

Electronic Supplementary Information

Graphene sheet anchored with high density TiO₂ nanocrystals and their application in quantum dot-sensitized solar cells

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Experimental details

Preparation of GO:

GO (graphene oxide) was prepared by a modified Hummer's method.^{1,2} In a typical procedure, 1 g graphite was added into a 250 mL conical flask containing 23 mL concentrated H₂SO₄ under stirring in ice bath. 3 g KMnO₄ was then added into the above mixture under stirring. After 30 min, the ice bath was removed and the dark green solution was stirred at 35°C for 1 h. Then, 46 mL distilled water was added to the reaction mixture and the flask was bathed in boiling water for another 30 min. Afterwards, 10 mL 30% H₂O₂ and 140 mL distilled water were added. The precipitation was centrifuged and washed repeatedly with 5% HCl and ethanol and finally dried in vacuum at 60°C.

Preparation of the reduced graphene oxide/TiO₂ heterostructures:

For the preparation of reduced graphene oxide wrapped with high density TiO₂ nanocrystals (RGT-H): 10 mg GO and 10 mg of hexadecyl trimethyl ammonium bromide (CTAB) were ultrasonically dispersed in 10 mL of N,N-dimethylformamide (DMF) and 30 mL of isopropanol to form a clear dispersion solution, then 1.0 mL tetrabutyl titanate (TBT) was added dropwise to the mixture with rigorous stirring. After a few minutes, the mixture was transferred into 50 mL Teflon-lined stainless steel reactor and heated at 180°C for 20 h. After cooled to room temperature, the gray precipitate was washed repeatedly with water and ethanol and dried at 40 °C. Finally, the samples were calcinated at 500°C for 2 h with a heating rate of 5°C min⁻¹ in N₂ atmosphere to obtain the final product.

For the preparation of reduced graphene oxide wrapped with low density TiO₂ nanoparticles (RGT-L): the product was synthesized *via* a similar process without using CTAB, while keeping the other conditions unchanged.

Preparation of the TiO₂ nanoparticles

0.5 mL, TBT was added dropwise to the mixture containing of 10 mL of DMF and 30 mL isopropanol with stirring. The mixture was transferred into 50 mL Teflon-lined stainless steel reactor and heated at 180 °C for 20 h. the final white product was washed repeatedly with water and ethanol and dried at 60 °C to obtain the nanoparticle powder.

Fabrication of the QDSSCs

Fluorine-doped tin oxide (FTO, 15 Ω/square, NSG, Japan) glass was immersed in 0.15 M TiCl₄ aqueous solution and kept in an 70 °C oil bath for 1 h to introduce a thin blocking layer on the FTO surface. The treated FTO was calcinated at 450 °C for 20 min. The paste preparation technique was adopted according to the literature.³ The prepared mixed paste was coated onto the FTO layer using a traditional doctor-blade method with adhesive tape as spacer and the film thickness are all controlled at 12 μm. Then, the coated film was calcinated at 450 °C for 30 min in air. The active areas of the films are controlled at 0.2 cm² by scratching off the excess film.

The modified version of chemical bath deposition method was applied to load the QDs on the TiO₂ photoanode.⁴ For the deposition of the CdS QDs: an aqueous solution with the composition of 0.02 mM CdCl₂, 0.14 mM thiourea, 0.07 mM NH₄Cl and 0.23 mM ammonia with a final pH of ~9.0 in the chemical bath at 10 °C for 1 hour. Afterwards, TiO₂/CdS films were immersed in an aqueous solution containing 0.026 mM CdSO₄, 0.04 mM N(CH₂COONa)₃ and 0.026 mM Na₂SeO₃ for 4.5 h in the same way. Both the QDs (CdS and CdSe) depositions films were fully washed with water. For the ZnS passivation, all the films which after sensitization were deposited by twice dipping alternatively into 0.1 M Zn(CH₃COO)₂ and 0.1 M Na₂S solutions for 1 min per dip, rinsing with deionized water between dips.

The QD-sensitized photoelectrode and counter electrode were sandwiched to form the cell, which was separated by adhesive tape spacer (~60 μm in thickness). Cu₂S on brass was used as a counter electrode according to the literature.⁵ The electrolyte composed of 1 M Na₂S and 1 M S in deionized water was injected into the cell *via* capillarity.

Material characterization

Morphology and crystallography of the samples were investigated by scanning electron microscope (SEM, JEOL, JSM-6390LV), high resolution transmission electron microscopy (HRTEM, JEOL, JSM-2100, 200 kV) and X-ray powder diffraction (XRD, Bruker D

diffractometer with Cu K α radiation). The Brunauer–Emmett–Teller (BET) specific surface areas and Barrett–Joyner–Halenda (BJH) pore size distributions of the samples were measured on a Surface Area Analyzer (Micromeritics Gemini 2380) at 77 K with N₂ gas as adsorbate.

Photovoltaic measurements

Photocurrent–voltage (I – V) curves of the DSSCs were measured using a Keithley 2400 sourcemeter, and the output power density of the xenon lamp solar simulator (Newport) was adjusted to 100 mWcm⁻² (AM1.5). Incident photon to current conversion efficiency (IPCE) was also measured on the 7-scspec system (Saifan Beijing) with a 1/4 m monochromator. The thickness of the photoanode films was measured on a profilometer (DEKTAK 150, Veeco Instruments Inc.). The Bode mode of electrochemical impedance spectroscopy (EIS) was recorded at room temperature in dark using a potentiostat (EG&G,M283) equipped with a frequency response detector (EG&G,FRD100). The plots were scanned in a frequency scanning from 100 kHz to 10 mHz and the alternating voltage amplitude was set at 10 mV

References

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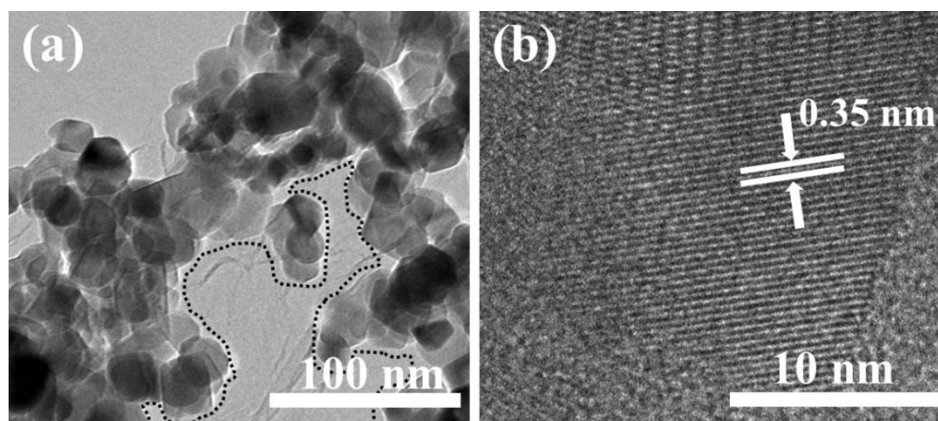


Fig. S1. (a) TEM and (b) HRTEM images of the RGT-L heterostructure prepared without CTAB.