Applied Chemical Engineering (2022) Volume 5 Issue 1
doi: 10.24294/ace.v5i1.1405

ORIGINAL RESEARCH ARTICLE

Photocatalytic performance of carbon nanotubes/activated carbon composite carrier carrying cadmium sulfide

Minghan Qu, Tong He, Tianyi Liu, Chensha Li*

School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China. E-mail: 2015068@hlju.edu.cn

ABSTRACT

The in-situ reaction process was used to prepare composite materials loaded with cadmium sulfide, which were respectively loaded by carbon nanotubes, activated carbon, and carbon nanotube/activated carbon composites for the study of photocatalytic degradation of methyl orange. The results show that when carbon nanotubes and activated carbon are used as carriers, the photocatalytic degradation reaction rate constants are 3.6 times and 8.8 times higher than those without a carrier. The photocatalytic performance of the carbon nanotube/activated carbon composite carrier with a mass ratio of 20:80 to support cadmium sulfide is significantly higher than that of cadmium sulfide supported by carbon nanotubes and activated carbon respectively, and its photocatalytic degradation reaction rate constant is 30%–40% higher than that under the condition of activated carbon alone as carrier. It shows that when the modified activated carbon is used as a photocatalyst carrier, carbon nanotubes have a significant effect in improving the efficiency of degrading organic matter.

Keywords: Carbon Nanotubes; Activated Carbon; Cadmium Sulfide; Methyl Orange

ARTICLE INFO

Received: 15 November 2021
Accepted: 29 December 2021
Available online: 9 January 2022

1. Introduction

Semiconductors have a special electronic structure: the lence band is full, the conduction band is idle, and the band gap is wide. The semiconductor photocatalyst generates electron-hole pairs under the action of visible light or ultraviolet light. When the energy of the photon is greater than or equal to the band gap, the valence band electrons are triggered to cross the forbidden band and enter the conduction band, and at the same time form corresponding holes on the valence band, which have strong redox properties. They directly react with organic matter or interact with surrounding media (O_2 or H_2O as electron acceptors) to produce highly active HO· free radicals, and then react with organic matter to degrade organic matter[1].

At present, among the photocatalysts, titanium oxide (TiO_2), cadmium sulfide (CdS) and zinc oxide (ZnO) are the most eye-catching. Compared with the other two semiconductor photocatalysts, CdS has unique advantages: the preparation process is simple, and the band gap (2.5 eV[2]) is lower than that of TiO_2 (3.2 eV[3]) and ZnO (3.4 eV[4]), so the wavelength range of light absorption is wider.

Suspension-type photocatalysts tend to condense in water and lose their activity, and hinder the penetration of light. It is difficult to separate and recover the catalyst. Therefore, fixed-type photocatalysts are more concerned. Commonly used carriers include glass balls, sea sand, zeolite, and activated carbon. Among them, activated carbon is most commonly used because of its superior performance[5]. Carbon nanotubes (CNTs) have a unique structure, nano-scale size, high effective specific surface area and the properties of presenting a conductor. They have superior performance in the fields related to energy storage, electronic materials and engineering materials[6–9], and are considered as a good carrier[10].

In this paper, take the difficult-to-degrade organic dye methyl orange[11] as an example, study the performance of photocatalytic degradation of organics by preparing the fixed cadmium sulfide semiconductor photocatalysts with carbon nanotubes and activated carbon (AC) as carriers. It is found that in the presence of the two types of carriers, the reaction rate of photocatalytic degradation is significantly higher than that without a carrier. The main mechanism is that both carriers have high specific surface area, effectively adsorb organic matter in the solution, and both can help to improve the photoelectric conversion efficiency of the semiconductor photocatalyst. Performance comparison shows that carbon nanotubes are better than activated carbon in improving the photoelectric conversion efficiency of cadmium sulfide, and the ability of activated carbon to adsorb organic matter in the liquid phase is higher than that of carbon nanotubes. The carbon nanotubes have a one-dimensional nanostructure, which is beneficial to improve the internal structure of activated carbon powder. The research results show that carbon nanotubes have potential advantages in the application of photocatalyst carriers due to their unique properties, and they also open up a new path for the application of carbon nanotubes.

2. Experimental method

Carbon nanotubes are prepared by catalytic cracking of propylene and treated with hydrofluoric acid and nitric acid to remove diatomaceous earth and nickel catalyst particles. The TEM picture of the pure multi-walled carbon nanotubes obtained is shown in **Figure 1**, which has a hollow tubular structure. The diameter is 40–50 nm. Activated carbon is provided by Shandong Huaguang Carbon Powder Factory.

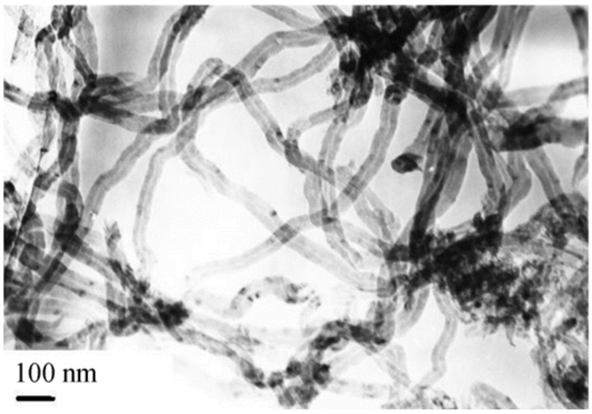


Figure 1. State of carbon nanotubes (CNTs) shown by transmission electron micrograph (TEM).

Preparation of photocatalyst: add a certain amount of carrier (carbon nanotubes, activated carbon or a mixture of carbon nanotubes and activated carbon with a mass ratio of 20:80) into $CdCl_2$ solution (400 mL, 0.0125 M), and stir for 30 min. While stirring, slowly add equimolar Na_2S solution (100 mL, 0.05 M) in a separatory funnel, and the dropping rate is controlled at 1 $mL \cdot min^{-1}$. After the addition, continue to stir for 2 h. Waitting for the reaction to end, filter with a nuclear pore membrane with a pore size of 0.4 μm and wash with deionized water. The obtained powder was dried in an oven at 80 °C, and finally ground and dispersed. The preparation of pure cadmium sulfide photocatalyst is similar to this process, but no other carrier is added.

Photocatalyst solid loading: weigh a certain amount of photocatalyst powder (the net content of cadmium sulfide is 1.4 g), mix it with a suspension of absolute ethanol and polytetrafluoroethylene (the net weight of which is 5% of the photocatalyst), then blow with hot air while stirring to volatilize the ethanol. After the viscosity of the solution increases, spread it evenly on the surface of the 10 cm × 9 cm cotton and linen fiber cloth, and use it for photocatalysis experiments after natural drying.

Photocatalytic reaction: the light source is backed by two ultraviolet lamps with a dominant wavelength of 365 nm and a power of 6 W. The rectangular reaction vessel is made of stainless steel, and the photocatalyst immobilized on the template is fixed by the iron clamp at the bottom of the vessel. The initial concentration of the methyl orange solution is 20 $mg \cdot L^{-1}$, the volume is 500 mL, and the distance between the liquid surface and the light source is 25 mm. Stir for 2 h to reach adsorption equilibrium, then turn on the UV lamp to start the photocatalytic reaction, take samples regularly, and measure the absorbance of the solution sample at the maximum absorption wavelength of methyl orange (λ_{max} = 465 nm) with a 721 UV spectrophotometer. 3 h later, stop the lighting and stirring.

Measure the absorbance of a methyl orange solution with a concentration of 0–20 mg·L^{-1}, and the fitted absorbance corresponding to the concentration relationship is:

$$C = -0.070\,2 + 14.163\,14A \quad (1)$$

The absorbance (A) is approximately proportional to the concentration of methyl orange (C). The degradation rate of methyl orange in the photocatalytic degradation reaction is:

$$\eta = (A_0 - A)/A_0 \times 100\% \quad (2)$$

In the formula: η is the degradation rate of methyl orange; A_0 and A are the absorbance values of the methyl orange solution at the initial and a certain moment, respectively.

Photocatalyst adsorption determination: the operation process is similar to the photocatalytic reaction, but the UV lamp is not turned on. When the photocatalyst immobilized on the template is placed at the bottom of the methyl orange solution, start stirring, and regular samples are selected to measure the absorbance, the calculated value by using formula (2) is the adsorption rate.

Photocurrent test of photocatalyst: distribute the photocatalyst evenly on the conductive glass (ITO) fixed by transparent tape to form a thin film, and then ballast a transparent glass to fix it. The aluminum wire penetrates the transparent tape into the film inside the photocatalyst, an ITO/photocatalyst electrode is thus formed. Use ST900 photometer to measure its photocurrent.

Sample characterization: JEOL–200CX transmission electron microscope, AMRAY–1910 field emission scanning electron microscope, and BRUK–ER D8 Advance polycrystalline X-ray diffractometer (Cu Kα, λ = 0.1540598 nm) were used to test the structure of the sample. The specific surface area is tested by the BET method, the pore size distribution is by the B.J.H method, and the instrument is SORPTOMAT-IC1990. ThermoQuest Italia S.P.A.

3. Experimental results and discussion

3.1 Physical properties of the photocatalyst sample

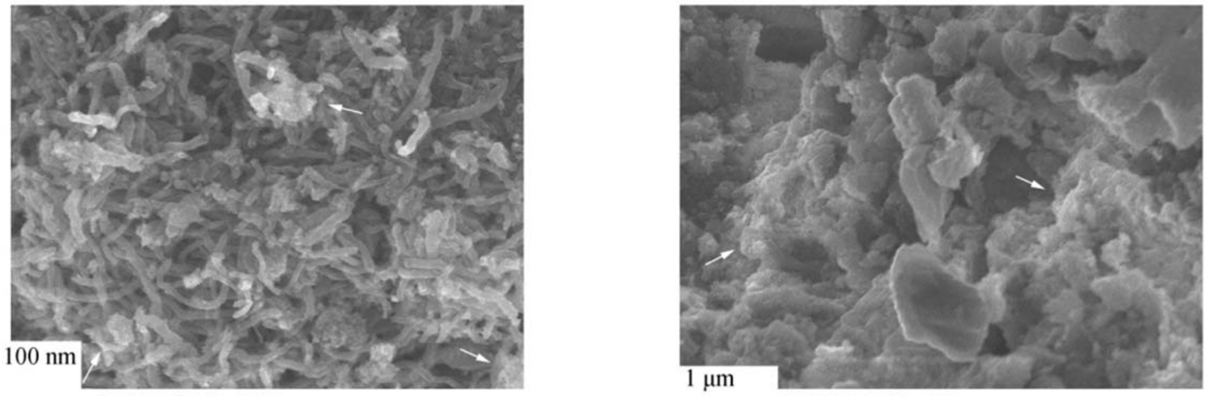
3.1.1 Structural properties

The material composition ratio of the prepared photocatalyst sample and the specific surface physical property parameters, including the specific surface area, specific pore volume, and micropore volume ratio are shown in **Table 1**. It can be seen from **Table 1** that the specific surface area and pore volume of pure CdS without loading materials are relatively small. The specific surface area of the activated carbon-supported CdS composite photocatalyst is higher than that of the carbon nanotube-supported CdS composite photocatalyst, but the ratio of the micropore volume of the former is much larger than the latter. The specific surface area and micropore volume ratio of CdS photocatalyst supported by carbon nanotube/activated carbon composite carrier are between those of the activated carbon-supported CdS composite photocatalyst and the carbon nanotube-supported CdS composite photocatalyst.

Table1. Specifications and specific area properties of prepared photocatalyst samples

Photocatalyst sample	**Weight ratio of CdS and carrier**	**Weight ratio of CNTs and AC**	**Specific area /(m^2·g^{-1})**	**Total pore volume/(cm^3\·g^{-1})**	**Volume ratio of micropores (diameter <2 nm)/%**
CdS			70.67	0.022	27.77
CdS–CNTs1	100:15		118.58	0.184	19.66
CdS–CNTs2	100:40		132.34	0.221	17.52
CdS–AC1	100:15		269.56	0.102	65.52
CdS–AC2	100:40		471.45	0.120	69.07
CdS–CNTs/AC–1	100:15	20:80	236.32	0.134	36.56
CdS–CNTs/AC–2	100:40	20:80	412.43	0.156	38.11

The SEM picture of CdS–CNTs1 and CdS–AC1 samples are shown in **Figure 2**. It can be seen from **Figure 2** that CdS particles are supported on the surface of carbon nanotubes and are evenly dispersed in the carbon nanotube population. The CdS particles loaded on the activated carbon are also uniformly dispersed in the activated carbon particle population.



(a) SEM of CdS–CNTs1
(The arrow refers to the CdS dispersed in the carrier)

(b) SEM of CdS–AC1
(The arrow refers to the CdS dispersed in the carrier)

Figure2. Scan electric microscopy (SEM).

The XRD test curve is shown in **Figure 3**. It can be seen from **Figure 3** that pure CdS, CdS supported by carbon nanotubes, and CdS supported by activated carbon are all cubic crystal phase structures, with diffraction peaks displayed at 26.5°, 43.70°, 51.82° and 71.10° respectively representing the 111, 220, 311 and 331 sides of the cadmium sulfide crystals[12]. The 111-side diffraction peaks of CdS of the latter two samples overlap with the 002-side diffraction peaks of carbon nanotubes and activated carbon respectively[13].

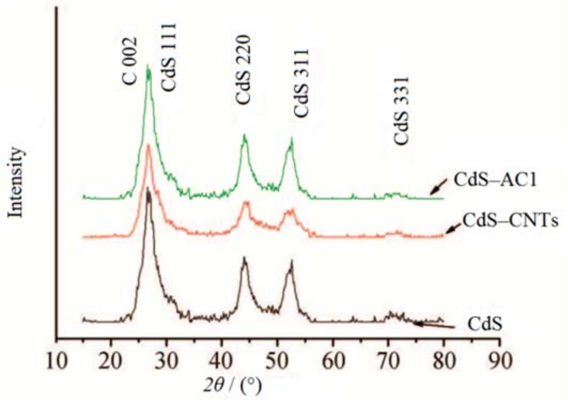


Figure 3. XRD measurement of CdS, CdS–CNTs1 and CdS–AC1.

3.1.2 Photoelectric conversion characteristics

Under the irradiation of ultraviolet light within a certain wavelength range, three samples of pure CdS, carbon nanotube-loaded CdS and activated carbon-loaded CdS all generate photocurrent, indicating that they all have photoelectric conversion properties (**Figure 4**).

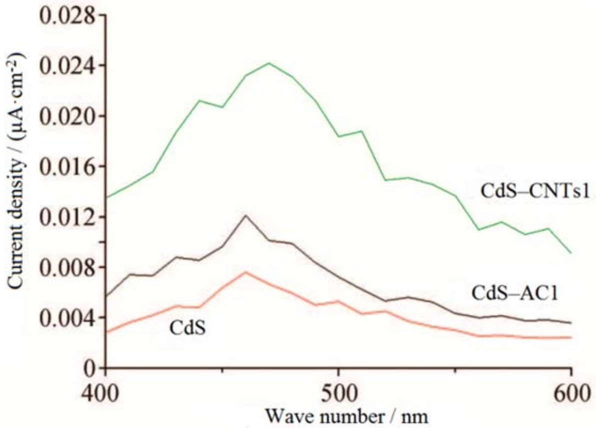


Figure 4. Photocurrent of the photocatalyst.
Note: The test samples are CdS, CdS–CNTs1 and CdS–AC1, and the net CdS content in each sample is equal.

It can be seen from **Figure 4** that the order of photoelectric conversion efficiency is: CdS–CNTs > CdS–AC > CdS. The reasons are as follows: (1) under ultraviolet light, the semiconductor CdS generates electrons and holes to form a photocurrent. Both carbon nanotubes and activated carbon have certain conductivity, which can absorb a part of photogenerated carriers, prevent electrons and holes and improve the photoelectric conversion efficiency; (2) the wall of the carbon nanotubes is composed of a curly graphitic carbon layer, and the degree of graphitization is relatively higher than that of activated carbon which is basically composed of amorphous carbon; (3) carbon nanotubes are one-dimensional nanomaterials with a large aspect ratio. In the stacked body, they can overlap each other to form a continuous network structure. Compared with the stacked body of granular materials, the contact resistance is smaller.

3.1.3 Absorptivity to organics in solution

Pure CdS has almost no adsorption capacity for methyl orange, as shown in **Figure 5**. It can be seen from **Figure 5** that the photocatalysts containing carbon nanotubes and activated carbon have significant adsorption of methyl orange, indicating that both carbon nanotubes and activated carbon have a significant ability to adsorb methyl orange, and the adsorption capacity of activated carbon is significantly higher than that of carbon nanotubes.

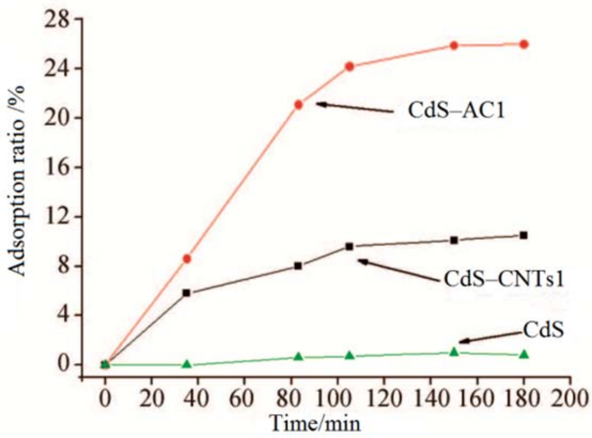


Figure 5. Adsorption of methyl orange of the template-fixed photocatalyst.

3.2 Photocatalytic performance

3.2.1 Photocatalytic performance of CdS-supported carbon nanotube photocatalyst

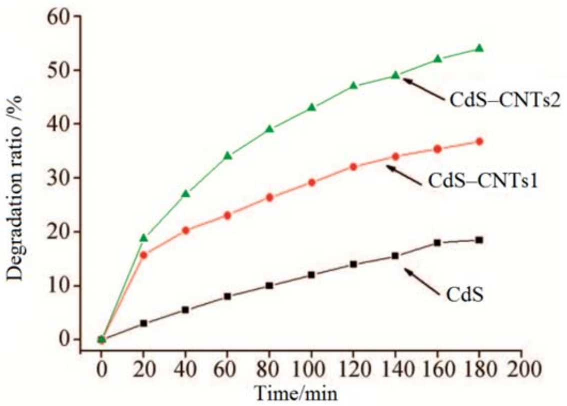


Figure 6. Degradation ratio of methyl orange caused by the CdS and CdS–CNTs photocatalyst.

The degradation rate curve of pure CdS and carbon nanotube-loaded CdS photocatalytic degradation of methyl orange is shown in **Figure 6**. If it meets the first-order reaction, it should have the following formula:

$$-\ln(C/C_0) = kt \quad (3)$$

In the formula: C_0 is the initial concentration of methyl orange; C is the concentration of methyl orange at a certain moment in the photocatalytic reaction; k is the reaction rate constant; t is the time. Since the concentration of methyl orange is approximately proportional to the absorbance, A/A_0 can be used instead of C/C_0. The rate constants and corresponding correlation coefficients of the photocatalytic reaction obtained by fitting are shown in **Table 2**. It can be seen from **Table 2** that the correlation coefficients are all close to 1, which is basically in line with the first-order reaction kinetic relationship.

Table 2. Measured reaction rate constant of the degradation of methyl orange

Photocatalyst sample	CdS	CdS–CNTs1	CdS–CNTs2	CdS–AC1	CdS–AC2	CdS–CNTs/AC–1	CdS–CNTs/AC–2
K (10^{-3} min^{-1})	1.21	2.68	4.31	7.66	10.55	10.47	13.42
Correlative coefficient (R)	0.9963	0.9640	0.9786	0.9894	0.9829	0.9854	0.9836

The photocatalytic degradation ability of carbon nanotubes carrying CdS to degrade methyl orange is significantly higher than that of pure CdS, and its photocatalytic ability increases as the ratio of carbon nanotubes to CdS increases (**Figure 6**). When the mass of carbon nanotubes in CdS–CNTs is 15% and 40% of the mass of CdS, respectively, the photocatalytic reaction rate constants are about 2.3 times and 3.6 times than that of pure CdS, respectively, as shown in **Table 2**. The reasons are as follows: (1) the photoelectric conversion efficiency of carbon nanotubes carrying CdS semiconductors is significantly higher than that of pure CdS (**Figure 4**). Due to the electrical conductivity of carbon nanotubes, photo-generated carriers generated under the action of ultraviolet light can be transferred into the carbon nanotubes. It reduces the recombination opportunities of electrons and holes, and improves the photocatalytic efficiency; (2) the carbon nanotubes have an adsorption effect on the methyl orange in the solution (**Figure 5**), so that the methyl orange is concentrated around the CdS carried, which improves photocatalytic degradation rate; (3) the nanometer diameter of carbon nanotubes, the special structure of one-dimensional nanomaterials and the effective specific surface area play an important role in improving the photocatalytic efficiency of the loaded CdS, so that the loaded CdS particles are evenly dispersed and can avoid mutual aggregation, the surface of CdS particles is effectively exposed, which increases the exposure to light and the contact area with the reactants in the solution; the inside of the accumulation of carbon nanotubes is a continuous network structure in the microscopic view, and the gaps between the carbon nanotubes are continuous[14]; (4) as the proportion of carbon nanotubes in the photocatalyst increases, the specific surface area and pore volume increase (**Table 1**), the dispersion of CdS particles increases, and the contact space with the reacting substance also increase, the photoelectric conversion efficiency and the adsorption of methyl orange in the solution will inevitably increase and strengthen.

3.2.2 Photocatalytic performance of activated carbon supported CdS photocatalyst

The degradation rate curves of pure CdS and activated carbon-supported CdS photocatalytic degradation of methyl orange are shown in **Figure 7**, and the rate constants and corresponding correlation coefficients of the fitted photocatalytic reactions are shown in **Table 2**. It can be seen from **Table 2** that the mechanism is similar to that of carbon nanotubes supporting CdS. The photocatalytic degradation of methyl orange by CdS supported on activated carbon is basically in line with the first-order reaction. When the mass of activated carbon in CdS–AC is 15% and 40% of the mass of CdS, respectively, the photocatalytic reaction rate constants are about 6.4 times and 8.8 times than that of pure CdS, respectively.

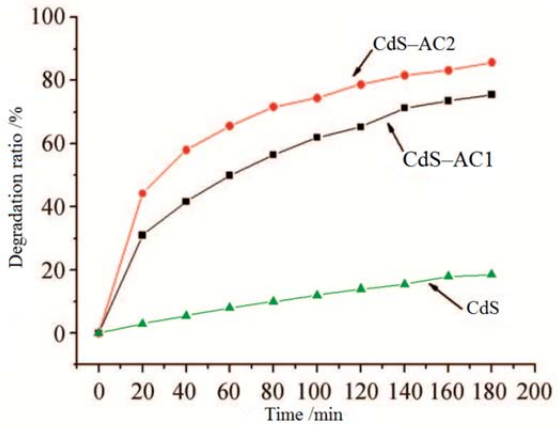


Figure 7. Degradation ratio of methyl orange caused by the CdS and CdS–AC photocatalyst.

3.2.3 Photocatalytic performance of CdS-supported photocatalyst on carbon nanotube/activated carbon composite carrier

The carbon nanotubes and activated carbon were composited at a mass ratio of 20:80, and the carbon nanotube/activated carbon composite carrier was used to prepare a semiconductor photocatalyst with CdS supported by the in-situ reaction in the solution, and the obtained photocatalytic reaction rate constant and correlation coefficient are shown in **Table 2**. It can be seen from **Table 2** that the photocatalytic degradation of methyl orange by the carbon nanotube/activated carbon composite carrier supporting CdS is basically in line with the first-order reaction. When the mass of the carrier is 15% and 40% of the mass of CdS respectively, the photocatalytic reaction rate constant of CdS–CNTs/AC is about 38% and 30% higher than that of CdS–AC, respectively, indicating that the composite carrier demonstrates the individual advantage of carbon nanotubes and activated carbon. The degradation rate curve of photocatalytic degradation of methyl orange is shown in **Figure 8**. It can be seen from **Figure 8** that when the mass ratio of CdS to the carrier is 100:15 and 100:40, the photocatalytic degradation rate of the CdS photocatalyst on the composite carrier is significantly higher than that of the carbon nanotubes and activated carbon supported CdS photocatalyst photocatalytic degradation rate of methyl orange.

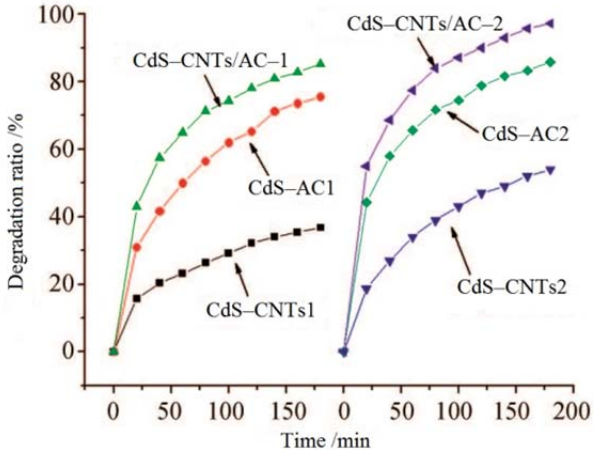


Figure 8. Degradation ratio of methyl orange caused by the CdS–CNTs/AC, CdS–CNTs and CdS–AC photocatalyst.

The reasons are as follows: (1) comparing the structure and specific surface characteristics of carbon nanotubes and activated carbon carriers, carbon nanotubes can form a continuous network structure with inter-connected gaps, which is conducive to the dispersion of CdS particles, surface exposure and the circulation of reactive substances. Although activated carbon has a higher specific surface area than carbon nanotubes, the proportion of micropores is very high. The proportion of micropores (<2 nm) supporting CdS photocatalyst is significantly higher than that of carbon nanotubes supporting CdS photocatalyst. The inner surface of the pores cannot be used for supporting particles and the contact between the supported particles and the organic matter in the solution. Moreover, the activated carbon is granular, and the activated carbon particles in the accumulation body are in close contact with each other, and the gaps are narrow, which is not conducive to the full exposure of the surface of the CdS particles and the circulation of reactive substances (**Table 1**). The microstructure of loose network and interconnecting gap formed between carbon nanotubes can improve the internal structure of the activated carbon deposits and increase the internal gaps in the activated carbon powder. Although the specific surface area of the composite carrier supported CdS photocatalyst is smaller than that of the activated carbon supported CdS photocatalyst, due to the specific surface area of the carbon nanotubes is smaller than that of the activated carbon, as a result, the proportion of micropores is significantly reduced and the pore volume is significantly increased. Therefore, it is beneficial to disperse CdS particles and promote the circulation of reaction substances and contact with the catalyst; (2) comparing the physical properties of carbon nanotube-supported CdS and activated carbon-supported CdS photocatalysts, it is found that the photoelectric conversion efficiency of the former is higher than that of the latter (**Figure 4**), the adsorption capacity of the latter is higher than that of the former (**Figure 5**). Therefore, the composite carrier supporting CdS photocatalyst can take advantage of the carbon nanotubes' respective advantages of higher photoelectric conversion efficiency and activated carbon's stronger ability to adsorb organics. The combined effect of these factors makes the semiconductor photocatalyst with CdS supported on the carbon nanotube/activated carbon composite carrier have a significantly higher photocatalytic degradation of organics than the semiconductor photocatalyst with CdS supported on carbon nanotubes or activated carbon alone.

4. Conclusion

The method of in-situ reaction in the solution is adopted to prepare a semiconductor photocatalyst with carbon nanotubes loaded with cadmium sulfide and activated carbon loaded with cadmium sulfide. The former is superior to the latter in terms of photoelectric conversion efficiency, and the latter has higher adsorption capacity and specific surface area for organics in the liquid phase than the former. Moreover, as a one-dimensional nanomaterial, carbon nanotubes have a special structure that helps to improve the internal structure of activated carbon powder. Combining carbon nanotubes with activated carbon can give full play to the advantages of the two carriers. The photocatalytic degradation of organic matter of the semiconductor photocatalyst with cadmium sulfide loaded on the carbon nanotube/activated carbon composite carrier is significantly higher than that of the semiconductor photocatalyst with cadmium sulfide loaded on carbon nanotubes or activated carbon alone.

After replacing 20% of the mass of activated carbon, this traditional photocatalyst carrier, with carbon nanotubes, it becomes a composite carrier supporting cadmium sulfide semiconductor photocatalyst. Compared with a single activated carbon supporting cadmium sulfide semiconductor photocatalyst, when the mass of the carrier is 15% and 40% of the mass of CdS, the reaction rate constant of the photocatalytic degradation of methyl orange in the former is about 38% and 30% higher than that of the latter, respectively.

Carbon nanotubes play a significant role in modifying activated carbon as a photocatalyst carrier and improving the efficiency of photocatalytic degradation of organics. The carrier composed of carbon nanotubes and activated carbon is a carrier with superior performance. It can also be used to support photocatalysts such as titanium oxide and zinc oxide to increase the reaction rate of photocatalytic degradation of organics.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

The project of National Natural Science Foundation of China (61275117); the project of Natural Science Foundation of Heilongjiang Province (LH2020E 106).

References

1. Arunachalam P, Nagai K, Amer MS, *et al.* Recent developments in the use of heterogeneous semiconductor photocatalyst based materials for a visible-light-induced water-splitting tem-a brief review. Catalysts 2021; 11(2): 1–27.
2. Sharma S, Dutta V, Raizada P, *et al.* Tailoring cadmium sulfide-based photocatalytic nanomaterials for water decontamination: A review. Environmental Chemistry Letters 2021; 19(1): 271–306.
3. Li B, Wu S, Gao X. Theoretical calculation of a TiO_2-based photocatalyst in the field of water splitting: A review. Nanotechnology Reviews 2020; 9(1): 1080–1103.
4. Shaba EY, Jacob JO, Tijani JO, *et al.* A critical review of synthesis parameters affecting the properties of zinc oxide nanoparticle and its application in wastewater treatment. Applied Water Science 2021; 11(2): 1–41.
5. Puma GL, Bono A, Krishnaiah D, *et al.* Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: A review paper. Journal of Hazardous Materials 2008; 157(2-3): 209–219.
6. Zhang Q, Huang J, Qian W, *et al.* The road for nanomaterials industry: A review of carbon nanotube production, post-treatment, and bulk applications for composites and energy storage. Small 2013; 9(8): 1237–1265.
7. Kandasamy SK, Kandasamy K. Recent advances in electrochemical performances of graphene composite (graphene-polyaniline/polypyrrole/activated carbon/carbon nanotube) electrode materials for supercapacitor: A review. Journal of Inorganic and Organometallic Polymers and Mmaterials 2018; 28(3): 559–584.
8. Barsan MM, Ghica ME, Brett CMA. Electrochemical sensors and biosensors based on redox polymer/carbon nanotube modified electrodes: A review. Analytica Chimica Acta 2015; 881: 1–23.
9. Liang Z, Ma Y, Song J, *et al.* Study on preparation of B/P/N/O co-doped carbon nanofibers and its properties for supercapacitors. Journal of Engineering of Heilongjiang University 2020; 11(2): 38–43.
10. Esteves LM, Oliveira HA, Passos FB. Carbon nanotubes as catalyst support in chemical vapor deposition reaction: A review. Journal of Industrial and Engineering Chemistry 2018; 65: 1–12.
11. Kumar R, Kumar G, Umar A. Zinc oxide nanomaterials for photocatalytic degradation of methyl orange: A review. Nanoscience and Nanotechnology Letters 2014; 6(8): 631–650.
12. Shivashankarappa A, Sanjay KR. Escherichia coli-based synthesis of cadmium sulfide nanoparticles, characterization, antimicrobial and cytotoxicity studies. Brazilian Journal of Microbi-

ology 2020; 51(3): 939–948.

13. Lv X, Zhang T, Luo Y, *et al.* Study on carbon nanotubes and activated carbon hybrids by pyrolysis of coal. Journal of Analytical and Applied Pyrolysis 2020; 146: 104717.
14. Gu WT, Yushin G. Review of nanostructured carbon materials for electrochemical capacitor applications: Advantages and limitations of activated carbon, carbide-derived carbon, zeolite-templated carbon, carbon aerogels, carbon nanotubes, onion-like carbon, and grapheme. WIREs: Energy and Environment 2014; 3(5): 424–473.