Improved activity for the photo-degradation by organic-inorganic composite photocatalysts

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Abstract. g-C3N4 and flowerlike ZnO organic–inorganic composite with varying the content of ZnO has been synthesized through facile mixing and heating method. The as-prepared ZnO samples were characterized by SEM images and BET surface area measurements and etc. The composite catalysts were characterized by BET surface area measurements, X-ray diffraction and etc. Under visible light irradiation, the activity of composite photocatalyst g-C3N4 and flowerlike ZnO organic–inorganic composite with 60% or 80% g-C3N4 for photo-degradation of MO is higher than that of either single-phase flowerlike ZnO or g-C3N4. The as-prepared g-C3N4 and flowerlike ZnO organic–inorganic composite exhibits an improved photo-degradation performance for MO due to the enhancement of electron–hole separation.

1. Introduction
In recent years for water splitting hydrogen generation or removal of contamination, the photocatalysis technique by using solar energy has a promising application. The photogenerated electron-hole pairs under light irradiation gives rise to the photooxidation-reduction reaction transfer. So far, to improve the photocatalytic performance, various techniques were studied for the photocatalyst, such as increasing surface area[1] and loading cocatalyst[2]. Recently, zinc oxide (ZnO) as a versatile material has attracted considerable attention in a wide range of applications, including catalysis, photodetectors, photoelectrochemical cells, biosensor and so forth.[3] Recently, it has been reported that the microstructures have great influence on these applications, including morphological characters and crystal size.[4] ZnO materials have been prepared with different morphologies, such as rods, cables, wires, and hierarchical nanostructures with high symmetries[5, 6]. In the many existing synthetic strategies[7,8], solvothermal or hydrothermal techniques have been widely used to be the effective approaches due to mild synthesis conditions and the facile operation[9].

An organic polymer photocatalyst, graphite-like carbon nitride (g-C3N4), has recently been reported [10, 11], which possesses water splitting and the removal of pollutants under visible light irradiation, and in the field of civil engineering, such photocatalysts have potential application for the low-cost advantage. Some composite catalysts such as g-C3N4/ Bi2WO6 [12], have shown better catalytic performance than that of single component catalyst. Therefore, it is expected to further improve the photocatalytic activity of g-C3N4 catalyst through forming composite photocatalysts.
In this paper, synthesis of the g-C₃N₄ and flowerlike ZnO organic–inorganic composite by simple mixing-heating method and the photo-degradation performance of MO by the composite catalysts have been studied. Based on the experimental results for the photo-degradation of MO, it was proposed for the possible mechanism on the improved photocatalytic performance.

2. Experimental
The starting materials utilized are zinc chloride, analysis purity grade), 26~28% NH₃·H₂O, absolute ethanol (Nanjing Chemical Reagent Co. Ltd.). Poly(styrene sulfonic acid) sodium salt was purchased from Alfa Aesar and used as received without further purification. Distilled water was used throughout the experiment.

In a typical process, zinc chloride and PSS was dissolved in the solution containing water and ethanol with a proportion, then the NH₃·H₂O was dropped in it at room temperature. The mixture was stirred for 30 min, then transferred into Teflon-lined stainless steel autoclave, and heated at 130 °C for 6 h. These samples were treated by centrifugation and thoroughly rinsed with water and ethanol several times, and then dried at 70 °C in an oven for subsequent characterization. The photocatalyst of g-C₃N₄ was prepared by directly heating melamine at 500 °C (heating rate: 20 °C/min) for 2 h, and the further deammoniation treatment was set at 520 °C for 2 h [11], respectively in the semi-closed system to prevent sublimation of melamine. The as-prepared ZnO and g-C₃N₄ powder samples were mixed by ball-milling and then calcined at 350 °C for 3 h in a muffle furnace.

Characterization of samples: The specific surface area of the as-prepared powders was obtained on a Micromeritics TriStar 3000 instrument (USA) at 77 K and Brunauer–Emmett–Teller (BET) equation were used to calculate the specific surface area. The products were characterized by X-ray diffraction (XRD) for phase identification on a Rigaku Ultima III diffractometer with Cu Kα radiation (λ = 0.154 nm, 40 kV, 40 mA) and a scan rate of 10 ° min⁻¹. Ultraviolet visible (UV–vis) diffuse reflection spectra were measured using a UV-vis spectrophotometer (Shimadzu UV-2550, Japan) and converted from reflection to absorbance by the Kubelka-Munk method.

The photocatalytic reaction was performed in a Pyrex reactor, and the methyl orange (MO) dye was used to test the photocatalytic activities of as-prepared samples. The catalyst (0.1 g) was dispersed in 100 mL MO aqueous solution. The light irradiation system contains a 300 W Xe lamp with a water filter to remove heating effects and cut-off filter L42 was used for visible light. The reaction solutions of the MO photodegradation on catalysts were first stirred in the dark for all experiments for 1 h to reach the adsorption–desorption equilibrium of MO. Using the UV-vis absorption spectra, the MO degradation efficiency was evaluated to measure the peak value of a maximum absorption at wavelength of 463 nm of MO solution.

3. Results and discussion
The SEM image provides information on the morphology and crystalline size. It is shown in Figure 1, that ZnO with flower-like morphology is composed of nanocrystalline ZnO rods, and the flower-like ZnO formed by the agglomeration of nanorods. The composite catalyst is composed of flower-like ZnO and g-C₃N₄. And from the XRD result, no impurity phases were detected, and the diffraction peaks are in good agreement with a typical wurtzite-type ZnO crystal (hexagonal, P6₃mc), JCPDS No.36-1451. The high resolution-SEM image provides further information on the morphology and crystalline size. It is shown in Figure 2, the ZnO nanorods are in the size of about 300-400 nm.
Figure 1. SEM image of the as-prepared ZnO sample prepared using zinc chloride as the precursor.

Figure 2. High resolution-SEM image of the as-prepared ZnO sample prepared using zinc chloride as the precursor.

For the investigation of the photo-degradation activity of g-C$_3$N$_4$ and flowerlike ZnO organic–inorganic composite photocatalyst, the pure ZnO, ZnO organic–inorganic composite and pure g-C$_3$N$_4$ samples were used as photocatalysts for the degradation of MO. It is shown from Figure 3, under visible light irradiation, the results of the degradation activities of MO over different photocatalysts are got. The 60 or 80 wt.% g-C$_3$N$_4$ and flowerlike ZnO organic–inorganic composite show much higher activity than that of pure g-C$_3$N$_4$, as shown in Figure 3. This clearly indicates that for the degradation of MO, the g-C$_3$N$_4$ and flowerlike ZnO composite was determined as an efficient visible-light-driven photocatalyst for the advantage of the formation of chemically bonded interfaces between the two materials by heating treatment.
Figure 3. Comparison of MO degradation over different photocatalysts: a, g-C$_3$N$_4$; b, g-C$_3$N$_4$ and ZnO composite with 80% g-C$_3$N$_4$; c, g-C$_3$N$_4$ and ZnO composite with 60% g-C$_3$N$_4$, under visible light irradiation.

4. Conclusion

In summary, g-C$_3$N$_4$ and flowerlike ZnO organic–inorganic composite photocatalysts with varying the content of g-C$_3$N$_4$ were synthesized. By coupling ZnO, the photocatalytic degradation result shows that the visible light-induced oxidation performance of MO with g-C$_3$N$_4$ was remarkably enhanced due to the effective separation of photogenerated electron-hole pairs.

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