Construction of ZnO Hollow Spheres Coupled with g-C₃N₄ as Enhanced Photocatalysts under Simulated Solar Light

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Abstract. Rapid photon-induced e⁻-h⁺ pairs recombination rate is a fatal factor restricting the photocatalytic performance of graphitic carbon nitride (g-C₃N₄). In this work, ZnO hollow spheres (ZnO HS) coupled with g-C₃N₄ photocatalysts were prepared by a simple mechanical agitation of the mixture of g-C₃N₄ and ZnO HS in ethanol solution. The as-prepared samples were systematically measured via were characterized by XRD, SEM, DRS, FT-IR and PL. As analysis from the PL test results, the g-C₃N₄/ZnO HS has much lower photo-generated e⁻-h⁺ pairs recombination rate than that of pure g-C₃N₄. Under the illumination of simulated solar light, the effect of ZnO HS concentration on the photocatalytic properties of as-prepared g-C₃N₄/ZnO HS photocatalysts with different ZnO amount was discussed by the degradation of methyl orange (MO) in detail. The optimum photodegradation performance of g-C₃N₄/ZnO HS with 5% ZnO HS is almost 47.43% higher than that of pristine g-C₃N₄. Our research results present a simple and convenient synthetic protocol for processing g-C₃N₄-based photocatalysts for the degradation of environmental pollutants.

1. Introduction
In recent years, semiconductor photocatalytic technology has attracted relatively great attention as one of green technologies to remove environmental contamination because of its potential advantage in low cost, harmless and high efficiency [1]. Up to now, various semiconductor materials with nanostructure have been explored exploited as photocatalysts for organic pollutants degradation by photocatalytic reaction [2-5]. Among the reported materials, graphitic carbon nitride (g-C₃N₄) has been regarded as a promising candidate, due to its easy availability and especially its intrinsic visible light response [6, 7]. However, its photodegradation activity is retarded by low quantum efficiency and high recombination rate of photogenerated electron-hole pairs [8]. Accordingly, various of strategies have been exploited to separate its photoreduced charges significantly with certain success such as coupling with other semiconductors [9], copolymerization [10], doping with metal or nonmetal elements [11]. Among those methods, forming heterojunction has emerged as a reliable route to promote the separation of photogenerated charges so that the photodegradation activity of g-C₃N₄ can be improved to a certain extent [12]. ZnO has a well-matched overlapping band-structure with g-C₃N₄, and then coupling ZnO with g-C₃N₄ has been verified to be an ideal system for showing enhanced visible-light driven photocatalytic degradation activity of Methylene blue (MB) [13].

In addition to the above we have discussed, previous studies demonstrate that the morphology and size of materials have an important influence on their photoelectric properties [14]. In recent years, ZnO with different micro-nanostructures have been reported, such as nanowires, nanofilm, hollow microspheres, etc [15-17]. Among them, the hollow-structured ZnO-based nanomaterials can improve
excellent photocatalytic activity by the fast separation of photogenerated charge carriers, the short charge diffusion distance and multiple reflections of light [18]. Moreover, the hollow structure makes the reactants easily transfer to the active sites, leading to the enhanced photocatalytic activity [19]. However, few studies reported on the synthesis and photocatalytic performance of g-C$_3$N$_4$/ZnO HS composite photocatalyst.

In the present work, g-C$_3$N$_4$/ZnO HS photocatalyst was prepared and analyzed in detail. The amount of ZnO hollow spheres loaded in the binary composite photocatalyst was changed to investigate its influence on the photocatalytic activity. The as-synthesized materials were systematically measured for their structure, morphology and optical properties by XRD, SEM, PL, FT-IR and DRS. Methyl orange (MO) was chosen as a model substance to evaluate the photodegradation activity of the as-prepared samples.

2. Experimental

2.1. Materials

The raw materials used in the experiments such as Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O), melamine (C$_3$N$_3$(NH$_2$)$_3$), urea (CO(NH$_2$)$_2$), glucose and absolute ethanol were analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd., China, and were employed as received.

2.2. Preparation of g-C$_3$N$_4$

Graphite-like C$_3$N$_4$ was first prepared by a thermal polymerization from melamine according to the reported methods [20]. Typically, certain amounts of melamine was placed in an alumina crucible and heated at 550°C for 2 h under air atmosphere.

2.3. Preparation of ZnO HS

In order to prepare ZnO HS, the carbon spheres were synthesized follows a reported process [21]. Briefly, certain amounts of glucose and deionized water were mixed. After vigorous stirring, the mixed solution was transferred to a teflon-lined stainless steel autoclave and maintained at 180°C for 4 h. After centrifugation, the dark brown products were obtained by drying at 80°C for one night. ZnO HS were further synthesized by the templating methods with the same molar ratio as the reported procedure [22]. In a briefly synthesis, the Znic source, precipitant agent urea and carbon template were added to deionized water in sequence. After continuously thermal treatment 90°C for 9 h, the puce precursor was obtained by centrifugation and washed with deionized water and ethanol, then dried at 60°C for 8 h. Finally, the white ZnO hollow spheres can be collected by calcinations of the precursor at 450°C for 3 h under air atmosphere.

2.4. Preparation of g-C$_3$N$_4$/ZnO HS Composites

The g-C$_3$N$_4$/ZnO HS composites were formed by mechanical agitation process. In a typical preparation, precalculated g-C$_3$N$_4$ and ZnO HS were dispersed in absolute ethanol by ultra-sonication for 1 h, followed by continuously stirring for 12 h. After centrifugation and drying at 70°C, the samples were collected by heating treatment at 500°C for 5 h. The mass percent of ZnO HS were 3 w.t.%, 5% w.t., 10w.t.%, 15 w.t.%, and 25w.t.%, and labeled as g-C$_3$N$_4$/ZnO (3%), g-C$_3$N$_4$/ZnO (5%), g-C$_3$N$_4$/ZnO (10%), g-C$_3$N$_4$/ZnO (15%), g-C$_3$N$_4$/ZnO (25%), respectively.

2.5. Characterization

All themono- and bi-component systems were systematically characterized by XRD (Shimadzu XRD-6100, Japan), SEM (Zeiss Sigma, Germany), PL (Zolix LSP-X500A), FT-IR (Spectrometer PerkinElmer Spectrum Two, USA) and DRS (lambda 750).

2.6. Evaluation of Photodegradation Efficiency

Photodegradation experiments were carried out in a photocatalytic reactor to assess the photodegradation efficiency of as-synthesized materials. The 500W xenon (Xe) lamp was utilized to
simulate the sunlight. The as-prepared photocatalyst was dispersed in an aqueous solution of MO (10 mg L\(^{-1}\)). Prior to the irradiation, the suspension was continuously stirred in the dark for 1 h to realize the adsorption/desorption equilibrium. Aliquots (3 mL) of sample were collected every 30 min intervals, and followed by centrifugation to separate the photocatalysts. The concentration was of MO solution was monitored via UV-vis spectrometer to record the maximum absorbance at 463 nm.

3. Results and Discussion

3.1. FT-IR analysis

Fourier transform infrared spectroscopy (FT-IR) is firstly used to identify components of the composites. Spectra of ZnO HS, pristine g-C\(_3\)N\(_4\) and g-C\(_3\)N\(_4\)/ZnO (5\%) composite are displayed in Figure 1. The peak at about 432 cm\(^{-1}\) in the ZnO HS sample is associated with the presence of bending vibration mode of Zn–O bond [23]. The broad band around 3416 cm\(^{-1}\) in the ZnO HS sample represents the stretching vibrations of OH, which is probably attributed to the adsorbed water molecules. The peak at about 810 cm\(^{-1}\) in g-C\(_3\)N\(_4\) sample is related to the bending vibration characteristic of heptazine units. The broad band around 1200–1700 cm\(^{-1}\) in g-C\(_3\)N\(_4\) sample is attributed to the typical stretching modes of CN heterocycles, another broad band around 3200 cm\(^{-1}\) in the same sample is assigned to the stretching vibration mode of amine groups [24]. However, the peaks related to ZnO HS in the g-C\(_3\)N\(_4\)/ZnO (5\%) composite are not detected, the introducing of ZnO HS in the g-C\(_3\)N\(_4\)/ZnO (5\%) sample has no influence on the absorption band of g-C\(_3\)N\(_4\), which should be ascribe to the much stronger IR response of pristine g-C\(_3\)N\(_4\) than that of ZnO HS.

![Figure 1. FT-IR patterns of pristine g-C\(_3\)N\(_4\), ZnO HS and g-C\(_3\)N\(_4\)/ZnO (5\%).](attachment:ftir.png)

3.2. Crystal Structures

The structure of g-C\(_3\)N\(_4\)/ZnO composite is further characterized by x-ray diffraction (XRD). Figure 2 shows the XRD patterns of g-C\(_3\)N\(_4\), ZnO HS and g-C\(_3\)N\(_4\)/ZnO with different ZnO mass percent. Unlike the FT-IR analysis, the different phase can be clearly distinguished in the XRD patterns. The diffraction peaks at around \(2\theta = 13.1\) and 27.4\(^\circ\) correspond to the (100) and (002) crystal planes of g-C\(_3\)N\(_4\), while the diffraction peaks at 20 value of 31.8, 34.3, 36.5, 47.3, 56.5 and 62.8\(^\circ\) correspond to the (100), (002), (101), (102), (110) and (103) crystal planes of the ZnO, respectively, the results are consistent with the previous reported [16, 25]. No other impure peaks are observed, indicating these
composites consist of both g-C\textsubscript{3}N\textsubscript{4} and ZnO HS. Furthermore, it is noted that the peaks intensities of g-C\textsubscript{3}N\textsubscript{4} weaken gradually with the increasing of the loading amount of ZnO content, while the peaks intensities of ZnO got strong.

Figure 2. XRD patterns of (a) ZnO HS, (b) pristine g-C\textsubscript{3}N\textsubscript{4}, (c) g-C\textsubscript{3}N\textsubscript{4}/ZnO (3\%), (d) g-C\textsubscript{3}N\textsubscript{4}/ZnO (5\%), (e) g-C\textsubscript{3}N\textsubscript{4}/ZnO (10\%), (f) g-C\textsubscript{3}N\textsubscript{4}/ZnO (15\%) and (g) g-C\textsubscript{3}N\textsubscript{4}/ZnO (25\%).

3.3. Morphology Characterizations
Figure 3 shows scanning electron microscopy (SEM) images of the as-prepared g-C\textsubscript{3}N\textsubscript{4}, ZnO and g-C\textsubscript{3}N\textsubscript{4}/ZnO (5\%) nanocomposites. The pristine g-C\textsubscript{3}N\textsubscript{4} sample exhibits a layered and sheet-like surface morphology from Figure 2a, which is consistent with the previous report [12]. Figure 2b reveals that small opening in the as-synthesized ZnO HS can be observed, indicating the hollow structure of the sphere. Figure 2c is the SEM image of g-C\textsubscript{3}N\textsubscript{4}/ZnO (5\%), it exhibited that ZnO HS are well attached with the g-C\textsubscript{3}N\textsubscript{4} and this interaction allowed for the charge transfer between ZnO HS and g-C\textsubscript{3}N\textsubscript{4}, restricting the recombination of photon-generated e\textsuperscript{−} - h\textsuperscript{+} pairs with the increasing of photodegradation efficiency.

Figure 3. SEM of (a) pristine g-C\textsubscript{3}N\textsubscript{4}, (b) ZnO, and (c) g-C\textsubscript{3}N\textsubscript{4}/ZnO (5\%).
3.4. UV−Vis Diffuses Reflectance Spectra (DRS)

The absorbance properties of ZnO HS, g-C₃N₄ and g-C₃N₄/ZnO HS composite with different ZnO HS mass ratios are analyzed by DRS, which are shown in Figure 4. As expected, the absorption edge is about at 400 nm for pure ZnO HS and 570 nm for pristine g-C₃N₄, the band gaps of pure ZnO HS and pristine g-C₃N₄ are considered to be 3.2 and 2.7 eV, respectively. The g-C₃N₄/ZnO composite samples still remain the similar absorption edge with g-C₃N₄, implying ZnO HS couples with g-C₃N₄ does not significantly change the band gap energies of g-C₃N₄. Nevertheless, the absorption intensity of g-C₃N₄/ZnO composite in the UV region increases compared with g-C₃N₄, which is attributed to the presence of ZnO HS. The composite samples hybrid absorption features of g-C₃N₄ and ZnO HS, which increases utilization of the solar spectrum and consequently leads to the enhancement of photocatalytic efficiency.

3.5. Photoluminescence (PL) Spectra

The PL spectra excited at 325 nm for pristine g-C₃N₄ and g-C₃N₄/ZnO (5%) are used to analyze the separation efficiency of the photo-generated e⁻−h⁺ pairs. As shown in Figure 5, pristine g-C₃N₄ presents an emission peak at 457 nm, and its intensity is higher, which is partially attributed to rapid photon-generated e⁻−h⁺ pairs recombination rate in the g-C₃N₄, but after introducing ZnO HS, the PL intensity decreases remarkably. The PL intensity of g-C₃N₄/ZnO (8%) is much lower than that of pristine g-C₃N₄, implying that high separation efficiency of photoinduced electrons and holes between g-C₃N₄ and ZnO HS, which always associated with the enhanced photocatalytic performance.

3.6. Photocatalytic Performance

The photocatalytic degradation of MO (10mg/L) under sunlight illumination using no catalyst, pure g-C₃N₄ and g-C₃N₄/ZnO HS with different ZnO HS concentration as photocatalyst was measured to prove the enhanced photodegradation efficiency, which is shown in Figure 6. In absence of catalyst, the concentration of MO does not show obvious change. Pure g-C₃N₄ and ZnO HS exhibit weak photodegradation efficiency for MO under sunlight irradiation. However, the photocatalytic activity of g-C₃N₄/ZnO composite is obviously enhanced compared to that of pristine g-C₃N₄ and ZnO HS, which is attributed to the formation of the heterojunction between g-C₃N₄ and ZnO HS. The photocatalytic activity increases as the loading ratio of ZnO HS rises up to 5%, yet it decreases with further increasing loading ratio of the ZnO HS. The g-C₃N₄/ZnO (5%) exhibits the best photocatalytic activity under simulated solar light irradiation within 180 min, which is nearly 47.43% higher than that of pure g-C₃N₄ and 43.42% higher than that of ZnO HS, respectively.
4. Summary
In summary, we have successfully prepared the ZnO HS by templating method and fabricated a series of g-C₃N₄/ZnO HS composite photocatalysts with different ZnO HS loading ratios via a simple mechanical agitation process. The formed composite photocatalysts exhibit obviously enhanced photocatalytic activities in MO degradation under simulated solar irradiation, owing to the synergistic effect of g-C₃N₄ and ZnO HS in composite photocatalysts. The optimal ZnO HS loading ratio with the highest photocatalytic activity is demonstrated to be 5%, which is almost 2.5 times higher than that of individual g-C₃N₄ and 2.3 times higher than that of individual ZnO HS, respectively. On the basis of the results, the novel g-C₃N₄/ZnO HS composite photocatalysts with efficient photocatalytic performance should be promising candidates for environmental remediation.
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References
[1] Kudo A, Miseki Y 2009 Chem. Soc. Rev. 38 253
[2] Sun C, Xu Q, Xie Y, et al. 2018 J. Mater. Chem. A 6 8289
[3] Cui D, Wang L, Xu K, et al. 2018 J. Mater. Chem. A 6 2193
[4] Chen L, Jiang D, He T, et al. 2013 CrystEngComm 15 7556
[5] Sawant S Y, Kim J Y, Han T H, et al. 2018 New. J. Chem. 42 1995
[6] Wang Y, Wang X, Antonietti M 2012 Angew. Chem., Int. Ed. 51 68
[7] Zheng Y, Liu J, Liang J, et al. 2012 Energy Environ. Sci. 5 6717
[8] Patnaik S, Martha S, Acharya S, Parida K M 2016 Inorg. Chem. Fron. 3 336
[9] Katsumata K, Motoyoshi R, Matsushita N, Okada K 2013 J. Hazard. Mater. 260 475
[10] Zheng D, Pang C, Liu Y, Wang X 2015 Chem. Commun. 51 9706
[11] Yan S C, Li Z S, Zou Z G 2010 Langmuir 26 3894
[12] Liu C, Li C, Fu X, et al. 2015 RSC Adv. 5 37275
[13] Chen D, Wang K, Ren T, et al. Dalton Trans. 43 13105
[14] Jia X, Tian M, Liu Y, et al. 2015 Appl. Phys. A 119 1179
[15] Liao L, Lu H B, Li J C, Liu C 2007 Appl. Phys. Lett. 91 173110
[16] Inamdar A I, Yuldashev S U, Jo Y C, et al. Thin Solid Films 562 269
[17] Li X B, Ma S Y, Li F M, et al. Mater. Lett. 100 119
[18] Nguyen C C, Vu N N, Do T O 2015 J. Mater. Chem. A 3 18345
[19] Nguyen C C, Dinh C T, Do T O 2017 RSC Adv. 7 3480
[20] Sun Y, Jiang J, Cao Y, et al. Mater. Lett. 212 288
[21] Xi J, Sun H, Wang D, et al. 2017 Appl. Catal. B: Environ. 225 291
[22] Lan S, Liu L, Li R, et al. 2014 Ind. Eng. Chem. Res. 53 3131
[23] Music S, Popovic S, Maljkovic M, Dragcevic E 2002 J. Alloys Compd. 347 324
[24] Bojdyš M J, Muller J O, Antonietti M, Thomas A 2008 Chem. Eur. J. 14 8177
[25] Wang X, Maeda K, Thomas A, et al. 2009 Nat. Mater. 8 76