

# Fabrication and Photocatalytic Properties of a Visible-light Responsive Nanohybrid Based on Self-assembling of Carboxyl Graphene and ZnAl Layered Double Hydroxides

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## Supporting Information

### Experiment details:

#### Preparation of exfoliated ZnAl-LDH nanosheets.

The precursor of ZnAl-layered double hydroxides (LDH) crystals in the nitrate form was prepared by the method of hexamethylenetetramine (HMT) hydrolysis.<sup>1</sup> Chemicals such as  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.06 mol),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.02 mol),  $\text{NaNO}_3$  (0.01 mol) and HMT (0.125 mol) were mixed together and dissolved into an aqueous solution of 250 cm<sup>3</sup> under vigorous stirring. The resulting suspension was stirred for 48 h at refluxing condition. The obtained LDH was recovered by filtration, washed with water, and dried at 50 °C in vacuum for 24 h.

The colloidal solution of exfoliated LDHs was achieved by vigorously stirring of LDH power (1.0 g/L) in the formamide for 7 days, and this reaction was under Ar atmosphere to avoid CO<sub>2</sub> contamination. The unexfoliated LDHs were removed by centrifugation at 3000 rpm. Then, a transparent colloidal solution was obtained, which can induce a clean Tyndall effect.

#### Preparation of carboxyl graphene colloidal solution

Graphene oxides (GO) was obtained by the oxidation of graphite powder using an improved Hummer's method.<sup>2</sup> 400 mL 9:1 mixture of concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  was added to a mixture of graphite flakes (3.0 g, 1 wt equiv). With stirring and cooling in an ice bath,  $\text{KMnO}_4$  (18.0 g, 6 wt equiv) was slowly added into the reaction mixture, producing a slight exotherm to 35 ~ 40 °C. The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (400 mL) containing 30%  $\text{H}_2\text{O}_2$  (3 mL). The solution was then filtered through a metal sieve (300 μm). The filtrate was centrifuged (8,000 rpm for 2 h), and the supernatant was decanted off. The remaining material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, 200 mL of ethanol, and water again until solution pH

reached 5.0 ~ 6.0. The resulting suspension was filtered with a 0.45  $\mu\text{m}$  membrane and then lyophilized to produce a fluffy GO powder. The obtained GO powder was dried at 50  $^{\circ}\text{C}$  in vacuum for 24 h.

The carboxyl graphene (CG) was synthesized from the obtained GO powder with chloroacetic acid under strongly basic conditions.<sup>3</sup> 0.5 g GO powder was dispersed in aqueous solution (2 mg/mL), and then bath sonicated for 1 h to give a clear solution. NaOH (1.2 g) and chloroacetic acid ( $\text{Cl-CH}_2\text{-COOH}$ ) (1.0 g) were added to the GO suspension and bath sonicated for 12 h to convert the OH groups to COOH via conjugation of acetic acid moieties giving GO-COOH. The resulting CG dispersion was washed, filtrated and dried at 50  $^{\circ}\text{C}$  in vacuum for 24 h. Then, a brown exfoliated solution was obtained by vigorously stirring of CG powder (0.5 g/L) for 24 h in the formamide under Ar atmosphere, and ultrasound treatment for 4 h. The obtained exfoliated also had a clean Tyndall light scattering.

#### **Preparation of CG/LDHs nanohybrid**

The colloidal solution of exfoliated LDH nanosheets was added dropwise into the CG solution with vigorously stirring under Ar atmosphere. Then, chocolate flocculent was obtained. The solid products were then centrifuged at 6000 rpm, washed with formamide and ethanol, and then vacuum dried at 60  $^{\circ}\text{C}$ . The final product used as photocatalyst was obtained by vacuum calcination of CG/LDHs nanohybrid at 700  $^{\circ}\text{C}$  for 1 h, labeled as rCG/LDO (rCG/layered double oxides) nanohybrid.

#### **Photocatalytic test**

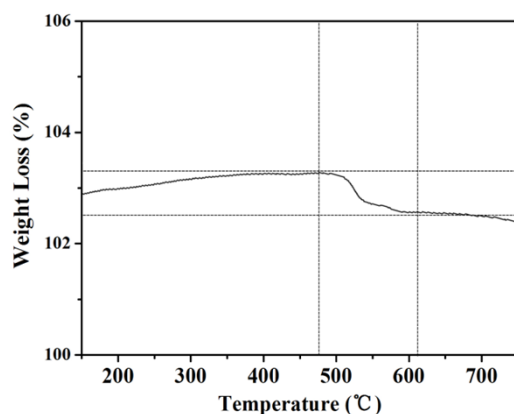
A 300 W Xe arc lamp (PLS-SXE) equipped with a cutoff filter ( $\lambda=420$  nm) was applied as visible light source, and the annular quartz reactor was thermostated at 25  $^{\circ}\text{C}$  by a circulating water jacket. The photocatalyst (50 mg) was suspended in 100 mL aqueous solution of 10  $\text{mg L}^{-1}$  methylene blue (MB) or 20  $\text{mg L}^{-1}$  Orange G (OG). The solution was stirred in dark for 30 min to establish an adsorption–desorption equilibrium. During the irradiation, samples were taken from the solutions at certain time intervals and

analyzed with a Shimadzu UV-2450 spectrophotometer.

## **Characterization**

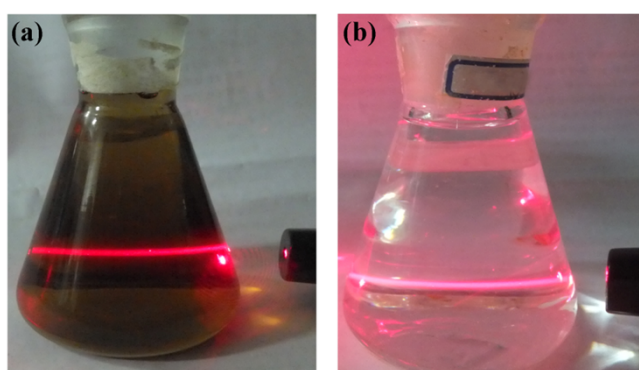
Thermogravimetric analysis (TGA) of the obtained product was carried out with a Mettler Toledo thermal analyzer to determine the percentage of graphene in the synthesized material. Five mg sample was first stabilized at 100 °C in air for 30 min and then heated from 100 °C to 750 °C at 5 °C min<sup>-1</sup> in 50 mL min<sup>-1</sup> of air. X-ray diffraction (XRD) patterns were measured with a Rigaku D/MAX-III A X-ray diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The microstructure of samples' external surface was observed by a field emission scanning electron microscope (SEM) (Hitachi, S-4700) with voltage of 20 kV and current of 10  $\mu$ A. SEM samples were prepared by drop-drying the samples from their aqueous suspensions onto silicon substrates. High resolution transmission electron microscopy (HRTEM) observations were carried out on a JEOL JEM-3010 electron microscope with an accelerating voltage of 200 kV. HRTEM samples were prepared by drop-drying the samples from their diluted aqueous suspensions onto copper grids. Atomic force microscopy (AFM) images were recorded on a Cypher S atomic force microscope (Asylum Research, Oxford Instruments) and AFM support substrate is clean exfoliated mica plate. The carboxyl graphene nanosheets suspension was conducted ultrasonic treatment for 4 h, and then dripped onto the mica surface. The substrate was washed briefly with D.I. water, blow-dried with air, and imaged by tapping mode AFM.

## Figures



**Fig. S1 TGA curve of rCG/LDO nanohybrid.**

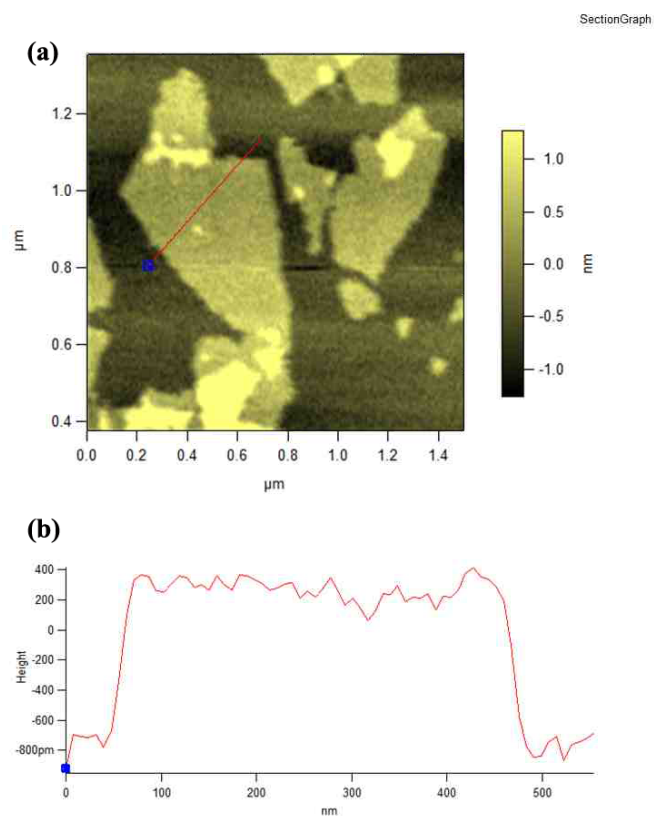
TGA was conducted to measure the percentage of rCG in the nanohybrid. No large mass loss was observed resulting from that rCG/LDO nanohybrid was obtained after high vacuum calcination at 700 °C. The slight increase of mass probably resulted from that the sample adsorbed moisture in the flowing air or baseline drift, and a similar phenomenon was observed for graphene/Ta<sub>2</sub>O<sub>5</sub> sample.<sup>4</sup> Rapid weight loss of 0.7% from rCG combustion in rCG/LDO nanohybrid occurred at temperatures ranging from 480 to 620 °C. Therefore, the ratio of rCG/LDO is approximately 0.7 wt%.



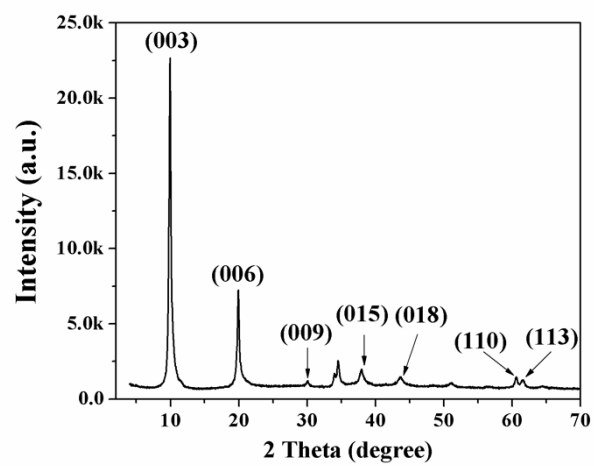
**Fig. S2** Photograph of the formamide solution of CG (a) and photograph of exfoliated LDHs nanosheets dispersed in formamide solution (b).

The obtained colloidal suspensions were very stable, and no sediment was observed upon long-term

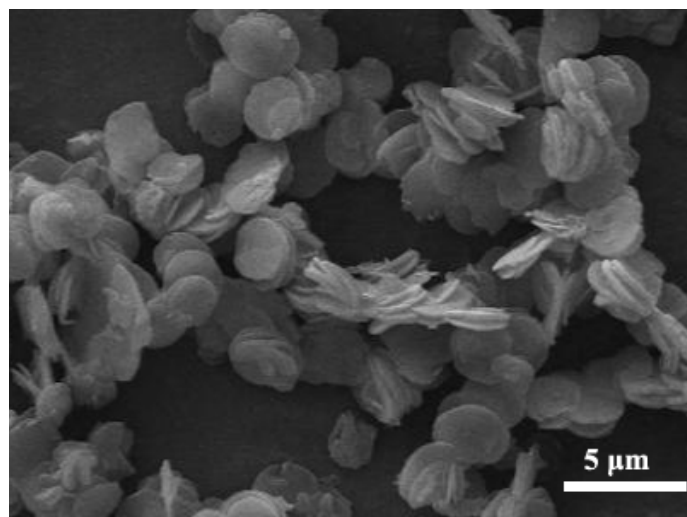
standing.



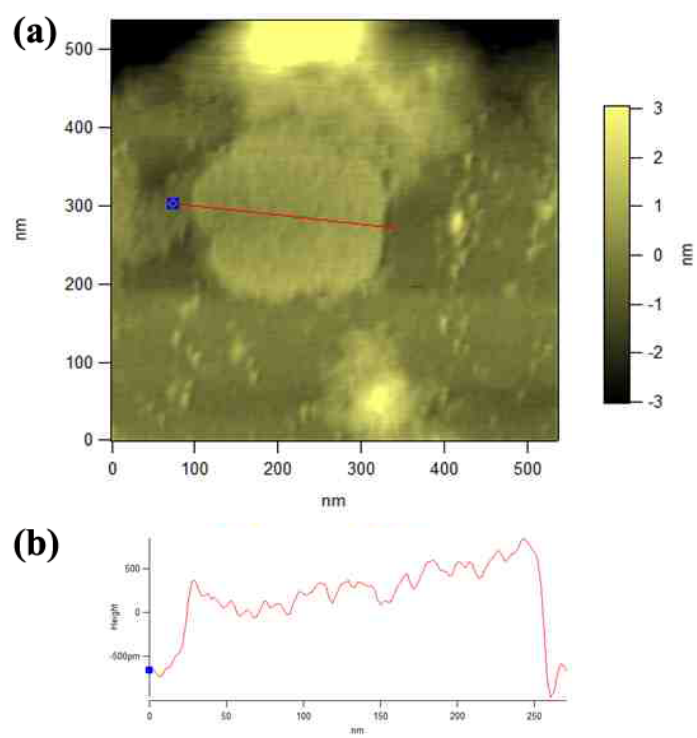
**Fig. S3** Tapping-mode AFM image of CG nanosheets (a) and their corresponding height profile (b).



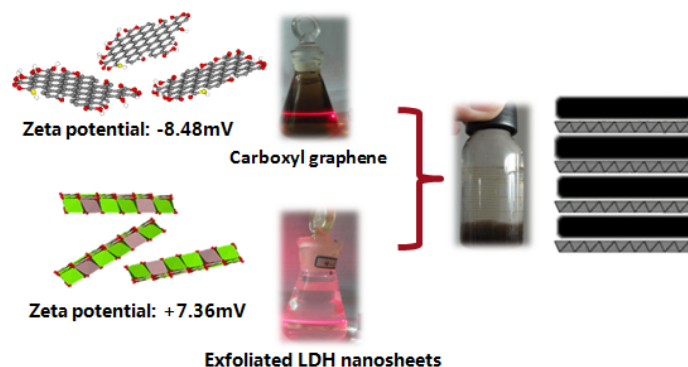
**Fig. S4** XRD pattern of pristine ZnAl-LDHs.



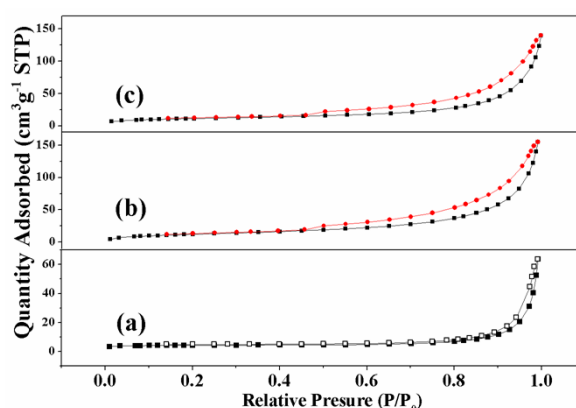
**Fig. S5** SEM image of pristine ZnAl-LDHs.



**Fig. S6** Tapping-mode AFM image of exfoliated LDH nanosheets (a) and their corresponding height profile (b).



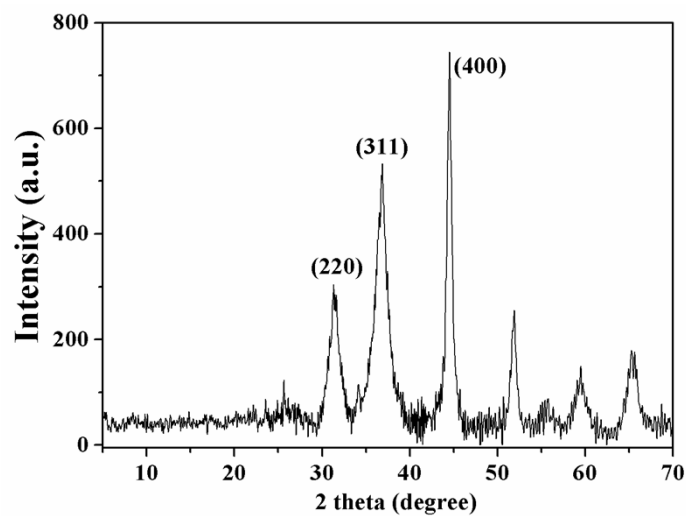
**Fig. S7** Schematic diagram of the process of electrostatical self-assembly between the negatively charged CG monolayer and the positively charged ZnAl-LDH nanosheets.



**Fig. S8** Nitrogen adsorption-desorption isotherms of samples: (a) ZnAl-LDH, (b) CG/LDH nanohybrid and (c) rCG/LDO nanohybrid.

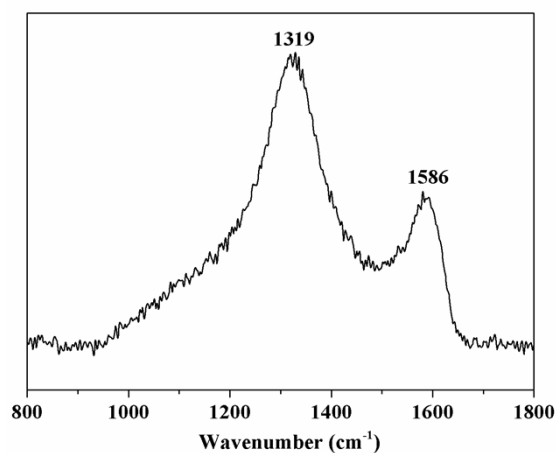
The pristine ZnAl-LDH presents a relatively weak adsorption of  $N_2$  with no distinct hysteresis loop, which can be classified into typical III adsorption-desorption isotherm. So ZnAl-LDH should not be porous materials. Both of nanohybrids (CG/LDH and rCG/LDO) show hysteresis loops at  $P/P_0 > 0.45$  and negligible  $N_2$  adsorption at  $P/P_0 < 0.40$ , indicating that most porosity arises from mesopores formed by the house-of-cards type stacking structure.<sup>5</sup> According to the IUPAC classification, the samples can be classified as Brunauer-Deming-Deaming-Teller (BDDT), typical IV adsorption-desorption isotherm, which is characteristic of mesoporous materials with three-dimensional interconnected pore geometry and a high energy of adsorption.





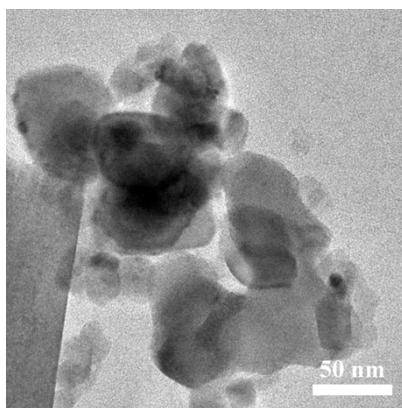
**Fig. S9** XRD pattern of rCG/LDO nanohybrid.

Upon vacuum calcining CG/LDH nanohybrid in a tube furnace at 700°C for 1 h, the XRD patterns (Fig. S9) indicated that the structure of CG/LDH nanohybrid has been destroyed and are consistent with previous studies of the thermal decomposition of LDHs,<sup>6</sup> which have shown that zinc oxide phases are formed by a topotactic transformation of the close-packed oxygen layers.<sup>7</sup> In the XRD patterns of the calcined CG/LDH nanohybrid, the peaks marked (220), (311) and (400) correspond to the characteristic reflections of a gahnite-like phase.



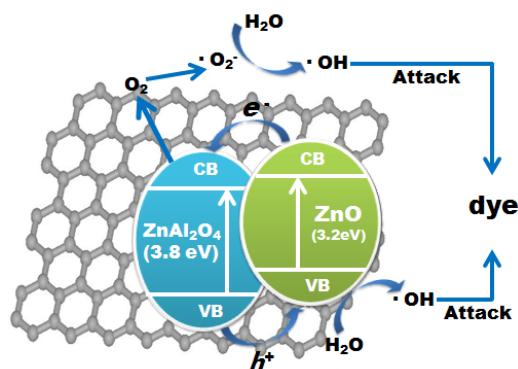
**Fig. S10** Raman spectra of rCG/LDO nanohybrid.

CG was used as a precursor to synthesize the nanohybrid, and would be converted into graphene after high vacuum calcination at 700°C for 1 h, which can be confirmed by the G band of the Raman spectra. The final product was obtained by high vacuum calcination of CG/LDHs nanohybrid at 700°C for 1 h. In order to investigate the C sp<sup>2</sup> of the calcined product, Raman spectra of CG/LDO was determined, as shown in Fig. S10. Compared with CG/LDH (without calcination), the D/G intensity ratio of rCG/LDO is larger, suggesting a decrease in the average size of the sp<sup>2</sup> domains upon reduction of the CG. As reported in the hybrid composite CG/LDH (Fig. 3) exhibits the characteristics G and D bands at 1328 and 1597 cm<sup>-1</sup>, respectively. Calcination caused the expected blue shift of the G band to 1586 cm<sup>-1</sup> corresponding to the conversion of CG into graphene.<sup>8, 9</sup> After high vacuum calcination, CG would transform into graphene: graphene-COOH → graphene + CO<sub>2</sub>.



**Fig. S11** TEM image of rCG/LDO nanohybrid.

The TEM image of rCG/LDO nanohybrid showed that the CG/LDH nanohybrid after vacuum calcination were in the form of translucent plate-like flakes, with an average diameter close to 50-90 nm.



**Fig. S12** Schematic representation of the photocatalytic degradation of dye in presence of rCG/LDO nanohybrid under visible light.

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