ZnO nanorod array/reduced graphene oxide substrate with enhanced performance in photocatalytic degradation

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A novel ZnO nanorod array/reduced graphene oxide (ZnO array/rGO) composite coating was synthesised via the combination of seed layers-growth and aqueous solution reaction for the formation of ZnO nanorod arrays, which was further combined with rGO using a simple water bath method. The results revealed that perpendicular arrays with hexagonal planes were successfully fabricated. The size and density of the arrays could be optimised by adjusting the reactant concentrations. The influence of the rGO fraction in the ZnO array/rGO composites on the photocatalytic degradation of the methylene blue under UV radiation was investigated. It was found that the photocatalytic performance could be significantly improved by adding rGO. The enhanced photocatalytic activities were attributed to the interactions between ZnO nanorod arrays and rGO nanosheets and subsequently effective separation of photo-generated electron-hole pairs via rGO as electron sinks. The ZnO array/rGO composites presented advantages including facile and green preparation, long photo-electron lifetime, easy particle agglomeration and recovery, and therefore is expected to be an ideal photocatalysts for the future utilisation.

1. Introduction: Nowadays, environmental issues, especially water pollution, have become more and more serious and attracted worldwide attention [1, 2]. Many efforts have been carried out to eliminate toxic organic or inorganic pollutants from effluents. Among these technologies, the photo-degradation technology using heterogeneous photocatalytic semiconductor materials is extensively utilised and has presented advantages in pollutants removal due to its low toxicity, high surface area and chemical stability etc. [3, 4]. ZnO, a kind of semiconductor material with wide bandgap of 3.37 eV and a large excition binding energy of 60 meV, has been widely used as a photocatalyst, which has been proven to demonstrate high photocatalytic activities [5]. However, the recombination of electron-hole pairs generated by high-energy photon, the particle agglomeration and the difficulty in separation as well as recovery of catalyst limit the application of this kind catalysts [6].

Graphene oxide (GO) with a two-dimensional layer structure is known as an excellent candidate to form reduced graphene oxide (rGO)/semiconductor photocatalyst, which has excellent electron-transport characteristics, chemical stability and high specific surface area. Many previous researches suggested that the ZnO/rGO nanocomposites with different morphologies of ZnO, including flower-like [7], sheet-like [8, 9], nanorod-flower [10], nanoparticles [6], nanorods [11] and arrays [12], could enhance photocatalytic performance. Han *et al.* [10] described an oriented hierarchical nanorod-flower ZnO with high exposing proportion of (001) active faces for the purpose to enhance photocatalytic activity. Even though nano-sized ZnO with high surface area can perform a higher photocatalytic activity, agglomeration and difficult recovery from the photocatalytic system are two critical issues, which restrict its practical application. Fu *et al.* [7] tried to design a micro-sized ZnO to improve the agglomeration of the ZnO. However, the micro-sized ZnO with a high surface area still exhibited a little mount of agglomeration. Therefore, we considered ZnO array as an ideal component with good dispersion in the composite photocatalysts. Until now, rare research has described the ZnO arrays-based rGO composite substrate and further investigated its photocatalytic performance. The bifunctional ZnO–rGO–Au substrate was developed by Wen *et al.* [12], in which the GO was reduced to rGO after UV irradiation. Recently, ZnO with other interesting morphologies of star, rod and hassock is also fabricated in our group and intends to compare the photocatalytic activities with the ZnO arrays after combination with rGO.

Herein, ZnO nanorod array/reduced graphene oxide (ZnO array/rGO) composite substrate was designed and fabricated via the combination of seed layers-growth and aqueous solution reaction for the formation of ZnO arrays, which was further combined with rGO using a simple water bath method. GO was reduced to rGO under gentle solution conditions. The microstructure and the effects of the rGO fraction on the photocatalytic degradation of methylene blue (MB) under UV radiation were investigated.

2. Experimental section: The synthesis and testing process includes four steps as illustrated in Fig. 1. Concretely, 25 ml of zinc acetate (0.02 mol/l) ethanol solution was stirred for 30 min at 58°C. 25 ml of sodium hydroxide (0.03 mol/l) ethanol solution was stirred for 30 min at room temperature and then added into the above solution with vigorous agitation for another 2 h to obtain the seeds solution. The seeding process was carried out by spinning coatings onto the glass substrate with seeds solution at 3000 rpm for 20 s. (Square pieces of 2.5 cm × 2.5 cm was used and cleaned by acetone, ethanol and deionised water, respectively) The seeded glass was then dried at 80°C for 5 min. This operation was repeated six times. The final glass was annealed at 400°C for 1 h. The seeded glass was diagonally put into the mixture of the aqueous solution of zinc nitrate (0.05 mol/l) and methenamine (0.05 mol/l) (v/v = 4:1) at 80°C for 24 h. Subsequently, the glass was washed by deionised water and dried in air. The above glasses were immersed into 0.25, 0.5 and 1.0 mg/ml GO aqueous solutions at 80°C for 30 min to obtain ZnO array/rGO composites (GO was purchased from Chengdu Organic Chemistry Co., Ltd.). In the process, the deoxygenation/dehydration reaction of GO may occur, resulting in the reduction of the GO to rGO [13].

The degradation of MB solution under UV light irradiation (with the wavelength of 200–400 nm) was used to evaluate the photocatalytic activities of ZnO array/rGO composites. Typically, the glass substrate was immersed into 60 ml of 10 mg/l concentration MB

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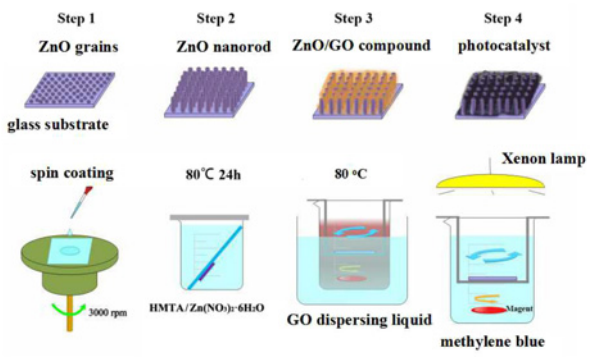


Fig. 1 *Scheme of the growth of ZnO array/rGO composites*

solution with stirring throughout the experiment. The dark adsorption/desorption time was set for 20 min. A 300 W Xenon arc lamp (CEL-HXF 300) was used as the light source and irradiated directly on the MB solution at a distance of 10 cm. The adsorption rate was measured at several minute intervals. The MB solution was taken out and measured using a UV–vis spectrometer. For characterisation, field emission scanning electron microscope was performed with the NANO NOVA SEM450. X-ray diffraction was performed with an X-ray diffractometer (XD-3A). Ultraviolet-visible (UV–vis) absorption spectra were measured with a Shimadzu UV-2201 spectrophotometer.

3. Results and discussion: As shown in Fig. 2, ZnO nanorod arrays exhibit the prospective geometry with hexagonal columns

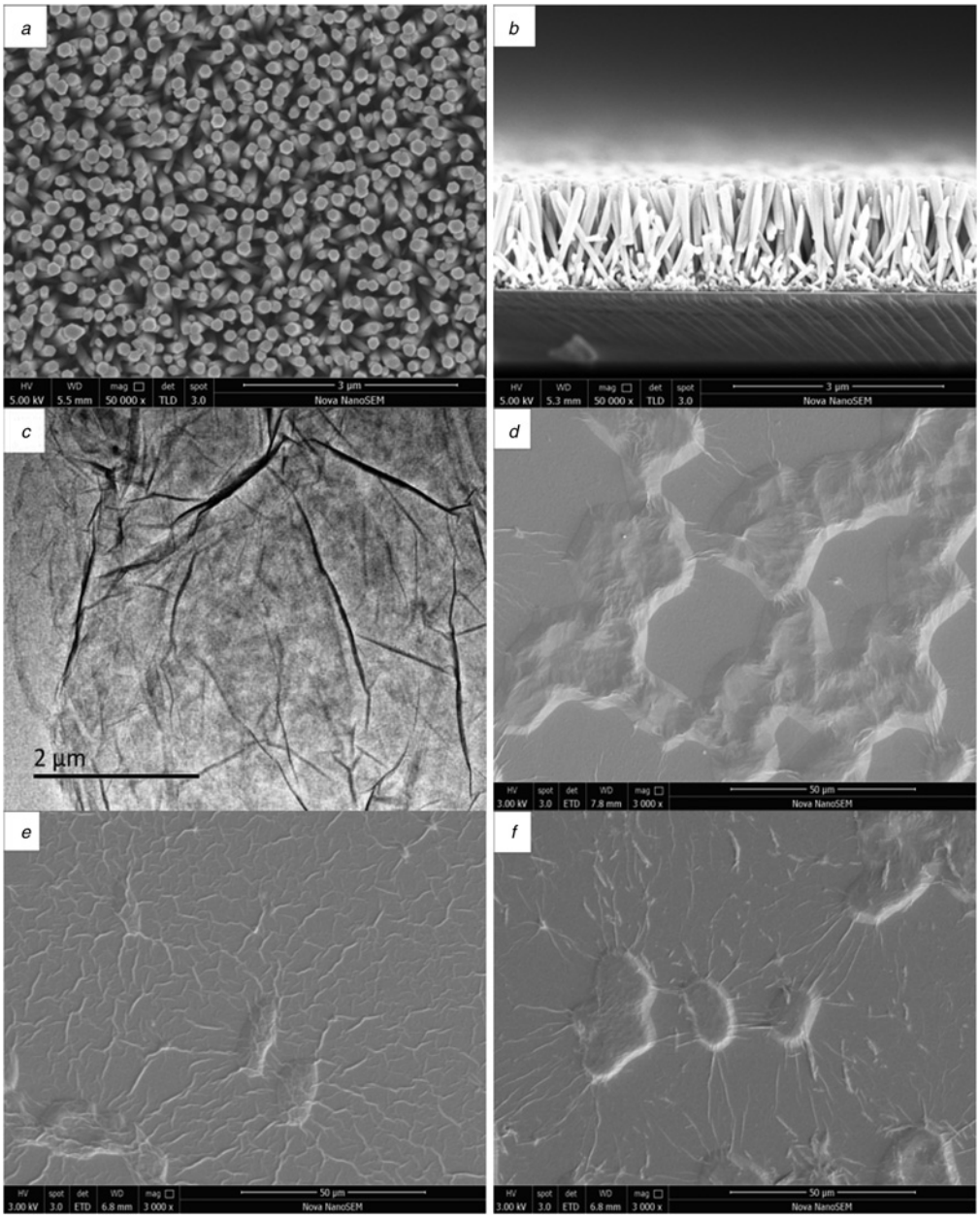


Fig. 2 *TEM and SEM images of the samples*
a ZnO nanorod arrays at a zinc nitrate concentration of 0.05 mol/l
b Cross-section of ZnO nanorod arrays
c GO
ZnO array/rGO composites with GO of
d 0.25 mg/ml
e 0.5 mg/ml
f 1.0 mg/ml

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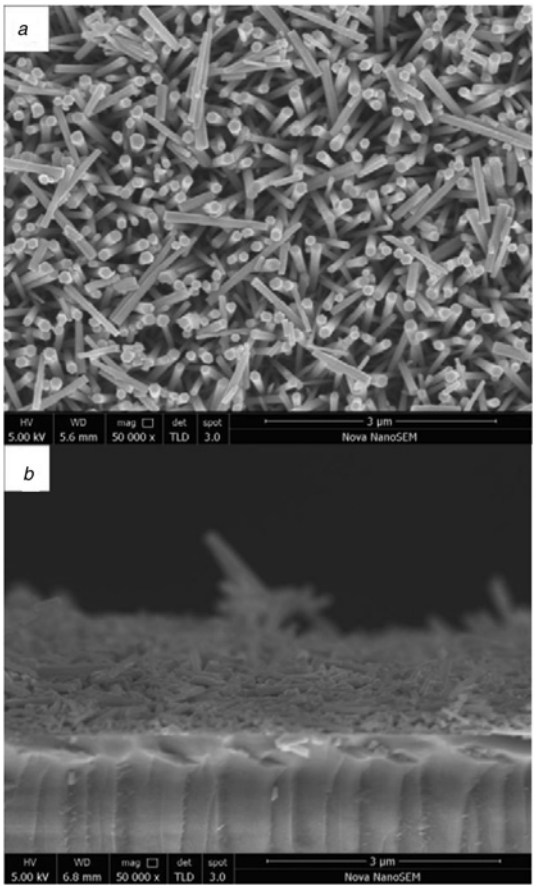


Fig. 3 *SEM images of the ZnO nanorod arrays*
a ZnO nanorod arrays at a zinc nitrate concentration of 0.025 mol/l
b Cross-section of ZnO nanorod arrays

(Fig. 2*a*) and good orientation to be perpendicular to the substrate (Fig. 2*b*) at a zinc nitrate concentration of 0.05 mol/l. For further modification of the ZnO arrays, crumpled GO nanosheets (Fig. 2*c*) were introduced for constructing the ZnO array/rGO composites. The as-prepared ZnO array/rGO composites at different GO concentrations are illustrated in Figs. 2*d–f*. It is obviously shown that the surface grain textures of the composites are quite different. At low GO concentrations (Fig. 2*d*), the composite coatings are relatively smooth except a few scattered humps located at the uneven ZnO arrays. The phenomenon also occurs in other samples with high GO concentrations, but the humps at low GO concentrations is the most outstanding owing to thin GO nanosheets. With the increase of GO concentrations (Figs. 2*e* and *f*), the lines of the coating become sharp and complex and the harsh surfaces of the coatings are subsequently revealed as a result of multilayer deposition of the GO on the ZnO arrays.

The relationship between the concentrations of zinc nitrate and the growth situation of the ZnO nanorod arrays has been investigated (Fig. 3). The results indicate that the perpendicular arrays are regularly generated, and both the size and the density of the arrays dramatically raise, with the increase of zinc nitrate concentration. At a low concentration of 0.025 mol/l, the ZnO nanorods of standing upright onto the substrate are rarely observed. It can be attributed to the ZnO nanorods with small diameter, which cannot support the successive growth of the nanorods.

Moreover, compared with the ZnO arrays, the ZnO array/rGO composites exhibit a better improvement of the UV light absorption with the red-shift of the absorption peak (Fig. 4*a*), probably in virtue of the interface interaction of the composites [13]. The enhancement of the light utilisation efficiency might be beneficial to the UV-light induced photocatalytic activity. Simultaneously, the

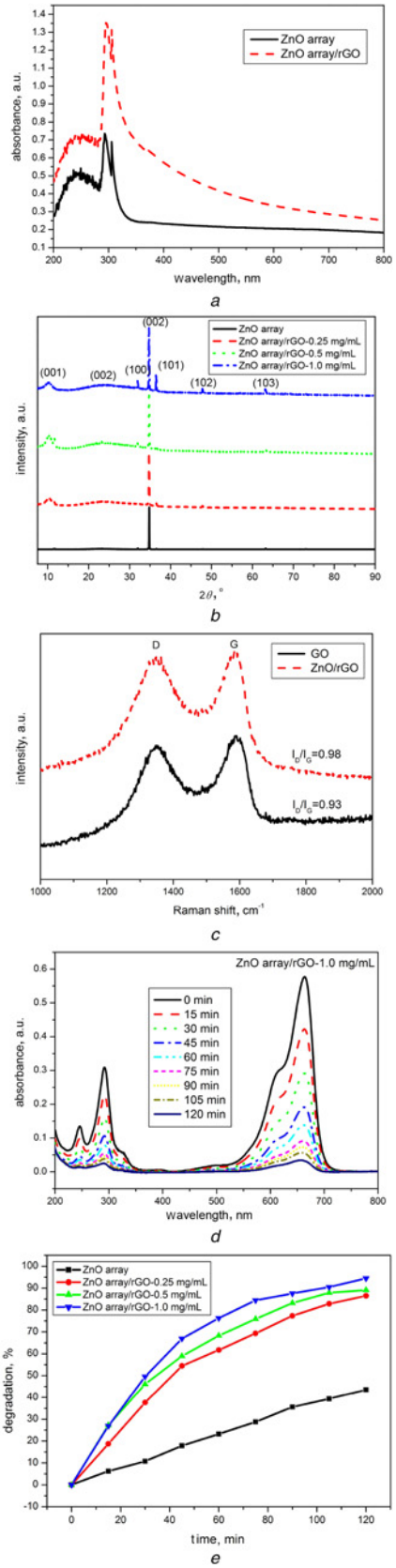


Fig. 4 *Optical, structural and photodegradation properties of the samples*
a UV–vis spectra of the samples
b XRD patterns of the samples
c Raman spectra of the samples
d Time-dependent absorption spectra of the MB solution in the presence of ZnO array/rGO composites with GO of 1.0 mg/ml
e Comparison of photocatalytic activities for the photocatalytic decolorisation of MB aqueous solution

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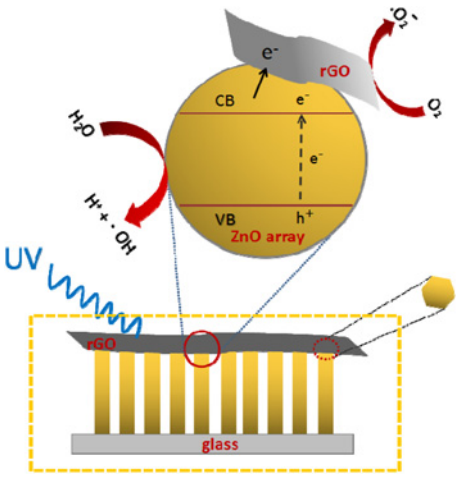


Fig. 5 *Mechanism representation of the ZnO array/rGO composites under UV light irradiation*

addition of the GO results in an enhanced absorption in visible-light ranges. Further information about the crystalline of the composites is provided by XRD (Fig. 4*b*). The typical diffraction peak at $2\theta = 34.4°$ appears, which can be indexed as (002) diffraction of ZnO. After GO addition with fixed reaction temperature, a broad diffraction peak at near 24° and a weak characteristic peak at 11° are observed and corresponded to the (002) and (001) diffraction of rGO, respectively, indicating the introduction of the GO and partial GO reduction with the weak characteristic peak at 11°.

The Raman spectra of the samples are presented in Fig. 4*c*. The GO exhibits two main bands at about 1352 cm^{-1} (D band) and 1589 cm^{-1} (G band). When the GO was compounded with ZnO and reduced to rGO, the D band and G band shifted to about 1349 and 1584 cm^{-1}, respectively. Moreover, the intensity ratio of the D to G band (I_D/I_G) is a response to the disorder/defects in graphene. It is clear that the I_D/I_G ratio of the GO is 0.93. The data increases to 0.98 in the ZnO array/rGO composites. It can be concluded that both the band shift and the increase of the I_D/I_G intensity [7, 13] indicate the reduction of the GO to rGO in the composites.

In order to evaluate the photocatalytic activity of the ZnO array/rGO composites, the representative time-dependent absorption spectrum of the MB solution were analysed, as shown in Fig. 4*d*. The MB is almost degraded in 2 h in the presence of ZnO array/rGO composites with 1.0 mg/ml GO. With comparison as presented in Fig. 4*e*, the degradation rates of MB achieves about 40, 80, 85 and 90% with the increase of GO concentrations from 0.25 to 1.0 mg/ml. These results indicate that high GO concentration could enhance the degradation activity of ZnO arrays.

Fig. 5 demonstrates a potential mechanism to explain the enhanced photocatalytic performance by ZnO nanorod arrays and rGO. When the UV light is incident on the surface of the composites, due to almost non-absorption of GO in ultraviolet range [12], the light can pass through the rGO and reach ZnO arrays to excite the photo-electron from the valence band to the conduction band of ZnO, remaining a hold in the valence band of ZnO. The photo-electron dynamically transfers to the rGO nanosheets on account of potential difference between ZnO and rGO [14], and therefore results in the decreased recombination rate of photo-generated electron-hole pairs. Further, the electrons in rGO reduce the dissolved oxygen molecule into reactive oxygen species. The superoxide radicals and the generated holes formed in ZnO arrays are the combined effect of the photo-degradation on the composites.

4. Conclusion: A ZnO nanorod array/reduced graphene oxide (ZnO array/rGO) composite substrate was designed via the fabrication of the ZnO arrays by the combination of the seed layers-growth and aqueous solution reaction, which was further combined with rGO using a simple water bath method. The composites exhibited enhanced photocatalytic activities on MB degradation under UV radiation. The interactions of the composites between ZnO naonorods and rGO sheets demonstrated the synergistic effects, preventing the electron-hole pair recombination, and improving enhanced photocatalytic performance of the composites. The fraction of GO in the composites was shown to be a key factor on the photocatalytic performance. The ZnO array/rGO composites could be regarded as a promising photocatalyst for environmental application.

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