



CdS nanoparticles decorated $K^+Ca_2Nb_3O_{10}^-$ nanosheets with enhanced photocatalytic activity

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ABSTRACT

Development of the novel photocatalyst with outstanding photocatalytic activity is of huge interest for photocatalytic degradation of organic pollution using solar energy. In this work, a new photocatalyst was achieved by CdS nanoparticles decorated $K^+Ca_2Nb_3O_{10}^-$ (KCNO) nanosheets. The as-fabricated CdS/KCNO hybrids exhibited well-defined morphology and enhanced photocatalytic activity than pristine KCNO. On the basis of the physicochemical characterization and photocatalytic performance test, it is believed that the CdS nanoparticles can effectively promote the photo-induced charge separation of KCNO nanosheets, and the relative mechanism has been investigated.

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1. Introduction

In recent years, photocatalysis has been considered as a promising technique to overcome the environmental pollution issue [1–7]. Development and fabrication of high-efficiency photocatalysts are of importance for the practical application of photocatalysis. Dion-Jacobson-type layered perovskite $K^+Ca_2Nb_3O_{10}^-$ (KCNO) nanosheet material, due to its large surface-to-volume ratio, unique optical and electronic properties, has attracted a lot of attention as the promising photocatalyst candidate for photocatalytic reaction [8,9]. However, the fast photo-induced charge combination seriously inhibits its photocatalytic activity. Thus, it is imperative to promote the charge separation efficiency to enhance the photocatalytic performance of KCNO nanosheets.

Up to now, great efforts for improving the charge separation of KCNO photocatalyst have been made [10]. In these approaches, construction of hybrid material has been considered as one of the most effective strategy. For instance, Jiang et al. [11] constructed $g-C_3N_4/K^+Ca_2Nb_3O_{10}^-$ 2D–2D nanosheet heterojunctions, and the as-prepared heterojunctions showed improved charge carrier charge separation efficiency and photocatalytic activity towards the degradation of organic pollutant. In the present work,

we for the first time report the construction of CdS/KCNO hybrids by decorating CdS nanoparticles on the surface of KCNO nanosheets with close contact interface. It is exhibited that the photocatalytic activity of KCNO nanosheets was significantly enhanced by the existence of CdS nanoparticles. The reason might be ascribed to the CdS nanoparticles can effectively facilitate the charge transfer ability and promote the charge separation in KCNO after the formation of CdS/KCNO hybrids.

2. Experiments

The detailed preparation methods, measurement and characterization, and photocatalytic activity tests were described in the [Supplementary materials](#).

3. Results and discussion

The morphologies of the KCNO and CdS/KCNO hybrids were analysed by TEM. As shown in Fig. 1a, the KCNO exhibits typical 2D nanosheet structure. The TEM image of CdS/KCNO hybrids (Fig. 1b and c) shows that a large number of CdS nanoparticles with an average of 25 nm anchored on the KCNO nanosheets with a good dispersion, indicating that the KCNO can act as a dispersion substrate for CdS nanoparticles. The HRTEM image (Fig. 1d) shows

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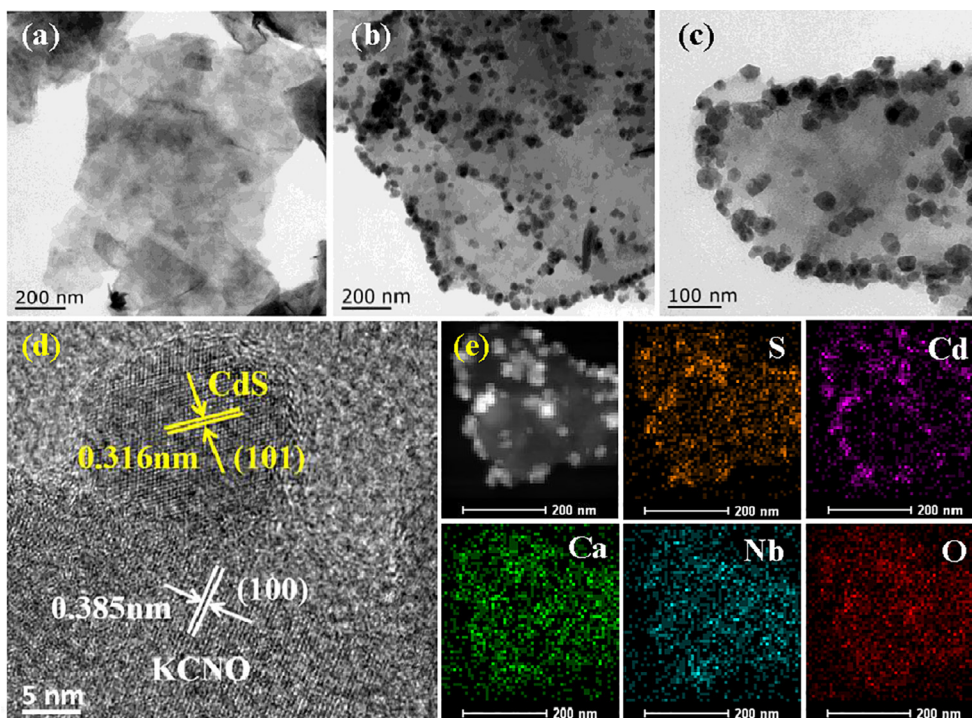


Fig. 1. TEM images of (a) KCNO, (b, c) CdS/KCNO hybrids, (d) HRTEM image of CdS/KCNO hybrids, and (e) HAADF-STEM images of CdS/KCNO hybrids and the corresponding EDX mapping.

that a close interface can be observed. The lattice fringe of the individual nanoparticle with d spacing of 0.316 nm can be assigned to the (1 0 1) plane of the hexagonal phase CdS, which is well consistent with the XRD patterns (Fig. S1, JCPDS no. 41-1049). The lattice fringe of the nanosheet with d spacing of 0.385 nm can be indexed to the (1 0 0) plane of perovskite KCNO. Furthermore, as exhibited in Fig. 1e, the elemental mapping reveals that the S, Cd, Ca, Nb, and O elements co-exist in the sample, which indicates the sample was composed of CdS and KCNO. Besides, it also suggests the CdS nanoparticles good dispersing on the surface of KCNO nanosheets. These results indicate the CdS/KCNO hybrids have been successfully prepared, which is also confirmed by the XPS analysis (Fig. S2).

The photocatalytic performances of the as-synthesized samples were assessed by monitoring the degradation of tetracycline hydrochloride (TC) aqueous solution under simulation solar light irradiation. In order to exclude the influence of adsorption over the photocatalysts, all of the photocatalysts and TC solution were stirring in the darkness for 60 min to reach absorption-desorption equilibrium. Fig. 2a exhibits the self-photolysis of TC is quite few and can almost be overlooked. The pristine KCNO nanosheets possess poor photocatalytic activity. Furthermore, though the pristine and physical-mixture of CdS nanoparticles and KCNO nanosheets exhibit a certain amount of degradation rate, the TC remove efficiencies are all only about 60%. It can be clearly found that the CdS/KCNO hybrids show the best photocatalytic performance and the TC remove efficiency is more than 90% within 60 min. The corresponding kinetic curves are shown in Fig. 2b. All of the photocatalytic degradation kinetic reactions were described by pseudo-first-order model [12], and the kinetic constant k , which is shown in Fig. 2c, indicate the CdS/KCNO hybrids have the highest photocatalytic activity than other samples. Besides, as exhibited in Fig. 2d, after four repeated cycles, the photocatalytic efficiency of CdS/KCNO hybrids kept well with the initial one, indicating its high stability during the photocatalytic degradation of TC. Moreover, in

comparison with the CdS nanoparticles (Fig. S3), the CdS/KCNO hybrids exhibited a higher stability.

To study the enhanced photocatalytic activity of CdS/KCNO hybrids, we first investigated its physicochemical performances. The UV-vis diffuse reflectance spectra (Fig. 3a) indicate that the KCNO is UV light nature, and CdS can response visible light. As shown in Fig. 3b, the band gaps of KCNO and CdS calculated from the UV-vis diffuse reflectance spectra are 3.4 eV and 2.2 eV, respectively. The surface areas of KCNO nanosheets and CdS/KCNO hybrids were evaluated by the nitrogen adsorption-desorption isotherms (Fig. 3c), and the BET surface areas of two samples are $31.9 \text{ m}^2 \text{ g}^{-1}$ and $19.6 \text{ m}^2 \text{ g}^{-1}$. Thus, the effect of surface area for the enhanced photocatalytic performance of hybrid photocatalyst can be excluded owing to its smaller surface area. The EIS spectra (Fig. 3d) show that the diameter of Nyquist semicircle in the high frequency region of CdS/KCNO hybrids is quite smaller than CdS and KCNO, proving the higher efficiency in the electron transfer process for the CdS/KCNO hybrids. In addition, the transient photocurrent response and the time-resolved fluorescence spectra further verified this result. As shown in Fig. 3e, in comparison with the CdS and KCNO, CdS/KCNO hybrids exhibit higher photocurrent intensity, indicating the accelerated charge transfer process. Fig. 3f shows the normalized decay profiles. The fluorescence lifetimes of CdS, KCNO and CdS/KCNO hybrids are 0.11 ns, 0.90 ns, and 1.41 ns, respectively, demonstrating the hybrid sample present the longest life time. This also suggests the recombination of photo-induced charges can be depressed by the formation of hybrid structure.

Furthermore, active species have been tested by the trapping experiment and ESR technique. As shown in the Fig. 4a, when the hole scavenger (AO), $\cdot\text{O}_2^-$ scavenger (BQ) and $\cdot\text{OH}$ scavenger ($t\text{-BuOH}$) added in the photocatalytic system, the photocatalytic activity were decreased, indicating that all the hole, $\cdot\text{O}_2^-$, and $\cdot\text{OH}$ are active species [13,14]. This result was further confirmed by the control experiment carried on the presence of N_2 atmosphere, which could form an anaerobic reaction system. Evidently, it can

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