A facile method for synthesis of graphene-coated hexagonal ZnO photocatalyst with enhanced photodegradation activity

Yunlong Zhang1,2, Yuzhi Zhang2,*
1 University of Chinese Academy of Sciences, Beijing 100049, China
2 The key Laboratory of Inorganic Coating Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, 200050

*Corresponding author e-mail: yzzhang@mail.sic.ac.cn

Abstract. A kind of hexagonal ZnO (HZO) was synthesized in N-methyl-2-pyrrolidone (NMP)/H2O mixed solvent for a high exposure of polar ±(0001) facets to get a high-efficiency photocatalyst. The amine-functionalized HZO particles were coated with graphene oxide (GO) by electrostatic force-induced self-assembly and thermal reduction to form HZO@Gr core/shell structure. The as-prepared HZO and HZO@Gr were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and UV-visible diffuse reflectance spectroscopy (UV-vis/DRS). The results indicate that the graphene on HZO@Gr remains high quality and the optical properties of the composite change a lot with sunlight absorption improving, bandgap and photoluminescence (PL) intensity decreasing. The obtained HZO photocatalyst shows good photocatalytic activity for methylene blue (MB) under UV-visible irradiation. Furthermore, the HZO@Gr photocatalyst exhibits the best photodegradation rate of MB reaching up to 98.2% within 50 minutes. The graphene-coated HZO structure could offer new directions which would further extend the scope for synthesis of various ZnO/graphene composites with improved properties useful for various applications.

1. Introduction
Currently, organic dyes and their effluents have become one of the main sources of water pollution due to the greater demand in industry such as textile, paper and plastic. Thus, it is of great significance to develop a high-efficiency, energy-saving and low-cost treatment method for the elimination of dyes in wastewater.

As one of the most important semiconductor photocatalysts, ZnO has attracted considerable interests because of its high photosensitivity and stability [1]. However, despite its great potential, the photocatalytic efficiency remains very low because of the fast recombination of the photogenerated electron-hole pairs in the single-phase semiconductor [2]. As a rising star of carbonaceous materials, graphene has become the focus of considerable interest for its great potential to enhance the photodegradation activity of ZnO [3]. According to recent research, there are mainly three factors that attribute to the increasing photocatalytic efficiency: the increasing adsorptivity of pollutants, extended light absorption range and efficient charge transportation and separation [4], which conquer the obstacles that hinder the photodegradation process.
Although it has synthesized a great diversity ZnO/graphene structure, the graphene-coated ZnO (ZnO@Gr) composites exhibit larger contact area and well composite effect. However, as presented in literatures [4-9], graphene with quantum-dot dimension acquired by reducing GO was broken to a great degree and the output of as-synthesized ZnO@Gr composite is relatively low so as not to be convenient to take characterization and eventually to be applied.

In this paper, a hexagonal ZnO@Gr core/shell structure was synthesized consisting of three steps: surface modification of ZnO particles with amine groups, coating of a GO shell on ZnO particles, and conversion of the GO shell to graphene. This technique is simple and readily capable of producing well-coated quantities of ZnO@Gr core/shell structure. The photodegradation tests of methylene blue (MB) showed that hexagonal ZnO displayed a certain ability of photocatalysis. The ZnO@Gr composites with core/shell structure exhibited obvious enhancement of photocatalytic activity.

2. Experimental and characterization procedures

2.1. Preparation

The GO sheets were prepared using the modified Hummers’ method, as reported elsewhere [10]. The exfoliated GO sheets were dispersed in deionized water. Then, the dispersion was centrifuged (8000 rpm for 20 min), and the supernatant was kept. 30 ml of the supernatant was evaporated and the remaining GO was weighed to calculate the concentration of GO sheets. Finally, the supernatant was diluted to 0.1 mg/ml dispersion with deionized water for storage.

A kind of hexagonal ZnO (HZO) powder was synthesized using a facile method. First, 100 ml N-methyl-2-pyrrolidone (NMP) and 100 ml deionized water was mixed in a 250 ml conical flask to form a homogenous solution and 4.5 g zinc acetate dehydrate (Zn(Ac)₂·2H₂O) was added to the above solution while continually stirring. Then, the mixed solution was heated to 95 °C in an oil bath and maintained for 4 hours. After that, the ZnO turbid liquid was washed with deionized water many times by centrifugation to remove the remaining NMP. Finally, the HZO was obtained after drying at 80 °C for 10 h.

The HZO@Gr core/shell structure was obtained by self-assembly of the obtained GO and amine-functionalized HZO. First, the surface of HZO was amine-functionalized in 2.5% amino-propyl-trimethoxysilane (APTM)/ethanol solution by sonication and subsequent roll-mixing at 60 °C for 10 hours. Then, we centrifuged the turbid liquid 3 times with ethanol to remove the remaining APTMS and dried the precipitation at 80 °C for 10 hours. After that, the amine-functionalized HZO (HZO-NH₂) particles were dispersed in deionized water, and the dispersion liquid was mixed with the GO solution described above while continually stirring. Subsequently, the mixed solution was heated to 60 °C and maintained for 10 hours. The product was centrifuged and washed 3 times to remove the dissociative GO. HZO@GO was obtained after drying at 80 °C for 10 hours. Finally, the HZO@GO was annealed at 500 °C in Ar for 2 hours to get the HZO@Gr powder.

2.2. Characterization

Scanning electron microscopy (SEM, Hitachi S-3400N), Field Emission SEM (FESEM, Magellan 400, FEI Company, USA) and high-resolution transmission electron microscope (HRTEM, Tecnai G2 F20, FEI Company, USA) were used to investigate the microstructure of ZnO and ZnO@Gr composite. Raman spectra were obtained by a DXR Raman Microscope with 532 nm laser excitation light. UV-visible diffuse reflectance spectroscopy was measured using a Hitachi U-3010UV-vis spectrophotometer. Photoluminescence spectra were also acquired using a Shimadzu RF-5301PC spectrophotometer, with the excitation wavelength set at 325 nm.

2.3. Evaluation of photocatalytic activity

The photodegradation process of MB was tracked based on the absorption spectroscopic technique. The samples (0.2 g/l) were dispersed in 100 ml MB aqueous solution (10 mg/l). The mixed suspensions were magnetically stirred for 1 h under dark at ambient conditions to get the absorption-desorption
equilibrium before irradiation. Then the suspensions were exposed to the light irradiation produced by a 300 W Xe lamp positioned at 36 cm away from the vessel. At 10 minutes intervals, 3 ml of the mixed suspensions were extracted and centrifuged to remove the photocatalyst. The degradation efficient of MB solution was analyzed by recording variations of the absorption located at maximum band using a UV-vis absorption spectrometer.

3. Results and discussion

3.1 Morphology of HZO@Gr

Figure 1a and b show the FESEM images of HZO@Gr composite. It can be seen the upturned layers of graphene on the surface of HZO particle in Figure 1a. The areas marked by the red dotted line indicate the color or height difference with graphene covering on the HZO surface so that the boundary of graphene can be seen. What’s more, the surface of HZO particle is covered by transparent graphene film which seems like being wrapped by some transparent plastic film and the wrinkle also can be seen (Fig. 1b). The detailed composite state of HZO and graphene can be seen from HRTEM in Figure 1c. There are about 3 layers of graphene at the edge zone of HZO, indicating that HZO particles are well coated by graphene. In addition, the magnification of Figure 1c (Fig. 1d) exhibits that the interplanar spacing in the crystalline petal is 0.26 nm, corresponding to the distance between two (002) planes of the hexagonal ZnO phase, indicating preferential growth along the [002] direction. What deserves to be mentioned is that there seldom exists free graphene in the observation of the SEM and TEM images because the graphene can be washed out by centrifugation while mounts of free graphene in the ZnO/graphene composites will decrease the photocatalysis efficiency.

![Figure 1](image_url)

**Figure 1.** (a, b) TEM images of HZO@Gr. (c) HRTEM image of HZO@Gr. (d) Magnified image of (d), revealing that the distance between two (002) planes of the hexagonal ZnO phase with the interplanar spacing in the crystalline petal is 0.26 nm.

3.2 Characterization of optical properties

The Raman spectra of GO, reduced GO (RGO) and HZO@Gr are shown in Fig. 2, which exhibit two prominent peaks, of the D band and G band, as well as a weak and broad 2D band. The RGO was obtained by thermal reduction of GO in the same processes with reducing HZO@GO. The G band is attributed to all sp² carbon forms and provides information on the in-plane vibration of sp² bonded carbon atoms while the D band suggests the presence of sp³ defects [9]. Generally, the ratio of the intensities (I_D/I_G) of the two bands D and G is used to provide additional information on the quality of nanostructured carbon-based materials. The ratio of the intensity are calculated to be about 0.94, 0.97 and 1.01 for HZO@Gr, RGO and GO, which indicates the high quality of graphene and the large distribution of sp² domains on the graphene [11,12]. It is possible that compared to the other ZnO particles, the graphene on the flat-surface HZO has less strain with HZO, ensuring it not easy to be damaged during the annealing process. What’s more, we observe that the G band of GO and RGO occur at 1576 and 1580 cm⁻¹, while the G band of HZO@Gr is located at 1592 cm⁻¹. The great up-shift of G band is a result of the p-type doping of graphene owing to the interaction with ZnO [9,13,14]. Electron charge transfer from graphene to ZnO occurs since the ZnO has a larger work function than graphene.
The flat surface of HZO and good quality of graphene will lead to intensive interaction between the interface and more p-type doping of graphene, thus resulting in the great up-shift of G band.

![Raman Spectra](image)

**Figure 2.** Raman spectra of HZO@Gr, reduced GO and GO.

The performance of UV-vis light absorption is an important factor for evaluating optical properties of photocatalysts. As shown in Fig. 3a, the absorption properties of HZO and HZO@Gr were measured by UV-visible spectroscopy and found that all the samples show the characteristic spectrum with their fundamental absorption sharp edge. The curves of \((\alpha h\nu)^2\) versus \(h\nu\) are derived from the UV-vis spectra. It indicates that HZO@Gr exhibit band gap energy of 3.22 eV, which is smaller than the 3.26 eV for HZO. This is indicative that the presence of graphene has some influence on the electronic energy level of ZnO [9]. In addition, HZO@Gr shows intense, broad background absorption in the visible light region. The increase of absorption in the visible light region is due to the presence of graphene, indicating the GO in the products has been well deoxygenated and reduced to graphene. These observations might suggest an increase of surface electric charge of the oxides in the composite due to graphene introduction, which may lead to modifications of the fundamental process of electron/hole pair formation during irradiation [14].

![UV-Vis Spectra](image)

**Figure 3.** (a) The plots of \((\alpha h\nu)^2\) versus \(h\nu\) derived from the UV-visible spectra (the inset). (b) The room temperature PL emission of HZO, HZO@Gr.

Figure 3b shows the Photoluminescence (PL) spectra acquired at room temperature and under excitation wavelength of 325 nm for HZO and HZO@Gr. We can see two obvious main emission peaks at 398 nm (3.11 eV) and 465 nm (2.57 eV) from the spectra of HZO. The UV emission of the products located at 398 nm is attributed to the band-edge emission resulting from the recombination of excitonic centers [16, 17]. The strong blue luminescence (465 nm) emission is more preferably attributed to the
bound excitons arising from the intrinsic defects such as oxygen vacancy [9, 18]. However, HZO@Gr show much weaker emission at 398 and 465 nm than HZO. These may result from the factors: (1) the introduction of graphene can eliminate the surface defects, and (2) the graphene can accept the photo-induced electron assuredly and improve the charge separation [9].

3.3 Photocatalytic property
The photocatalytic experiments were carried out in order to study the photocatalytic properties of as-prepared samples with different shapes. The results of the MB degradation efficiency in a series of experimental conditions are summarized in Figure 4. The degradation efficiency of MB in the presence of commercial ZnO (CZO) is 41% after 50 min of irradiation. However, HZO was found to exhibit obvious increasing efficiency, and the photocatalytic efficiency reached to 69% after 50 min. Compared with the irregular shape of CZO, HZO particles own hexagonal shape with thin thickness, which could generate considerable internal electric field and facilitate the separation of photogenerated electron-hole pairs [19]. The enhanced separation efficiency of photogenerated charges could increase the photodegradation activity of ZnO. What’s more, the photocatalytic efficiency of HZO@Gr exhibits prominent enhancement compared with the graphene-uncovered HZO and CZO, reaching 98.2% at 50 min. The photocatalytic superiority of the graphene-coated HZO samples can be attributed to their interaction between graphene and the surface of HZO, thus affect the surface electron behavior of HZO under the UV-visible irradiation. As a result, the band gap of HZO@Gr and recombination possibility of photogenerated electron-hole pairs decreased, and the reduced graphene with large specific surface area and a number of oxygenic groups allow good access of MB molecules to their surface in photocatalytic system [3], which account for the increase of the photodegradation activity of HZO@Gr.

![Figure 4. Photodegradation efficiency of MB over commercial ZnO (CZO), HZO, HZO@Gr and blank, respectively](image)

4. Conclusion
We have provided a unique and facile route to synthesize core/shell HZO@Gr photocatalyst. A kind of hexagonal ZnO was synthesized for a better photocatalytic efficiency Graphene shells were formed by uniformly coating GO on the surface of surface-modified HZO particles through electrostatic-force-induced self-assembly followed by the thermal reduction of GO. For the hexagonal prism shape of HZO and unique HZO@Gr core/shell structure, the graphene remained high quality and the optical properties of the composite changed a lot. The synthesized HZO sample has already exhibited good photocatalytic ability. While the photocatalytic efficiency of graphene-coated HZO@Gr photocatalyst showed a considerable increase that the MB dye decomposed 98.2% within 50 minutes. Hence, synthesizing the polar facets dominant HZO and coating graphene on it could offer new directions which would further extend the scope for synthesis of various ZnO/graphene composites as well as other nano metal oxides/graphene composites with improved properties useful for various applications.
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