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Coloading of TiO_2 and C_3N_4 on kaolinite nanotubes for obviously improved photocatalytic performance in degradation of methylene blue dye

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ABSTRACT

kaolinite nanotubes (KNTs) were firstly used to coload TiO_2 nanoparticles and carbon nitride (C_3N_4) nanosheets for photocatalytic degradation of methylene blue (MB) dye. The influence of C_3N_4 amount on the photocatalytic activity of composites was evaluated. The optimum sample showed an ultrahigh efficiency/effective mass ratio that is 18.8 and 24.7 times higher than these of pure TiO_2 and C_3N_4 references, respectively. The enhancement of photocatalytic performance for clay-semiconductor composites can be attributed to the Z-scheme transport of photoproduced electrons and the good dispersion of catalyst particles on KNTs. The work provides an example that KNTs can be used as a promising support with very little catalysts but high photocatalytic performance.

1. Introduction

The nanotubes have attracted a great deal of attention since the discovery of carbon nanotubes (CNTs) by Iijma in 1990s [1] due to several unique features, for example large special surface area (SSA), tunable surface loading chemistry and high mechanical strength. Halloysite, one star member in the clay family, has similar tubular morphology to CNTs [2]. Compared to CNTs, halloysite nanotubes (HNTs) are economically accessible and have many unique characteristics including high stability and resistance against organic solvents, ease of disposal, different outside and inside chemical properties and adequate hydroxyl groups on the surface, that endue HNTs with versatile applications such as sustained release of biologically active molecules, strengthening of polymer, and supporting small functional guests [2,3].

However, halloysite has far less reserves around the world than kaolinite, another member in clay family with a similar layer structure [4,5]. Kaolinite has a tendency to curve because of the mismatch between aluminum–oxygen octahedral sheet and silicon–oxygen tetrahedral sheet. Thus the weakness of hydrogen bonds between adjacent layers will promote the rolling of the kaolinite layer [6], and numerous studies have been performed over the last few decades in synthesis of halloysite-like KNTs [2,7].

In photocatalytic reaction, to decrease aggregation of nanoparticles and expose enough active sites is a key point to achieve a high catalytic performance. Therefore, catalysts with smaller size are usually loaded on larger supports to improve their dispersion and recyclability [8]. Due to the similar features to HNTs, KNTs material becomes a promising candidate for supporting catalyst nanoparticles with improved photocatalytic activity. KNTs have been successfully used as support of iron porphyrins catalyst, filler of polylactide polymer, magnetic adsorbent of MB [9–11]. However, the studies especially on KNTs loading more than one catalysts with heterojunction have not been found until now.

Here, we reported a new application of KNTs in coloading TiO_2 nanoparticles and C_3N_4 nanosheets for degradation of MB dye. The results show that the obtained composites could achieve an ultrahigh efficiency/effective-mass ratio compared to pure TiO_2 and C_3N_4. The reason for improved photocatalytic performance was studied in detail by analysis of morphology, structure, optical properties and radical trapping properties of obtained samples.

2. Experimental

KNTs were synthesized by a solvothermal routine as previously reported with a slight modification [12,13]. Loading anatase TiO_2

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on KNTs (T/KNTs) was achieved by a sol-gel method without further high-temperature calcination [3]. C_3N_4 nanosheets were produced by a liquid exfoliation route from bulk g-C_3N_4 in water [14] and then deposited on T/KNTs composite through a simple mixing routine [15] to get C_3N_4-TiO_2 coloaded composite (CT/KNTs). All experimental details can be found in Supplementary Information.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the as-prepared samples. Kaolinite gives a characteristic (0 0 1) basal reflection of 0.71 nm. For KNTs resulting from weakening of interlayer attractive force led by intercalation of cetyltrimethylammonium chloride (CTAC), 1.92 and 1.27 nm reflections corresponding to (0 0 2) and (0 0 3) planes of kaolinite – CTAC composite indicate successful entrance of CTAC into interlayer space of kaolinite [16]. TiO_2 shows a typical 0.35 nm reflection related to (1 0 1) plane of anatase. C_3N_4 shows a 0.33 nm reflection due to (0 0 2) interlayer stacking and a 0.69 nm reflection led by (1 0 0) in-plane packing. For CT/KNTs composites, the (0 0 2) and (0 0 3) reflections in KNTs disappear, indicating that CTAC molecules were removed from interlayer space, and 0.80 nm peak may correspond to an immediate hydrate [5]. The characteristic peaks at 0.35 and 0.33 nm suggest the successful loading of TiO_2 and C_3N_4 on KNTs. The low intensity of the reflections that are attributed to C_3N_4 without increasing with the amount of C_3N_4 can be ascribed to the poor crystallization and small amount of C_3N_4 [17].

The transmission electron microscopy (TEM) image clearly shows the formation of KNTs (Fig. 2a) from initial pseudo-hexagonal plates of kaolinite (Fig.S1a). The increased SSA of KNTs

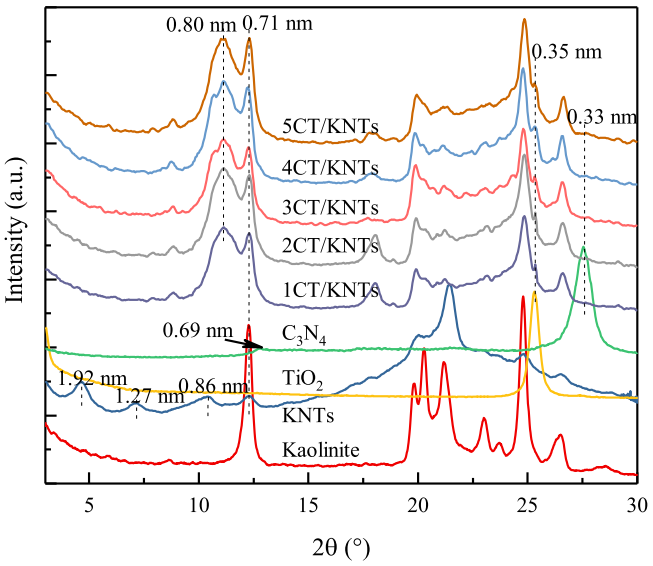

Fig. 1. XRD patterns of obtained samples.

compared to kaolinite further confirms this (Fig.S2). The TiO_2 particles of several nanometers similar to pure reference (Fig.S1b) are uniformly distributed on the surface of KNTs (Fig. 2b). After further loading C_3N_4, the approximatively round C_3N_4 plates of about 70–160 nm appear on KNTs besides TiO_2 nanoparticles (Figs. 2c and S1c), without changing the nanotube morphology. The high-resolution TEM (HRTEM) image of 3CT/KNTs further confirms the coloading of two catalysts with different morphologies and the formation of heterogeneous interface between them (Fig. 2d).

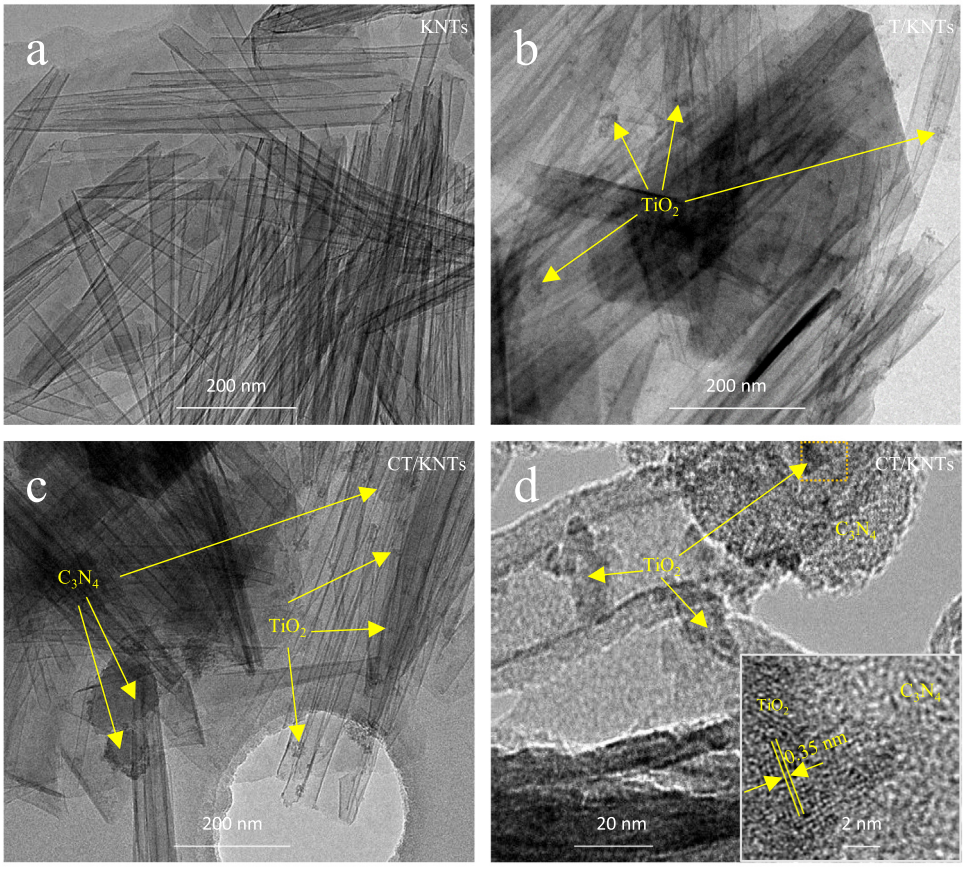

Fig. 2. TEM images of (a) KNTs, (b) T/KNTs, (c) 3CT/KNTs and (d) HRTEM of 3CT/KNTs.