***In-situ* growth of g-C₃N₄ layer on ZnO nanoparticles with enhanced photocatalytic performances under visible light irradiation**

Le Wang^{a*}, Chao Ma^b, Zheng Guo^d, Yangyong Lv^a, Weiwei Chen^a, Zheng Chang^c, Qipeng Yuan^{c*},
Hui Ming^a, Jinshui Wang^{a*}

Abstract

We proposed a facile method to prepare ZnO@g-C₃N₄ core/shell type photocatalyst *via* a two-step calcination. Thin layer of g-C₃N₄ was homogeneously coated on ZnO nanoparticles with well-defined heretro-interface, which reduces the charge transfer resistance and results in distinct PL quenching. Therefore, the as-prepared ZnO@g-C₃N₄ demonstrates significant photocatalytic improvement under visible-light irradiation than ZnO (~35 times) and g-C₃N₄ (~5 times) due to the effective charge separation and suppressed carrier recombination. Moreover the ZnO@g-C₃N₄ photocatalyst shows high stability which retains ~90 % of the activity after 5-cycle reuse.

Keywords: ZnO; g-C₃N₄; Semiconductors; Nanocomposites; Photocatalyst

1. Introduction

ZnO is recognized as a group of promising materials for photo-catalysis and photovoltaics [1-3]. However, ZnO exhibits low photocatalytic activity under of visible light owing to its wide band gap of 3.37 eV. On the other hand, as the incident photons are absorbed, the as-generated electron-hole pairs would migrate from the generation site to the catalyst surface, during which the charge carries would confront with rapid recombination, which largely limited its photocatalytic activity [4,5]. In addition, the photo-corrosion and chemical instability of ZnO nanocrystal also hinder its practical application [6,7]. Therefore, it is anticipated that ZnO could become an excellent photocatalyst if the optical absorption of ZnO could be extended from UV region to visible region, the recombination of the photo-excited electron-hole pairs could be suppressed and the stability of the ZnO could be substantially improved.

Graphite-like C_3N_4 (g- C_3N_4) is an all-organic delocalized π conjugative structured material with band gap of ~ 2.7 eV [8], which could be used as high performance photocatalyst under visible-light. In addition, due to the delocalized π - π structure, g- C_3N_4 also possesses rapid photo-induced charge separation and relatively slow charge recombination property in the electron transfer process [9]. Meanwhile, the g- C_3N_4 is regarded as the most stable allotrope among the carbon nitride materials under ambient conditions as well as in high acid or base solutions due to the strong covalent bonds between carbon and nitride atoms [10]. Therefore, the modification of g- C_3N_4 could give rise to nanocomposites with visible-light activity, better charge separation and relatively slow charge recombination, and enhanced photo- or chemical- stability.

Based on these considerations, many ZnO/g- C_3N_4 hybrid materials were prepared for various applications, such as visible-light photo-degradation, photovoltage device, CO_2 capture and so on. [11-13]. Although many strategies were developed to prepare g- C_3N_4 based hybrid materials, these methods generally involve the first preparation of g- C_3N_4 before the hybridization [14-16]. Herein, we proposed a facile method to prepare ZnO@g- C_3N_4 core/shell type nanocomposites *via* two-step calculation, which could *in situ* grow g- C_3N_4 layer on ZnO surface with high efficiency. In addition, the as-prepared sample shows improved photocatalytic activity of RhB degradation under visible-light (>400 nm) with high cycling stability. Moreover, this method could potentially

serves as a general strategy to fabricate other g-C₃N₄ based hybrid materials.

2. Experimental

0.5 g Zn(Ac)₂•2H₂O was dispersed into 40 mL absolute ethanol under vigorous stirring, and the suspension was transferred into 50 mL Teflon-lined autoclave and heated at 180 °C for 4 h. The white powder were rinsed with distilled water and absolute ethanol, and finally dried in vacuum. 1.0 g Urea was dissolved in distilled water to form a clear solution and 1.0 g as-prepared ZnO was added to form white suspension which was stirred under room temperature for 2 days to evaporate the water. The as-yield white powder was transferred in to an alumina ceramic boat (uncovered) and the sample was treated in Muffle furnace at 130 °C for 30 min. then, the temperature was elevated to 500 °C with a heating rate of ~10 °C min⁻¹ and maintained for 2 h. After cooling, yellowish powder product were produced. Pure g-C₃N₄ was prepared by a similar method without adding ZnO.

The products were characterized by X-ray powder diffraction (XRD, Rigaku), transmission electron microscopy (TEM, JEOL, JSM2100), Energy dispersive X-ray spectroscopy (EDS, EDAX Inc.). Photoluminescence (PL) measurements were performed on Hitachi F-7000 and the excitation wavelength is 325 nm. The Fourier transform infrared spectroscopy was characterized by (FTIR, FTS-40) and electrochemical impedance spectroscopy (EIS) was performed on CHI 660D workstation (Shanghai Chenhua) according to reported method [14]. The photocatalytic properties of the samples (20 mg) were evaluated by degrading Rhodamine B (RhB, 50mL, 5mg/L) under visible-light irradiation ($\lambda > 400$ nm). The mixture solutions were firstly stirred in dark for 20 min to reach the adsorption equivalence before irradiation. The degradation of RhB was monitored by checking the absorbance at 553 nm every 10 min.

3. Results and discussion

Fig. 1. TEM images of (a) g-C₃N₄, (b, c) ZnO nanoparticles, and (d, e, f) ZnO@g-C₃N₄.

Fig. 1a shows the TEM image of g-C₃N₄, which resembles previous literatures [17]. **Fig. 1b** depicts the as-prepared ZnO have particle size of 30-50 nm with highly crystallized prism-like shapes. HRTEM image in **Fig. 1c** shows surface of ZnO is clear and the lattice fringes with d-spacing of ~0.26 nm corresponds to the (001) planes. **Fig. 1d** indicates the ZnO@g-C₃N₄ particles are slightly aggregated and some of them are linked together, which probably results from the high temperature treatment. Moreover, **Fig. 1e** shows that an amorphous layer was observed homogeneously coated on ZnO nanoparticle with thickness of ~2 nm. [11,12] As depicted in **Fig. 1f**, the inter-planar spacing is of ~0.26 nm which corresponds to wurtzite structured ZnO.

Fig. 2. (a) XRD patterns, (b) EDS spectra and (c) Photoluminescence spectra of as-prepared samples (d) illustration of the band alignment in ZnO@g-C₃N₄.

The XRD peak found in g-C₃N₄ at ~27.4 ° can be indexed to (0 0 2) diffraction planes [13]. While, the curves for ZnO reveals that the sample is highly crystallized with wurtzite phase (Fig. 2a). It is interesting that no characteristic diffraction peak belonging to g-C₃N₄ is detected in the composites, indicating the g-C₃N₄ proportion is quite low or the g-C₃N₄ is uniformly coated on the ZnO nanoparticles, which prevents the long range order stacking pattern [11]. The existence of g-C₃N₄ is confirmed by the EDS investigation (Fig. 2b). The main elements simultaneously detected in ZnO@g-C₃N₄ includes Zn, O deriving from ZnO and C, N originate from g-C₃N₄, which provides powerful evidence for the existence of g-C₃N₄. FTIR spectra show that the peak at 400-550 cm⁻¹ correspondings to Zn-O bending vibrations. Meanwhile, the peaks at 1200-1700 cm⁻¹ related to the C-N and C=N stretching vibrations, respectively, and the peak at ~800 cm⁻¹ is related to the s-triazine ring vibrations (Fig. 2c). It can be seen clearly that the characteristic peaks of g-C₃N₄ presented in ZnO/g-C₃N₄ shifted to lower wave number, which suggests the covalent bond between g-C₃N₄ and ZnO [11]. The EIS test shows the Nyquist semicircle of ZnO@g-C₃N₄ is smaller than that of g-C₃N₄ and ZnO, which indicates ZnO@g-C₃N₄ has lower charge transfer resistance [14] (Fig. 2d). The PL spectra shows g-C₃N₄ exhibits strong photoluminescence at ~460 nm due to the $\pi \rightarrow \pi^*$ electronic transition [14], and the emission centered at ~390 nm represents the near-band-edge recombination of ZnO (Fig. 2e). The PL intensity for ZnO@g-C₃N₄ is much lower both at the UV and visible-light regions, which implies the ZnO@g-C₃N₄ has lower recombination rate [13]. The PL together with the EIS tests indicate that the effective charge separation and transfer at the g-C₃N₄ and ZnO interface could suppresses the direct recombination of the photo-generated electrons and holes, which improves the photocatalytic properties (Fig. 2f).

Fig.3 (a) Photocatalytic degradation of RhB solution using different photocatalysts under visible-light irradiation; (b) The $\ln(C/C_0)$ in function of time curves; (c) different scavengers on the degradation of RhB and (d) recyclability of ZnO@g-C₃N₄.

The photocatalytic performances were investigated using RhB as simulating pollutant under visible-light irradiation. It is obvious that ZnO@g-C₃N₄ exhibits much better activity (**Fig. 3a**). The degradation data were fitted according to the pseudo-first-order kinetic equation $\ln(C/C_0)=-kt$, (**Fig. 3b**). The apparent rate constant of the dye photodegradation could be determined as $\sim 0.0024 \text{ min}^{-1}$ for ZnO, $\sim 0.0157 \text{ min}^{-1}$ for g-C₃N₄ and $\sim 0.0831 \text{ min}^{-1}$ for ZnO@g-C₃N₄, which indicates the activity of ZnO@g-C₃N₄ is **~ 35 times higher than ZnO** and ~ 5 times higher than g-C₃N₄. The oxidative species in the photocatalytic process were detected using t-BuOH as radical scavenger and EDTA-2Na as hole scavenger. t-BuOH only caused a small change in the photodegradation rate, but the photocatalytic activity was greatly suppressed by EDTA-2Na (**Fig. 3c**) [18]. The results suggested that the photogenerated holes were the main oxidative species. The stability of ZnO@g-C₃N₄ was evaluated by successive experiments. In the testing, the used photocatalyst was added into fresh RhB solutions for each cycle and the photocatalytic activity retained over 90% of its original activity value after five successive cycles.

4. Conclusion

A facile two-step calcination method was developed to prepared ZnO@g-C₃N₄ core-shell type photocatalyst which significantly enhances the visible-light harvesting efficiency and stability. The photocatalytic activity of ZnO@g-C₃N₄ under visible light is ~ 5 time higher than g-C₃N₄ and **~ 35 times higher** than ZnO, which originates from the electron transfer from g-C₃N₄ to ZnO and the suppressed charge recombination. Moreover, the photocatalyst shows excellent stability and activity retains over 90% after 5 cycle reuse. This method could be potentially adopted as a general strategy to prepare other g-C₃N₄ based hybrid materials.

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