Electronic Supplementary Material

TiO_2 Nanocrystals Grown on Graphene as Advanced Photocatalytic Hybrid Materials

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Synthesis of GO

GO was made by a modified Hummers' method (Refs. [15–18] in the main text). Expandable graphite (1 g, Graftech) was ground with NaCl (50 g) for 10 min. Afterwards, NaCl was washed away with water using vacuum filtration. The graphite was heated at 70 ℃ in an oven for 10 min to remove any remaining water. The dried solid was then combined with 23 mL of concentrated sulfuric acid in a 250 mL round bottom flask and stirred at room temperature for 24 h. Next, 500 mg of $NaNO_3$ was added to the suspension and allowed to dissolve for 5 min. The flask was then placed in an ice bath and 3000 mg of $KMnO_4$ was added while the temperature was kept below 20 ℃. The solution was then heated at 35–40 ℃ for 30 min. Afterwards, 3 mL of water was added to the flask. Another 3 mL of water was added 5 min later. After another 5 min, 40 mL of water was added. The suspension heated up during this time. After 15 min, 140 mL of water and 10 mL of 30% H_2O_2 were added to the flask to end the reaction. This suspension was stirred at room temperature for 5 min. The suspension was then repeatedly centrifuged and washed first with 5% HCl solution and then with water. The collected precipitate was mixed with 150 mL of water and bath sonicated for 20 min. After centrifuging at 5000 r/m for 5 min, a brown homogeneous supernatant was obtained.

Synthesis of graphene/TiO_2 hybrid

In a typical reaction, 3.5 mg of GO was dissolved in EtOH/water (70 mL/5 mL). The suspension was heated to 80 ℃ with stirring. Then a solution of $Ti(BuO)_4$ (0.18 mL) and H_2SO_4 (0.075 mL) in 5 mL of EtOH was injected in and the mixture was kept stirring at 80 ℃ for 12 h. The reaction mixture was then cooled down and the composite was collected by centrifugation and washed with water. In the second step of the synthesis, the washed composite was dispersed in water/DMF (25 mL/0.5 mL). The suspension was transferred to a 40 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 200 ℃ for 20 h. The final product was collected by centrifugation and washed with water. The mass of dried hybrid was 35 mg, composed of ~31.5 mg of TiO_2 and ~3.5 mg of GO (~10% of GO by mass in the hybrid). The mass of TiO_2 in the hybrid was determined by removing GO from the hybrid by calcination at 500 ℃ for 3 h. The mass of GO was obtained by comparing the mass of the GO/TiO_2 hybrid with the remaining mass of TiO_2 measured.

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Synthesis of free TiO_2 nanocrystals

In a typical reaction, a EtOH/water (70 mL/5 mL) mixed solvent was heated to 80 ℃ with stirring. Then a solution of $Ti(BuO)_4$ (0.18 mL) with H_2SO_4 (0.075 mL) in 5 mL of EtOH was injected in and the mixture was kept stirring at 80 ℃ for 12 h. The reaction was then cooled down and the solid was collected by centrifugation and washed with water. In the second step of the synthesis, the washed solid was dispersed in water/DMF (25 mL/0.5 mL). The suspension was transferred to a 40 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 200 ℃ for 20 h. The final product was collected by centrifugation and washed with water. The mass of the dried white powdery TiO_2 product was ~ 31 mg.

Synthesis of graphene/P25 mixture

In a typical reaction, 1.5 mg of GO was dissolved in EtOH/water (20 mL/10 mL). Then 13.5 mg of P25 (Degussa) was added to the solution, and the mixture was stirred at room temperature. After stirring for 2 h, the mixture was transferred to a 40 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 120 ℃ for 3 h. The final product was collected by centrifugation and washed with water. The mass of the dried mixture was about 15 mg, composed of ~13.5 mg of P25 and ~1.5 mg of GO (~10% of GO by mass in the hybrid).

Photocatalytic activity measurements

The photocatalytic activities of the graphene/TiO_2 hybrid, free TiO_2 synthesized in the same way in the absence of GO, P25 (Degussa) and the P25/GO mixture were compared by measuring the photodegradation of rhodamine B. In a typical measurement, the four samples each containing about 6.3 mg of TiO_2 were suspended in 100 mL portions of an 0.03 mmol/L aqueous solution of rhodamine B. The suspension was stirred in the dark for 2 h to allow for sufficient mixing with rhodamine B. Then the stirred suspension was illuminated with a 100 W high pressure mercury lamp (Carl Zeiss, HBO 100 W/2). The concentration change of rhodamine B was monitored by measuring the UV–vis absorption of the suspensions at regular intervals. The suspension was centrifuged at 10 000 r/m for 10 min to remove the TiO_2 or graphene/TiO_2 hybrid before UV–vis measurements. The peak absorbance of rhodamine B (at 553 nm) was used to determine its concentration. Photodegradation of methylene blue was conducted in the same way by using 50 mL portions of a 0.03 mmol/L aqueous solution of methylene blue.

Characterization

Scanning electron microscopy (SEM) was carried out using an FEI XL 30 Sirion microscope. Transmission electron microscopy (TEM) was carried out using an FEI Tecnai G2 F20 transmission electron microscope. Atomic force microscopy (AFM) images were taken on a Veeco MultiMode NanoScope instrument. X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert instrument. Surface area of the samples was measured by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherms at 77 K with a Micromeritics ASAP 2020 instrument.

Sample preparation for AFM, SEM, TEM, and XRD

AFM samples were prepared by soaking a silicon substrate in a GO suspension. SEM samples were prepared by drop-drying the samples from their aqueous suspensions onto silicon substrates. TEM samples were prepared by drop-drying the samples from their diluted aqueous suspensions onto copper grids coated with holey carbon. XRD samples were prepared by drop-drying the samples from their aqueous suspensions onto glass substrates.

Supplementary Figures

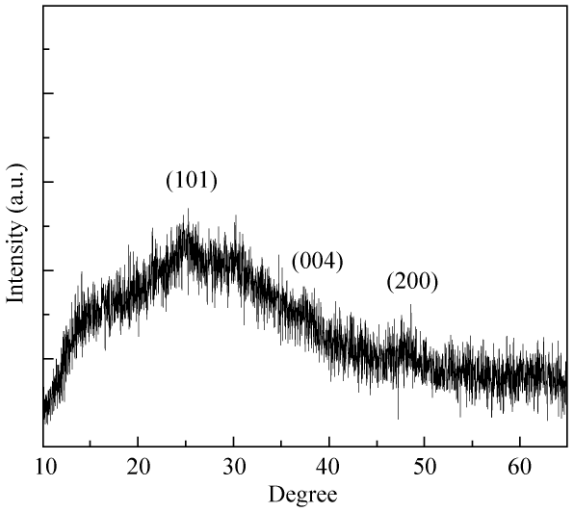

Figure S-1 XRD pattern of the TiO_2/GO hybrid after the first synthesis step at 80 ˚C. The product showed very low crystallinity, but weak signals can be seen corresponding to the anatase TiO_2 phase

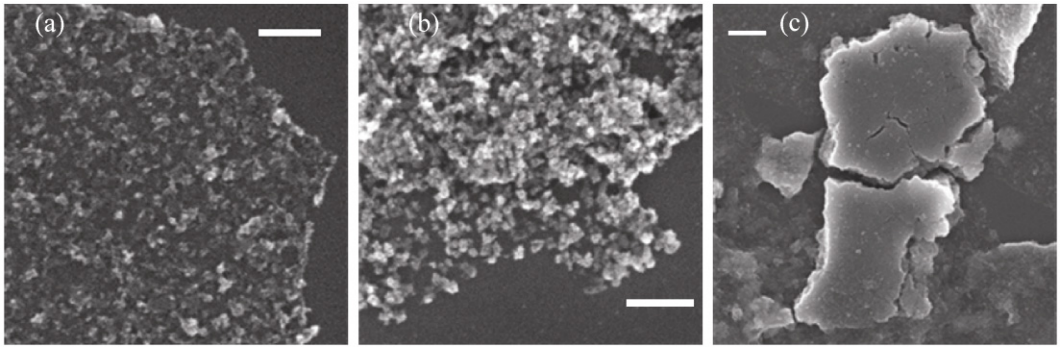

Figure S-2 SEM images of the products of the first step in the preparation of TiO_2/GO hybrids using different EtOH/water ratios of (a) 15:1, (b) 3:1, (c) 0:1 (by volume). The scale bars are 100 nm for (a) and (b), and 400 nm for (c). When the relative amount of water was increased, the size of the TiO_2 coated particles on the GO sheets became larger and some TiO_2 particles did not tightly bind to the graphene sheets. When water alone was used as solvent (c), although there were some TiO_2 particles coated on GO, large aggregates of free TiO_2 particles grown in solution were observed

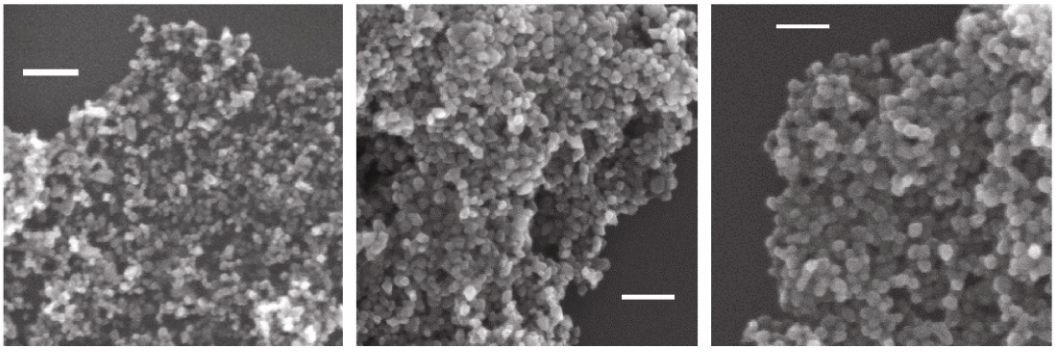

Figure S-3 SEM images of TiO_2/GO hybrids prepared by using different EtOH/water ratios in the first step: from left to right: 15/1, 10/1, 3/1 (by volume ratio). The scale bars are 100 nm. The average size of the TiO_2 nanocrystals depended on the EtOH/water ratio in the first reaction step, increasing from ~15 nm in EtOH/water (15/1) to ~30 nm in EtOH/water (3/1)

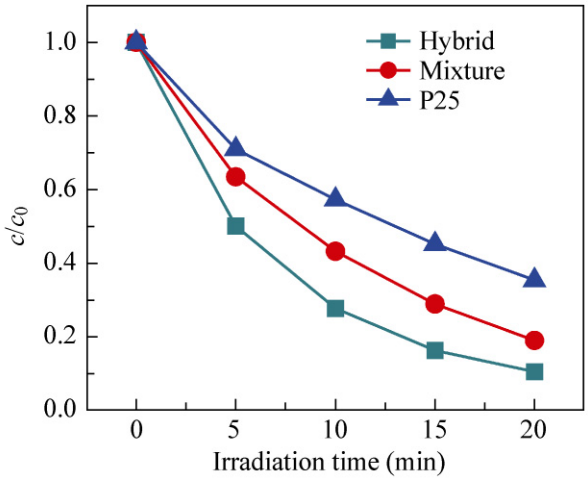

Figure S-4 Photocatalytic degradation of methylene blue monitored as plots of normalized concentration change versus irradiation time in the presence of P25, TiO_2/GO hybrid and GO/P25 mixture

Supplementary Table

Table S-1 BET surface areas of free TiO_2, P25 and different graphene/TiO_2 nanocrystal hybrids

Sample	P25	Free TiO_2	Hybrid from EtOH/water = 15/1	Hybrid from EtOH/water = 10/1	Hybrid from EtOH/water = 3/1
Surface area (m^2/g)	58	121	190	180	145