Supporting Information

Controlled Growth of $LaFeO_3$ Nanoparticles on Reduced Graphene Oxide for Highly Efficient Photocatalysis

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Experimental Section:

Materials. Iron (III) nitrate hydrate ($Fe(NO_3)_3·9H_2O$, ≥98.5%), lanthanum nitrate hydrate($La(NO_3)_3·6H_2O$), and citrate acid hydrate($C_6H_8O_7·H_2O$) were purchased from Sinopharm Chemical Reagent Corp. Graphite powder (< 20μm), TiO_2 nanopowder, MB and RhB were purchased from Aldrich. All chemicals were analytical grade and used as received. Deionized water was used in all experiments.

Synthesis of rGO. GO was synthesized based on a modified Hummers' method[1]. Typically, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (30:3.3 mL) was added to a mixture of graphite powder (0.25 g, 1 wt equiv) and $KMnO_4$ (1.5 g, 6 wt equiv). The suspension was then stirred magnetically and heated at 50 °C for 12 h before it is cooled to room temperature. The reaction mixture was poured onto ice with 30% H_2O_2 (2.5 mL) and was then centrifuged (4000 rpm for 5 min) to decant the supernatant. The remaining solid material was washed with 110 mL of 30% HCl, and 200 mL of water three times until the pH of the solution was stabilized at 6-7 (for each wash, the mixture was centrifuged (5000 rpm for 5 min) to decant the supernatant). The solid material was suspended in water and dialyzed for 48 h. After water removal (via centrifugation), the solid was further suspended in 200 ml of ethanol and was subject to ultra-sonication for 3 h. The undispersed solid precipitate was separated from the solution by centrifugation (1000 rpm for 5 min). The GO dispersion (25.0 mL, 0.05 wt %) was mixed with 25 mL of water, 11 μL of hydrazine solution (80 wt %), and 175 μL of ammonia solution (28 wt %) in a glass vial. After vigorously shaken for a few minutes, the vial was put in a water bath (95 °C) for 1 h.

Synthesis of $LaFeO_3$-rGO. 0.1 g of $Fe(NO_3)_3·9H_2O$, 0.1 g of $La(NO_3)_3·6H_2O$, 0.25 g of $C_6H_8O_7·H_2O$ were dissolved in 2 mL H_2O by 10 min ultrasonication. 120 mg of GO was added to the above solution, which was subject to further ultrasonication for 60 min. The solvent was evaporated at 80 °C, and the powder was calcinated at a designated temperature between 300 °C and 900 °C under an Ar flow (30 s.c.c.m.) for 15 h to obtain $LaFeO_3$ NPs on rGO. Pure $LaFeO_3$ NPs and $LaFeO_3$ NPs on porous C ($LaFeO_3$-C) were synthesized by the same process.

Characterization. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 microscope (Japan) operating at 10 kV. Energy-dispersive X-ray (EDX) analysis was performed on a Hitachi S-4800 EDX instrument. Transmission electron microscopy (TEM) images were acquired on a Tecnai G^2 20 ST microscope operated at 200 kV. The TEM samples were prepared by dropping ethanol dispersion of the NPs onto the holey carbon coated Cu grids and by ethanol evaporation. The X-ray diffraction (XRD) patterns were recorded on a Bruke D2 diffractometer with monochromatized Cu Kα (30 kV, 10 mA). Metal components of NPs were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a IRIS Intrepid II XDL. Fourier transformed infrared (FTIR) spectra were scanned on an Excalibur 3100 FTIR spectrometer with powder-pressed KBr pellets. Raman spectra were obtained from a Via-Reflex Raman spectrometer using the 532 nm Ar ion laser as excitation source (the sample was deposited on a glass wafer). Nitrogen sorption isotherms were measured at 77 K using a Micromeritics Quadrasorb SI-MP analyzer (USA). Before measurements, the samples were degassed under vacuum at 180 °C. The Brunauer−Emmett−Teller (BET) method was used to calculate the specific surface areas of the powder. The pore size distributions were obtained from the isotherms using the Barrett−Joyner−Halenda (BJH) model. The UV-vis absorption spectra were measured at room temperature on the U-4100 spectrophotometer (Hitachi, Japan).

Measurements of photo-catalytic activity. The photo-catalytic activities of the $LaFeO_3$ NP catalysts were analyzed by photocatalytic degradation of MB and RhB under.visible light. Typically, 10 mg of $LaFeO_3$-rGO were added into 100 mL of MB aqueous solution (0.5 mg/L) and RhB aqueous solution (1.25 mg/L) respectively. Before illumination, the suspension was stirred in the dark for 2 h. Then the dispersion was irradiated by a 300 W xenon arc lamp with a UV-cutoff filter (≥400 nm). At regular irradiation intervals of 10 min, the dispersion was sampled (4 mL), centrifuged, and the concentration of MB or RhB was determined by the characteristic UV-vis absorption at 664 nm (MB) or 553 nm (RhB).

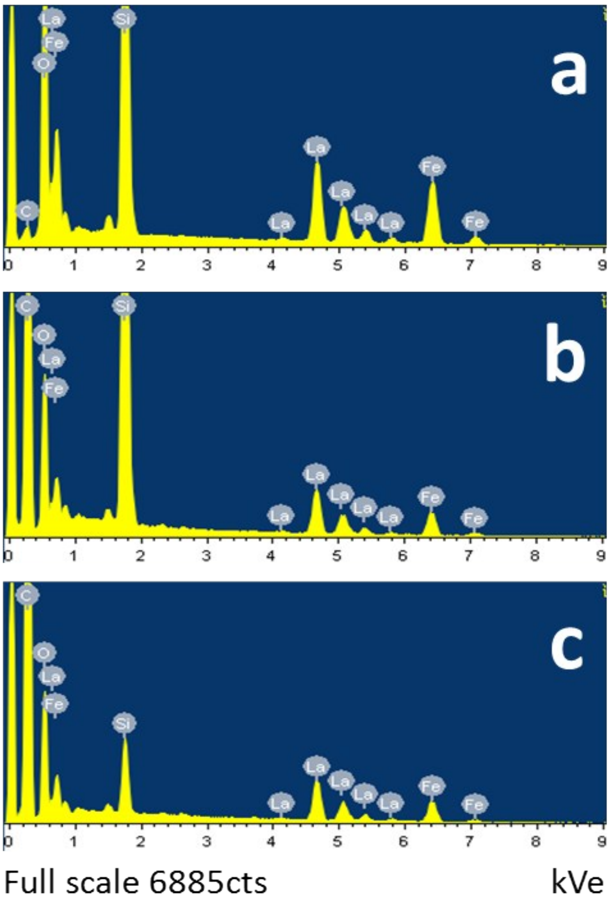

Figure S1. EDX of (a) pure $LaFeO_3$, (b) $LaFeO_3$-C, and (c) $LaFeO_3$-rGO NPs.

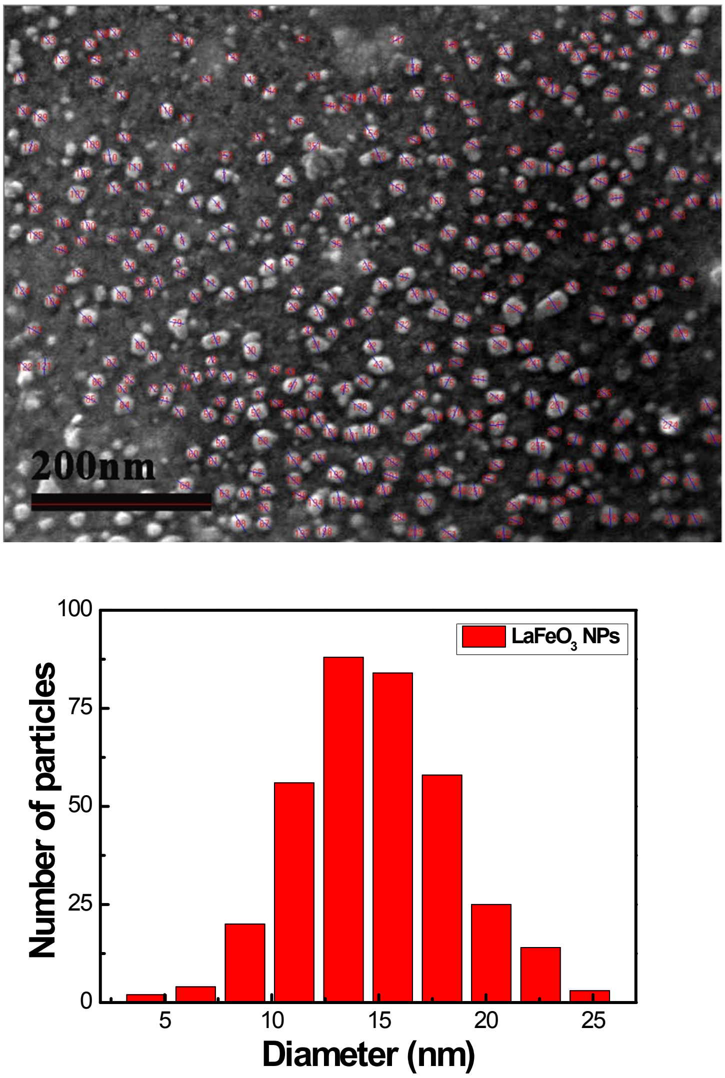

Figure S2. Statistical analysis of $LaFeO_3$-rGO NPs within the selected rectangular area and the particle size distribution histogram showing that the average diameter of the NP s is ~15 nm.

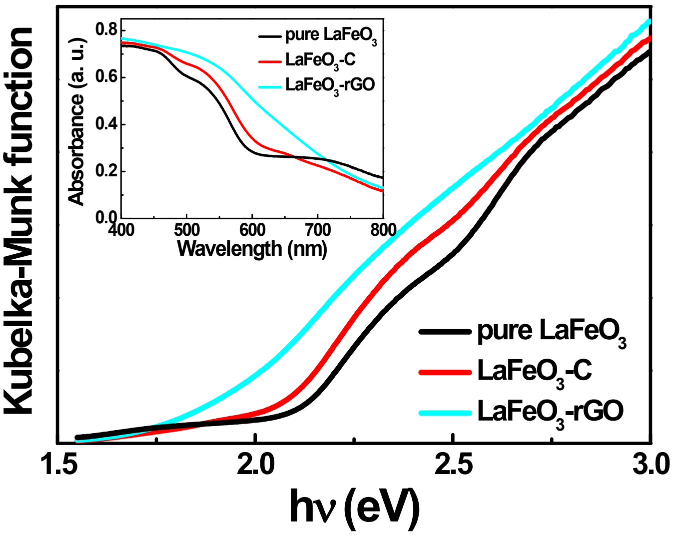

Figure S3. Estimated bandgap of the pure $LaFeO_3$, $LaFeO_3$-C, and $LaFeO_3$-rGO NPs by Kubelka-Munk function. The inset is UV–vis absorption spectra of the pure $LaFeO_3$, $LaFeO_3$-C and $LaFeO_3$-rGO NPs.

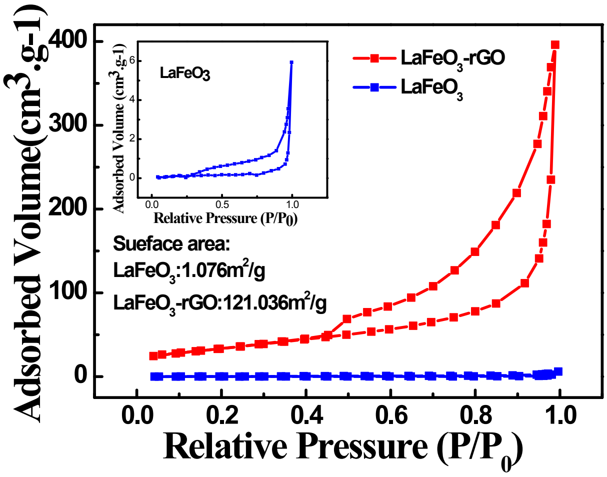

Figure S4. Nitrogen adsorption-desorption isotherms of pure $LaFeO_3$ and $LaFeO_3$-rGO NPs.

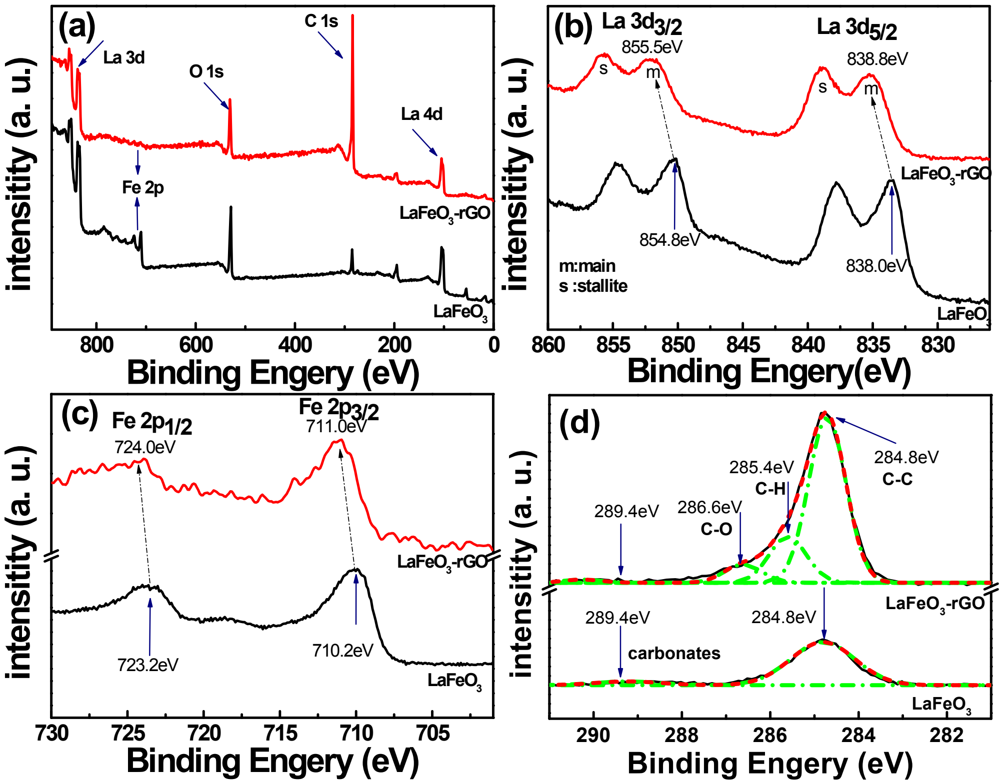

Fig. S5. X-ray photoelectron spectra (XPS) of the pure $LaFeO_3$ and $LaFeO_3$-rGO NPs: (a) the survey spectra and the spectra of (b) La 3d, (c) Fe 2p, and (d) C 1s.

Reference

1 D.C. Marcano, D.V. Kosynkin, J. M. Berlin, A. Sinitskii, Z.Z. Sun, A. Slesarev, L. B. Alemany, W.Lu, J.M. Tour. *ACS. Nano.* 2010, **4**, 4806.