomposition of Ag_2CO_3 , which greatly improved the photocatalytic performance of the latter [32]. Typical examples of heterostructured Ag_2CO_3 composites include $\text{Ag}_2\text{CO}_3/\text{TiO}_2$ [33], $\text{g-C}_3\text{N}_4/\text{Ag}_2\text{CO}_3$ [34,35], $\text{AgCl}/\text{Ag}_2\text{CO}_3$ [36], $\text{Ag}_2\text{CO}_3/\text{Bi}_2\text{O}_3$ [37], $\text{Ag}_2\text{S}/\text{Ag}_2\text{CO}_3$ [38], $\text{ZnO}/\text{AgI}/\text{Ag}_2\text{CO}_3$ [39], graphene oxide/ Ag_2CO_3 [40] and $\text{Ag}_2\text{CO}_3/\text{SrCO}_3$ [41]. Other effective methods to inhibit the photocorrosion of Ag_2CO_3 include adding AgNO_3 to the Ag_2CO_3 reaction system [42] and the formation of a plasma resonance structure [43]. Recently, new composites such as reduced graphene oxide/ Ag_2CO_3 [44], $\text{Ag}_2\text{O}/\text{Ag}_2\text{CO}_3/\text{MWNTs}$ [45], Z-scheme $\text{Ag}_2\text{CO}_3/\text{N-doped graphene}$ [46] and an $\text{Ag}_3\text{PO}_4/\text{Ag}_2\text{CO}_3$ p-n heterojunction [47] have also been reported.

The unique physicochemical properties of carbon quantum dots (CQDs) have aroused great interest in terms of improvement of the photocatalytic performance of catalysts. CQDs are a form of carbon-based material with good water-solubility and the strong ability to accelerate the transfer of photogenerated electrons [48–51], enabling them to significantly boost photocatalytic performance. For example, an enhanced photocatalytic performance was observed over CQDs/ $\text{Ag}/\text{Ag}_2\text{O}$ [52], N-CQDs/ Ag_3PO_4 [53] and CQDs/ Ag_3PO_4 [54]. Moreover, the doping of N atoms into CQDs can allow a more effective delocalization of the photogenerated charge, thus promoting the transfer of electrons, while preserving the intrinsic characteristics of CQDs [51]. Therefore, a high photocatalytic performance can be expected by coupling N-doped CQDs (N-CQDs) into Ag_2CO_3 crystals.

In this study, solutions of N-CQDs and of bare CQDs were successfully prepared by a simple hydrothermal method. For the first time, trace amounts of N-CQDs or CQDs were coupled with Ag_2CO_3 , producing N-CQDs/ Ag_2CO_3 or CQDs/ Ag_2CO_3 composite nanocrystals. The relationships between photocatalytic performance and N-CQDs content were investigated. Interestingly, the presence of trace amounts of N-CQDs influenced the crystal growth of Ag_2CO_3 and greatly promoted the separation of photogenerated electrons and holes, leading to a large enhancement in photocatalytic performance.

2. Experimental

2.1. Catalyst synthesis

All chemicals used were of analytical grade and purchased from Sigma Aldrich. N-CQDs were prepared according to the

method reported in the literature with minor modifications [55]. Typically, a specific amount of solid citric acid (0.42 g) was dissolved in 10 mL of deionized (DI) water, then, 8 mmol urea was added into the above solution to form a clear solution. After that, the solution was transferred into a 20 mL Teflon-lined stainless steel autoclave and maintained at 200 °C for 5 h. After cooling, a yellow solution was obtained and the solution was centrifugated to remove the residue. Finally, a yellow N-CQDs solution was obtained by diluting the above solution 100 times. The undoped CQDs solution was prepared by the same process but without adding urea.

N-CQDs/ Ag_2CO_3 was synthesized by the precipitation method. In a typical synthesis, AgNO_3 (2.2 mmol) and a certain amount of N-CQDs solution (0, 1, 3, 5 and 10 mL) were dissolved in DI water. The total volume of solution was kept at 35 mL for all samples. After stirring for 30 min, 15 mL of Na_2CO_3 was added dropwise to the above solution and further stirred for 1 h. The precipitate was collected by filtration, and washed with DI water and absolute alcohol several times. Then, the samples were dried at 80 °C under vacuum. CQDs/ Ag_2CO_3 was prepared by the same process.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the samples were obtained with a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation at 40 kV and 40 mA. The morphology of the catalyst was analyzed by scanning electron microscopy (SEM) on an XL 30 scanning electron microscope (Holland Philips). Transmission electron microscopy (TEM) was performed on a JEOL-2100F microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 470 FT-IR spectrometer (USA) using samples pressed by a KBr disk preparation apparatus. The BET surface areas of the samples were measured on an automatic analyzer (Micromeritics, ASAP 2020) at liquid nitrogen temperature. The light absorption properties of the samples were tested by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) on a UV-vis spectrophotometer (UV-2550, Shimadzu) and referenced to BaSO_4 . Photocurrent tests and electrochemical impedance spectroscopy (EIS) were carried out on an electrochemical workstation (CHI-660E, China). The curve of the relationship between photocurrent and time was measured under a 500-W Xe lamp as the excitation light source. The electrolyte was 0.1 mol/L Na_2SO_4 solution. Pt was used as the auxiliary electrode and Ag/AgCl was used as the reference electrode.

2.3. Photocatalytic activity measurement

Aromatic compounds are a major class of hazardous pollutants in waste water, being harmful to the environment and aquatic life. In this study, the representative organic pollutant phenol was chosen as the degradation target to evaluate the photocatalytic activity of the fabricated samples. A 350-W Xe lamp with 420 nm long-pass filter was used as the visible light source. Typically, 0.020 g of photocatalyst was added into 50

mL of phenol solution with a phenol concentration of $C_0 = 0.020$ g/L. The suspension was irradiated under the light source after magnetically stirring in the dark for 40 min to reach the adsorption–desorption equilibrium. Aliquots (3 mL) of the suspension were sampled and subjected to high-speed centrifugation. The concentration of phenol was measured by UV-vis spectrophotometry, and the degradation rate of phenol was calculated from the change in its concentration relative to C_0 .

3. Results and discussion

3.1. Crystal properties

The XRD patterns of Ag_2CO_3 , N-CQDs/ Ag_2CO_3 and CQDs/ Ag_2CO_3 are presented in Fig. 1. Bare Ag_2CO_3 shows intense diffraction peaks at $2\theta = 18.7^\circ$, 20.6° , 32.7° , 33.8° , 37.2° and 39.5° . These diffraction peaks correspond to the crystal planes of (020), (110), (-101), (130), (200) and (031), respectively, for the Ag_2CO_3 monoclinic phase (JCPDS 012-0766). When N-CQDs or CQDs solution was added to the Ag_2CO_3 crystal growth system, the obtained QDs/ Ag_2CO_3 composites displayed almost identical diffraction peaks to bare Ag_2CO_3 . However, careful observation reveals the appearance of two new peaks at $2\theta = 19.4^\circ$ and 34.1° in all samples. These two peaks correspond to the hexagonal crystal phase of Ag_2CO_3 (JCPDS 031-1237). This result shows that the presence of quantum dots during the Ag_2CO_3 growth process slightly modified the resulting Ag_2CO_3 crystal phase. However, no diffraction peaks from the N-CQDs or CQDs themselves were detected, because the QDs were present in only trace amounts.

The average crystal size of the samples was estimated using the Scherrer equation. The equation was solved using the data from the strongest diffraction peak, at $2\theta = 33.8^\circ$. The results are shown in Table 1. The addition of quantum dots in the preparation process resulted in a slight decrease in the average crystallite size of Ag_2CO_3 , indicating that the QDs not only affected the structure of the crystal phase but also the particle size.

Fig. 1. XRD patterns of Ag_2CO_3 , N-CQDs/ Ag_2CO_3 and CQDs/ Ag_2CO_3 samples.

Table 1

Average crystal sizes of the prepared samples.

Sample	Crystal size (nm)
Ag_2CO_3	51.5
1N-CQDs/ Ag_2CO_3	47.6
3N-CQDs/ Ag_2CO_3	41.3
5N-CQDs/ Ag_2CO_3	45.1
10N-CQDs/ Ag_2CO_3	49.5
3CQDs/ Ag_2CO_3	46.1

Table 2

Specific surface areas of the prepared samples.

Sample	A_{BET} (m^2/g)
Ag_2CO_3	0.16
1N-CQDs/ Ag_2CO_3	3.48
3N-CQDs/ Ag_2CO_3	5.47
5N-CQDs/ Ag_2CO_3	6.41
10N-CQDs/ Ag_2CO_3	6.33
3CQDs/ Ag_2CO_3	4.89

3.2. Specific surface area

The surface areas of the prepared samples were determined by nitrogen physisorption and the results are shown in Table 2. As can be seen, the surface area of pure Ag_2CO_3 was very small (~ 0.16 m^2/g). The addition of carbon-based quantum dots induced an obvious increase in surface area (in the range of 3–6 m^2/g). The above SEM analysis demonstrated that the introduction of quantum dots markedly changed the morphological structure of the samples and caused a large decrease in particle size, which is likely to be the main reason for the increase in surface area.

3.3. Morphological structure

The morphological structures of the prepared samples were analyzed by SEM and TEM. Fig. 2(a) and (b) show the SEM images of pure Ag_2CO_3 and 3N-CQDs/ Ag_2CO_3 . We can see from Fig. 2(a) that bare Ag_2CO_3 is composed of irregular rod-like particles. In Fig. 2(b), the obtained 3N-CQDs/ Ag_2CO_3 shows a much smaller particle size than that of pure Ag_2CO_3 . Moreover, the morphology of 3N-CQDs/ Ag_2CO_3 is more irregular, indicating that the introduction of N-CQDs greatly affected the nucleation and crystal growth of Ag_2CO_3 . The low-magnification TEM image of 3N-CQDs/ Ag_2CO_3 is shown in Fig. 2(c), which appears to depict large Ag_2CO_3 particles surrounded by many smaller particles. In previous studies, the particle sizes of N-CQDs have been measured in the range of a few nanometers [48]. Therefore, it was inferred that these small particles could be N-CQDs. To confirm this deduction, high-resolution (HR) TEM imaging was carried out. In the HRTEM image (Fig. 2(d)), clear crystal spacings of around 0.264 nm can be observed. These lattice spacings correspond to the (130) crystal plane of Ag_2CO_3 . In a different magnified image, an interplanar spacing of 0.230 nm could be observed for one of the small particles. This spacing

Fig. 2. SEM images of pure Ag_2CO_3 (a) and 3N-CQDs/ Ag_2CO_3 (b); TEM (c) and HRTEM (d) images of 3N-CQDs/ Ag_2CO_3 ; (e)–(h) element mapping images of Ag, C, O and N.

corresponds to the (1120) lattice fringes of graphene [56,57], which further confirms the presence of N-CQDs. In Fig. 2(d), the embedded picture shows a clear crystal spacing of 0.206 nm, corresponding to the (131) crystal plane of Ag_2CO_3 , which indicates that the N-CQDs were in close contact with Ag_2CO_3 nanoparticles.

Fig. 2(e)–(h) are the element mapping images of clusters of several particles in 3N-CQDs/ Ag_2CO_3 . We can clearly see that the elements Ag, C, O and N are homogeneously distributed throughout the 3N-CQDs/ Ag_2CO_3 particles, indicating the coupling of the N-CQDs with the Ag_2CO_3 crystals.

3.4. Light absorption

Fig. 3 shows the UV-vis absorption spectra of the fabricated CQDs and N-CQDs solutions. The CQDs solution shows strong absorption in the range of 200 to 264 nm. For the N-CQDs solution, a new absorption at around 328 nm appears, which confirms the successful doping of N into the CQDs.

The UV-vis DRS spectra of all the samples are shown in Fig. 4(a). As can be seen, pure Ag_2CO_3 exhibits strong absorption of UV and visible light. In the visible light region, the absorption

Fig. 3. UV-vis absorption spectra of the CQDs and N-CQDs solutions.

performance of the composite photocatalyst was slightly weakened after coupling with CQDs and N-CQDs. Note that the increase of N-CQDs content within a certain range actually enhanced the absorption ability of the sample in the visible region. However, above that range, the light absorption of Ag_2CO_3 was slightly weakened with increasing N-CQDs content. This is consistent with a previous study [58], which found that excess N-CQDs could accumulate over the catalyst surface and block the absorption of light.

For each sample, $(\alpha h\nu)^2$ was plotted versus $h\nu$ (the energy of the absorbed light) in order to calculate the band gaps, as shown in Fig. 4(b). The band gap energies of Ag_2CO_3 , 3N-CQDs/ Ag_2CO_3 and 3CQDs/ Ag_2CO_3 were estimated from the intercept of the tangent to the plot as 2.76, 1.95 and 2.51 eV, respectively. Fig. 4(c) displays photographs of the three prepared samples. The successive color change between those three samples, from yellow-green to dark brown to ash black, provides further evidence of the structural change of the fabricated composite samples caused by the presence of CQDs or N-CQDs.

3.5. FT-IR analysis

Fig. 5 displays the FT-IR spectra of the fabricated samples. Firstly, Fig. 5(a) reveals the presence of several functional groups, i.e., O–H, N–H, C=O, C–O and C=N/C–N, on the surface of the N-CQDs. The broad peak around 3440 cm^{-1} is attributed to the stretching vibration of O–H and N–H. The absorption peaks at 1045 and 1664 cm^{-1} are assigned to the C–O and C=O stretching vibrations [57]. The peak at 1385 cm^{-1} belongs to the C=N/C–N in-plane stretching vibration [59], indicating the presence of doped nitrogen in the CQDs. It can be seen from Fig. 5(b) that all the samples have a strong absorption peak at about 3400 cm^{-1} , which arises from the stretching vibrations of surface $\cdot\text{OH}$ on the samples [60]. Another weak peak at about 1640 cm^{-1} is the bending vibration of H–O–H for adsorbed water. The characteristic absorption bands of CO_3^{2-} are mainly found at 1449 , 1382 , 883 and 705 cm^{-1} [61]. Compared with

Fig. 4. UV-vis absorption spectra (a) and $(\alpha h\nu)^2$ versus $h\nu$ curves of Ag_2CO_3 , N-CQDs/ Ag_2CO_3 and CQDs/ Ag_2CO_3 samples (b); (c) Representative photographs of the prepared samples.

pure Ag_2CO_3 , the absorption band at about 3400 cm^{-1} is wider and stronger for the composites containing coupled quantum dots. This result shows that the presence of carbon-based QDs enriches the quantity of surface $-\text{OH}$ groups. In the photocatalytic process, $-\text{OH}$ groups can react with photogenerated holes to produce $\cdot\text{OH}$ radicals, which are important active species in the photocatalytic reaction.

3.6. Raman spectra

Fig. 6 shows the Raman spectra of pure Ag_2CO_3 and 3N-CQDs/ Ag_2CO_3 . Pure Ag_2CO_3 exhibits six characteristic Raman peaks at around 702 , 804 , 924 , 1062 , 1167 and 1397 cm^{-1} .

After the introduction of N-CQDs, the intensity of these characteristic peaks for 3N-CQDs/ Ag_2CO_3 becomes markedly weaker, possibly because of the coverage of N-CQDs over the surface of Ag_2CO_3 . Moreover, two weak peaks at about 1342 and 1532 cm^{-1} can be seen in the Raman spectrum of 3N-CQDs/ Ag_2CO_3 . These peaks are attributed to the D-band and G-band, respectively, of the N-CQDs [62].

3.7. XPS analysis

The survey spectrum and high-resolution XPS of N-CQDs/ Ag_2CO_3 are shown in Fig. 7. The spectra in Fig. 7(a) reveal the presence of Ag, O, N and C. The binding energies at

Fig. 5. FT-IR spectra of the prepared samples. (a) N-CQDs; (b) Ag_2CO_3 , N-CQDs/ Ag_2CO_3 and CQDs/ Ag_2CO_3 .

Fig. 6. Raman spectra of pure Ag_2CO_3 and 3N-CQDs/ Ag_2CO_3 .

531.3, 399.6 and 284.7 eV correspond to O 1s, N 1s and C 1s, respectively. In Fig. 7(b), the two peaks at 374.3 and 368.2 eV in the Ag 3d spectrum correspond to $\text{Ag } 3d_{3/2}$ and $\text{Ag } 3d_{5/2}$, which confirms the existence of Ag^+ in N-CQDs/ Ag_2CO_3 . The O 1s peak at 531.3 eV in Fig. 7(c) is attributed to the O^{2-} in the Ag_2CO_3 . Fig. 7(d) shows three peaks in the C 1s spectrum. The peak at 284.7 eV is attributed to the C atoms in Ag_2CO_3 . The peaks at 286.3 and 288.9 eV correspond to the C–O/C–N and C=O/C=N bonds, respectively [63]. The N 1s spectrum (Fig. 7(e)) contains four peaks at 400.7, 399.8, 398.9 and 396.9 eV, which are assigned to the N–H, N–O, C=N and C–N bonds, respectively [64].

Fig. 8. Photocurrent density induced under simulated solar light irradiation (Xe lamp).

3.8. Photocurrent test

To analyze the separation efficiency of photogenerated electrons and holes, the photocurrent responses of the samples were tested on an electrochemical workstation. A specific amount of sample (15 mg) was ultrasonically dispersed and then evenly coated on conductive glass sheets. The light-induced current intensity of each sample was measured under the same bias voltage of 0.5 V and the obtained results are shown in Fig. 8. As can be seen, the photocurrent intensity was greatly improved for all samples containing N-CQDs. The

Fig. 7. XPS spectra of N-CQDs/ Ag_2CO_3 . (a) Survey spectrum; high-resolution spectra: (b) Ag 3d; (c) O 1s; (d) C 1s; (e) N 1s.

Fig. 9. Electrochemical impedance spectra of pure Ag_2CO_3 , 3CQDs/ Ag_2CO_3 , and 3N-CQDs/ Ag_2CO_3 .

sample of 3N-CQDs/ Ag_2CO_3 , prepared by adding 3 mL of N-CQDs solution, showed the largest improvement in photocurrent intensity. However, with a further increase in N-CQDs content, the photocurrent intensity decreased sharply.

3.9. EIS test

The AC impedance test is an effective technique to measure the charge transfer resistance and separation efficiency of the photogenerated charge in a photocatalyst during the photocatalytic reaction. Fig. 9 shows the Nyquist plots of the pure Ag_2CO_3 , 3CQDs/ Ag_2CO_3 and 3N-CQDs/ Ag_2CO_3 . As can be seen, the semicircle diameter of 3N-CQDs/ Ag_2CO_3 is much smaller than these of pure Ag_2CO_3 and 3CQDs/ Ag_2CO_3 , and the semicircle diameter of 3CQDs/ Ag_2CO_3 is smaller than that of pure Ag_2CO_3 . In the AC impedance test [65], a smaller semicircle indicates a smaller charge transfer resistance. Therefore, the results in Fig. 9 demonstrate that the charge transfer resistance of Ag_2CO_3 during the photochemical reaction was reduced after the addition of quantum dots, and the separation efficiency of photogenerated electrons and holes was promoted. These effects were greatest for 3N-CQDs/ Ag_2CO_3 , i.e., the sample synthesized by the introduction of 3 mL of N-CQDs solution during

the fabrication process. This finding is consistent with the above photocurrent test.

3.10. Photocatalytic performance

In this experiment, phenol was chosen as the degradation target under visible light ($\lambda \geq 420$ nm) illumination. As shown in Fig. 10, a blank test was conducted to confirm that phenol could not be degraded under visible light irradiation in the absence of a photocatalyst. As shown in Fig. 10(a), pure Ag_2CO_3 exhibited weak photocatalytic activity. After coupling with N-CQDs, an obvious increase in degradation activity was obtained over the N-CQDs/ Ag_2CO_3 composites. Moreover, the photocatalytic activity was closely related to the N-CQDs content. In the fabrication of N-CQDs/ Ag_2CO_3 , the addition of 1–3 mL N-CQDs solution resulted in an obvious increase in photocatalytic activity over the obtained N-CQDs/ Ag_2CO_3 . However, the addition of greater amounts of N-CQDs solution, i.e., to obtain 5N-CQDs/ Ag_2CO_3 and 10N-CQDs/ Ag_2CO_3 , negatively affected the photocatalytic activity. This is illustrated in Fig. 10(b), which shows the degradation rate of phenol over different samples after 150 min light irradiation. Fig. 10(c) compares the photocatalytic activities of two samples fabricated with the addition of equal volumes of either N-CQDs or CQDs solution, respectively, as well as the activity of pure Ag_2CO_3 . As can be seen, the addition of either species of quantum dots improved the photocatalytic activity of Ag_2CO_3 ; however, the effect of N-CQDs was greater than that of CQDs. The degradation rate of phenol over 3N-CQDs/ Ag_2CO_3 was roughly twice that of 3CQDs/ Ag_2CO_3 after 150 min light illumination.

As described in the introduction, an insurmountable problem for Ag_2CO_3 is its poor stability against corrosion during the process of photocatalysis. Fig. 11 shows the results of stability tests of Ag_2CO_3 and 3N-CQDs/ Ag_2CO_3 . The activity of Ag_2CO_3 was almost completely lost after just three runs because of photocorrosion resulting from metallic Ag formation. In contrast, even after three successive cycles, 3N-CQDs/ Ag_2CO_3 still achieved a 27% degradation rate for phenol after 150 min visible light irradiation, indicating its relatively high stability.

To determine which active species play(s) the major role in the photoreaction process, tests were carried out involving the degradation of methyl orange (MO) in the presence of

Fig. 10. (a) Photocatalytic degradation of phenol over Ag_2CO_3 and N-CQDs/ Ag_2CO_3 ; (b) Phenol degradation rates over Ag_2CO_3 and N-CQDs/ Ag_2CO_3 ; (c) Phenol degradation rates over Ag_2CO_3 , 3N-CQDs/ Ag_2CO_3 and 3CQDs/ Ag_2CO_3 .

Fig. 11. Stability test of Ag₂CO₃ and 3N-CQDs/Ag₂CO₃ in phenol degradation.

Fig. 12. Effects of addition of radical-capture agents on the degradation of MO over N-CQDs/Ag₂CO₃.

free-radical scavengers. The results are shown in Fig. 12. As can be seen, the degradation rate of MO over N-CQDs/Ag₂CO₃ was heavily suppressed by the addition of scavengers for $\cdot\text{O}_2^-$ radicals, holes and $\cdot\text{OH}$ radicals (*p*-benzoquinone, BQ; disodium ethylene diamine tetraacetate, Na₂-EDTA; and *tert*-butanol, TBA, respectively), indicating that $\cdot\text{O}_2^-$, holes and $\cdot\text{OH}$ may all have participated in the degradation of MO. However, the greatest reduction in degradation rate occurred in the presence of TBA, which implies that $\cdot\text{OH}$ was the main active species in phenol degradation.

Based on the above experimental results, a photocatalytic reaction mechanism over this N-CQDs/Ag₂CO₃ composite system was proposed (Fig. 13). The superior photocatalytic performance over N-CQDs/Ag₂CO₃ can be attributed to two causes. Firstly, the addition of N-CQDs solution during the crystallization process of Ag₂CO₃ resulted in a distinct decrease in Ag₂CO₃ particle size and a large increase in surface area, which benefits light-harvesting and the adsorption of reactant molecules. Secondly, the presence of N-CQDs greatly promoted the separation of photogenerated electrons and holes. These photogenerated charge carriers were then captured by O₂ and OH⁻ to generate

Fig. 13. Photocatalytic mechanism of N-CQDs/Ag₂CO₃ for enhanced photocatalytic performance.

active species ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$) that were able to decompose phenol. Compared with bare CQDs, the presence of N atoms in N-CQDs induced more effective charge delocalization to promote the transfer of electrons, resulting in the high activity of N-CQDs/Ag₂CO₃.

4. Conclusions

N-CQDs/Ag₂CO₃ composite crystals were successfully prepared by a simple precipitation method. TEM and Raman spectroscopy analysis confirmed that the N-CQDs adhered over the surface of the Ag₂CO₃ crystals. Small crystal size and large specific surface area were obtained for the N-CQDs/Ag₂CO₃ composites. Moreover, the presence of N-CQDs reduced the charge transfer resistance and improved the separation rate of photo-generated electrons and holes. The highest photocatalytic performance in phenol degradation was obtained over 3N-CQDs/Ag₂CO₃, i.e., the sample synthesized using 3 mL of N-CQDs solution. This research could provide new insights into the design and fabrication of highly efficient Ag-based semiconductor photocatalysts for environmental purification.

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Graphical Abstract

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Boosting the photocatalytic performance of Ag_2CO_3 crystals in phenol degradation via coupling with trace N-CQDs

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NCQDs/ Ag_2CO_3 composite crystals were successfully prepared by using simple precipitation method. The presence of NCQDs can improve the light absorption and increase the specific surface area of Ag_2CO_3 , and largely promote the separation of photogenerated carries to boost photocatalytic performance with trace NCQDs.

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复合微量NCQDs对提高Ag₂CO₃半导体降解苯酚的光催化性能研究

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摘要: 半导体光催化具有无毒、无污染、低能耗等优点, 广泛应用于水溶液中染料、药物分子的降解等. 其中Ag₂CO₃半导体因其较窄的带隙能和显著的可见光吸收性能而引起广泛关注. 但是Ag₂CO₃在光照下极不稳定. 目前, 主要是通过引入其它半导体等材料与其进行复合来提其催化活性与稳定性.

本文以一种具有良好的水溶性以及能够加快电子转移能力的碳量子点(CQDs)和氮掺杂的碳量子点(NCQDs)作为复合材料, 利用简单的沉淀法制备出了CQDs/Ag₂CO₃、NCQDs/Ag₂CO₃等复合材料. 结果表明, CQDs和NCQDs的存在能够很好的提升光催化性能. 而且发现NCQDs除了具有碳量子点的特性外, 还能够诱导电荷离域, 更加有效的促进电子的转移. 利用X射线衍射、扫描电镜、透射电镜、N₂物理吸附、元素成像、紫外-可见光漫反射吸收光谱、红外光谱以及光电流和交流阻抗测试等手段对所制备的CQDs/Ag₂CO₃和NCQDs/Ag₂CO₃进行了表征. 结果表明, 量子点的存在能够有效增大Ag₂CO₃的比表面积. 紫外-可见漫反射吸收结果说明, 量子点的存在还能够一定程度上增大样品的可见光吸收性能. 而光电流和交流阻抗测试结果证明, 量子点的存在能显著降低载流子的迁移阻力, 提高光生电子与空穴的分离效率. 在量子点相同含量下, NCQDs能够更加有效的转移载流子. 以350 W氙灯加可见光滤光片($\lambda \geq 420$ nm)作为光源进行光催化降解苯酚的性能测试. 结果表明, NCQDs/Ag₂CO₃比CQDs/Ag₂CO₃表现出更高的活性, 其对苯酚的降解率约为后者的2倍; 同时NCQDs/Ag₂CO₃还具有更佳的性能. 自由基捕获试验说明, 在光催化过程中, 主要的活性物种为·OH与·O₂⁻. NCQDs能够提高Ag₂CO₃活性与稳定性的原因在于, NCQDs能够提高了催化剂的比表面积, 增强光催化剂的光吸收性能. 另外NCQDs能够比CQDs更有效的转移电子, 提高光生e⁻和h⁺的分离效率, 产生更多的光催化降解活性物种.

关键词: Ag₂CO₃; 氮掺杂碳量子点; 光催化; 活性与稳定性; 苯酚

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