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N-doped graphene-cadmium sulfide nanoplates and their improved photocatalytic performance

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Cadmium sulfide nanoplates and N-doped graphene composites (CdS NP/NG) were synthesized for use as photocatalysts. Photocatalytic testing showed that both the two dimensional (2D) nanostructure and nitrogen-doping of graphene contributed to its excellent photocatalytic performance. Here, the 2D nanostructure provided a large number of active sites and the nitrogen-doping of graphene could improve its electronic properties. This work offers a new insight for obtaining a highly efficient CdS/graphene photocatalyst.

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Keywords: N-doped, Graphene, Photocatalytic performance

1. Introduction

Photocatalysts have gained considerable interest due to their potential for environmental clean-up[1-2]. Cadmium sulfide (CdS) nanoplates have been found to be an efficient photocatalyst, since two-dimensional (2D) CdS can provide abundant active sites[3]. However, rapid recombination of charge carriers and photocorrosion seriously impede its applications[4].

Graphene can improve the electrical conductivity and promote effective electron-hole separation in the composite, making it an excellent candidate to solve the above mentioned problems[5-6]. Thus, graphene-based composites are a new type of photocatalysts, with great potential[7-8]. It has been widely researched that doping with a heteroatom (e.g., N, B, S, and P) can improve the physicochemical properties of graphene. Graphene doped with nitrogen provides electron carriers for the conduction band and improves the electronic conductivity, due to the introduction of N-doped defects and functionalized groups[9-10]. Therefore, N-doping of graphene could be a viable approach to overcome the drawbacks of CdS.

Considering all the aforementioned issues collectively, a composite catalyst, N-doped graphene decorated with CdS nanoplates, could achieve highly improved photocatalytic performance. The CdS nanoplates provide abundant active sites and N-doped graphene promotes electron transfer in the composites. However, to the best of our knowledge, this aspect has seldom been focused upon.

Herein, N-doped graphene/CdS nanoplates were prepared using microwave method. The photocatalytic performance of N-doped graphene/CdS towards degradation of methyl orange under visible light irradiation was tested.

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2. Experimental details

2.1. Preparation of nitrogen-doped graphene

GO (100 mg) and 3,4-diaminopyridine (5 mg) were dispersed in 100 mL of deionized solution and heated overnight in an oven at 120 ºC. After cooling to room temperature, Soxhlet extraction of the reaction mixture with water, tetrahydrofuran, and methanol, followed by drying at 80 ºC for 10 h, provided the product, which was labeled as NG.

2.2. Preparation of samples

NG (0.05 g) was dispersed in 100 mL solution mixture of deionized water: ethylene glycol (1:1 (v/v)) by ultrasonication for 30 min. Cadmium acetate dihydrate ($Cd(AC)_2.2H_2O$, 4 mmol) and thiourea (H_2NCSNH_2, 4 mmol) were added to above solution. The reaction mixture was continuously stirred for 1 h and transferred into a microwave reactor. After reacting at 180 ºC for 30 min, the solid product was washed several times with de-ionized water, dried in a vacuum oven at 80 ºC, and labeled as Cd NP/NG. For comparative study, CdS NP were prepared using the same method, but without the addition of graphene. CdS NP/G was also obtained by the same method, but using GO instead of NG.

2.3. Characterization

The morphologies and structures of the products were characterized by transmission electron microscopy (SEM, JEM-2100), S4800), transmission electron microscopy (TEM, JEM-2100F), and X-ray diffractometry (XRD, D5000, using Cu K-radiation source). The graphitization of the samples was studied by Raman spectroscopy (J-Y, T6400). The optical properties were analyzed by UV-vis spectrometer (UV-2550). The surface composition was further analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063).

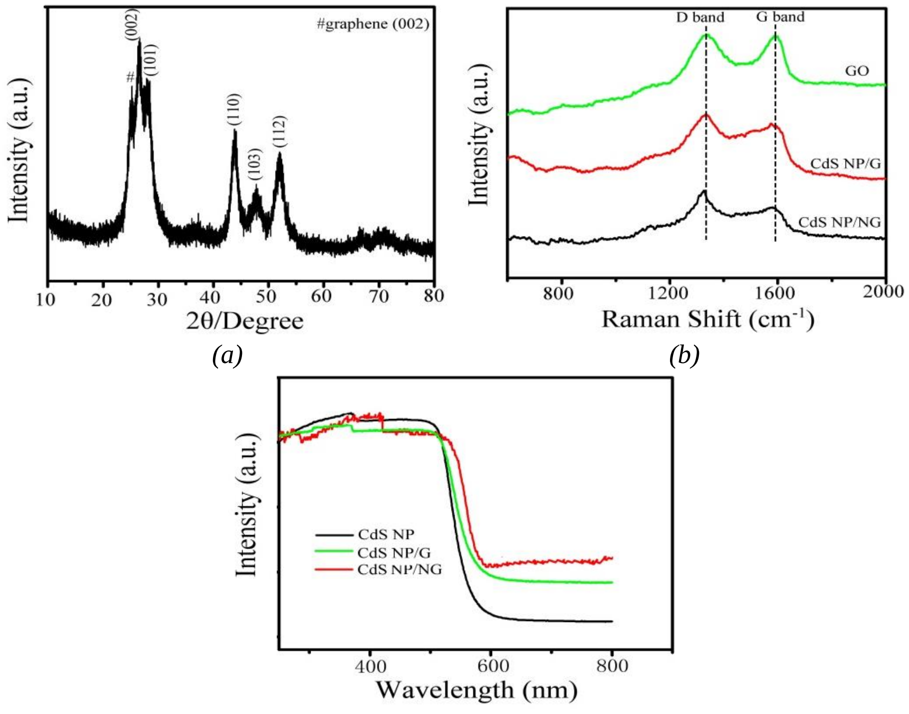
2.4. Photocatalytic experiment

Typically, photocatalyst powder (20 mg) was dispersed in methyl orange (MO) aqueous solution (20 mg/L, 300 mL). Prior to irradiation, the suspension was magnetically stirred in the dark for 1 h to attain adsorption/desorption equilibrium. Then the suspension was irradiated by xenon lamp (300 W). At regular intervals of 20 min, 4 mL of the suspension was withdrawn and the concentration was monitored by UV-vis spectrophotometry (UV-2550) at λ_{max} = 465 nm.

3. Results and discussion

Fig. 1a showed the X-ray diffraction (XRD) pattern of CdS NP/NG sample and the characteristic peaks at about 26.6°, 27.9°, 43.7°, 47.7°, and 52.0°, corresponded to the (002), (101), (110), (003), and (112) planes of CdS phase (JCPDS No. 41-1049)[11]. The peak at about 25.2° could be attributed to the (002) plane of graphene[12]. The results proved the effective formation of the N-doped graphene and CdS composites.

The graphitization and composition of the samples were further confirmed by Raman spectroscopy as shown in Fig. 1b. All the samples showed sharp peaks at 1327.2 and 1581.3 cm^{-1}, corresponding to the D and G peaks. The I_D/I_G values of GO, CdS NP/G, and CdS NP/NG were 1.03, 1.08, 1.16, respectively. Obviously, CdS NP/NG showed the highest I_D/I_G value. This could be attributed to the large topological defects in graphitic structure, due to doping of graphene with nitrogen atoms[13].



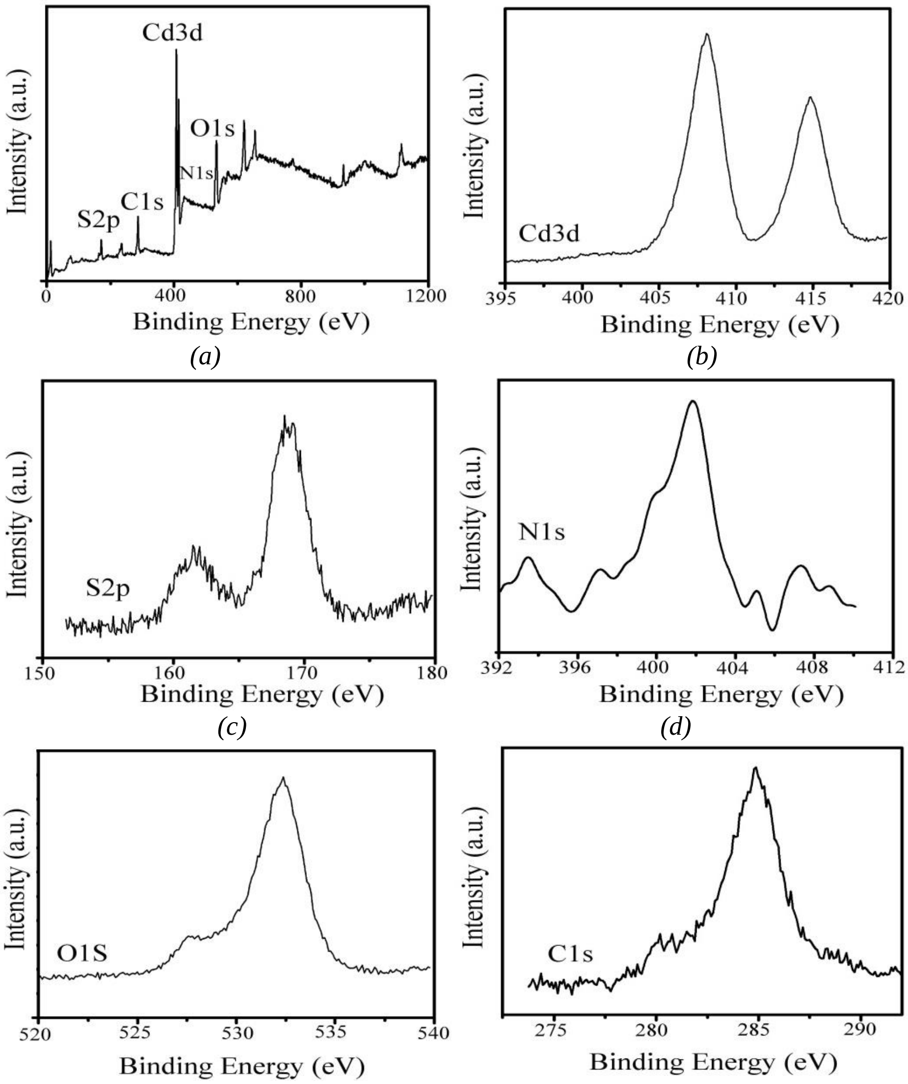
(a) (b)

(c)

Fig. 1. (a)XRD, (b)Raman spectra, (c) UV/Vis diffuse reflectance spectra of the composites.

The optical properties of composites were investigated by UV-vis spectra (Fig. 1c). Bare CdS NP showed an absorption edge at 580 nm. Compared with CdS NP, optical absorption band edge was shifted towards the higher wavelength in CdS NP/G and CdS NP/NG, which was due to the strong interfacial interaction between graphene and CdS NP. In addition, CdS NP/NG composites exhibit a significantly enhanced light absorption over the visible light region from 600 to 800 nm and the ability to effectively utilize visible light can increase the production of photogenerated electrons.

XPS analysis was conducted to determine the elemental composition of CdS NP/NG (Fig. 2). Peaks for C 1s, Cd 2p, S 2p, N 1s, and O 1s confirmed the presence of C, Cd, S, N, and O elements. Fig. 2b showed the high-resolution Cd 3d spectrum. Peaks at 408.08 eV and 414.88 eV could be assigned to the binding energies of Cd 3d5/2 and Cd 3d3/2, respectively. Fig. 2c shows the high-resolution S2p spectrum, wherein the peaks for S 2p3/2 and S 2p1/2 of S^{2-} ions appeared at 161.48 and 168.48 eV, respectively. These findings confirmed the formation of a Cd-S bond[14]. The N 1s peaks at 398.4 eV and 401.8 indicated the presence of pyridinic- and quaternary-nitrogen functional groups on the graphene surface (Fig. 2d). This proved the successful doping of nitrogen in graphene[9]. Fig. 2e showed the O 1s spectrum with the peak at 532.38 eV assigned to the carbonyl and carboxyl groups. Meanwhile the C 1s (Fig. 2f) spectrum showed a main peak at 284.88 eV, which was assigned to C-C bond after the reduction of GO[15]. Thus, the effective transformation of photo-generated electrons from CdS to graphene could be achieved.



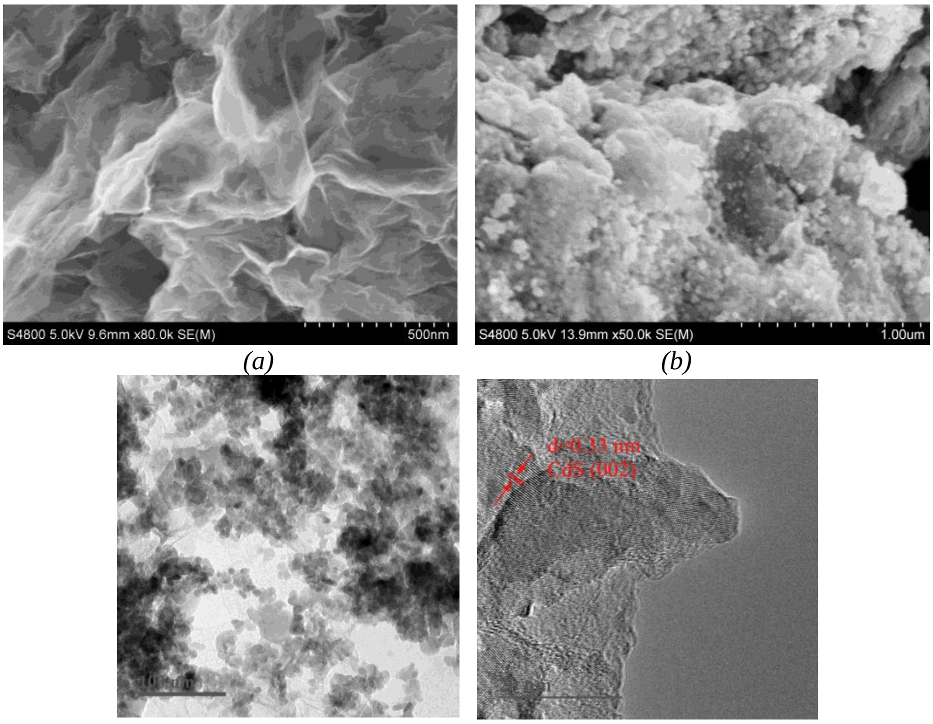
(a) (b)

(c) (d)

(e) (f)

Fig. 2. Typical XPS spectra of the CdS NP/NG composite: (a) survey spectra, (b) Cd 3d region XPS spectrum, (c) S 2 p region XPS spectrum, (d) N 1s s region XPS spectrum, (e) O1s region XPS spectrum, (f) C1s region XPS spectrum.

The morphologies and microstructures of the samples were investigated by SEM, TEM, and HRTEM (Fig. 3). SEM image (Fig. 3a) showed a crumpled silk-like morphology of graphene. SEM image (Fig. 3b) of CdS NP/NG showed good dispersion of nanosized CdS particles on the surface of graphene due to their intimate contact between them. TEM images (Fig. 3c) showed that the nanoparticles were tens of nanometers in size and had plate-shaped morphology. High-resolution transmission electron microscopic (HRTEM) image in Fig. 3d showed a typical layered structure with d-spacing of 0.33 nm, corresponding to the (002) plane of CdS[16].



(a) *(b)*

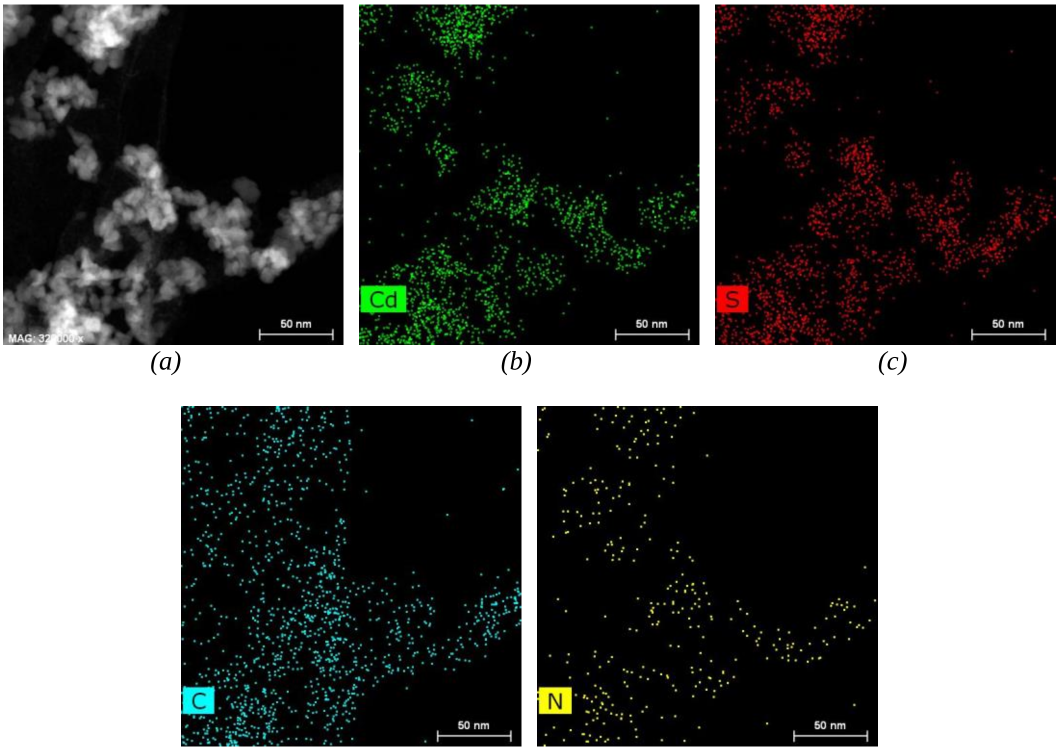
(c) *(d)*

Fig. 3. (a)SEM of graphene, (b) SEM, (c)TEM, (d)HRTEM images of CdS NP/NG.

TEM elemental mapping (Fig. 4a) showed graphene surface decorated with CdS nanoplates. Mapping of cadmium, sulfur, nitrogen, and carbon elements were shown in Fig. 4b, c, d, and e, respectively. The dispersions of cadmium and sulfur elements were consistent with the nanoplate morphology and hence confirmed the formation of CdS nanoplates (Fig. 4b and c). Content of carbon element was consistent with the graphene sheet (Fig. 4d). However, the dispersion of the element nitrogen was almost the same as that of the element carbon and it further confirmed the nitrogen doping in the graphene (Fig. 4e).

The photocatalytic activities of the synthesized nanocomposite were tested. Fig. 5 showed that the photocatalytic degradation rates of MO by NG, CdS NP, CdS NP/G, and CdS NP/NG were 17.9%, 64.8%, 77.8%, and 84.4%, respectively. Hence, amongst all, CdS NP/NG showed the highest degradation rate. This was due to the unique advantage provided by the 2D nanostructure with a large number of active sites. Moreover, nitrogen-doping of graphene provided added advantage in modulating the electronic properties of the composites[9].

Fig. 6 clearly showed the mechanism diagram of CdS NP/NG composites. The light was absorbed by the CdS NP, generating the photogenerated electron and hole pairs in the valence and conduction bands of the CdS, respectively[17]. When CdS NP was anchored on the surface of graphene, graphene can be used as one ideal electron sink[18]. Especially, N atom in the N-doped graphene had the extra p-electrons, endowing graphene the metallic properties with the improved conductivity[19]. Thus, the photogenerated electrons in the conduction band of CdS could easily migrate into the surface of N-graphene and electron-hole recombination were effectively retarded. Finally, O_2 captured the photogenerated-electrons and was reduced to $.O^{2-}$. Both $.O^{2-}$ and holes were active for the degradation of MO[20].



(a) (b) (c)

(d) (e)

Fig. 4. (a)TEM of EDS mapping of selected area, (b) element Cd mapping, (c) element S mapping, (d) element C mapping, (e) element N mapping of CdS NP/NG.

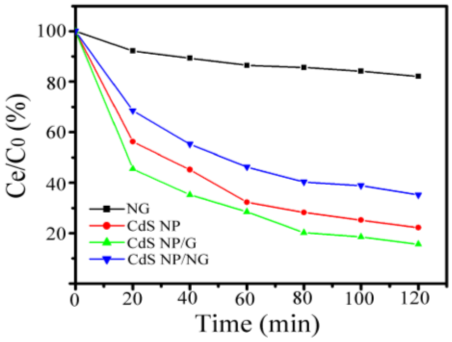


Fig. 5. Photocatalytic degradation efficiency of MO with different catalysts under visible light.

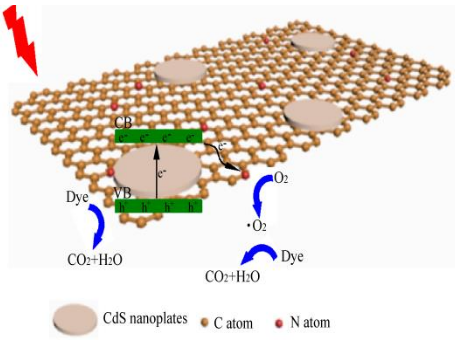


Fig. 6. Proposed photocatalytic mechanism of CdS NP/NG.

4 Conclusions

In summary, an efficient visible-light driven N-doped graphene composite, CdS NP/NG, was successfully synthesized via microwave method. The synergistic effects could be achieved due to the presence of abundant number of active sites on their nanoplate structures and the excellent carrier transport ability achieved by the nitrogen doped-graphene in the composites. This work could provide new insights into the understanding of other high-performance graphene-based photocatalysts.

Acknowledgments

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