

SUPPORTING INFORMATION

Charge transfer and surface defect healing within ZnO nanoparticle decorated graphene hybrid materials

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Synthesis of ZnO nanoparticles

In order to synthesis ZnO nanoparticles (NPs), we used solid state method where the details have been already published elsewhere¹. Here, we simply summarize the synthesis method as follows: To the fine pestled, dry Zn(SO₄)·7H₂O (0.1 mol, 179.45 g/mol) was added fine pestled NaOH (0.2 mol, 40.01 g/mol) and grounded for another 30 min. Afterwards the paste was resuspended with 50 mL millipore water, filtered and washed three times with ethanol (abs). The received white powder was dried for 2 h at 80 °C and annealed at 300°C. Finally, ZnO product was pestled.

TrGO-ZnO and GO-ZnO hybrid material syntheses

The syntheses of GO and TrGO were described in our former work². For the synthesis of TrGO-ZnO, firstly, 5 mg TrGO was dispersed in 15 ml DMF by sonication for 30 min. After that, the TrGO solution was centrifuged at 1000 rpm for 2 min to remove bigger TrGO agglomerated particles which were not well dispersed. The resulting TrGO solution was used for synthesis of TrGO-ZnO hybrid. Subsequently, 50 mg ZnO NPs were dispersed in the as-received TrGO solution in a 50 ml glass vial by sonication for 15 min. A homogeneous solution of TrGO and ZnO NPs was obtained and was held at 100°C in an oil bath under continuous stirring for 1 hour for self-assembly decoration. As a result, ZnO decorated TrGO was obtained and collected by centrifuged at 2000 rpm for 5 min. The TrGO-ZnO powder was then dried at 90 °C in an air-circulated oven for 2h.

GO-ZnO hybrid was synthesized using the same procedure as described above for TrGO-ZnO.

The dried TrGO-ZnO and GO-ZnO powders were subjected to EPR spectroscopy and Photoluminescence (PL) spectroscopy experiments, as described below.

Table 1: Starting materials for the synthesis.

Chemical	Manufacturer	Grade
NaOH	Roth	99 %
Zn(SO ₄)·7H ₂ O	Aldrich	99.9 %
Ethanol (abs.)	Analar Normapur	99.9 %
DMF	Scharlau Chemie S.A	HPLC reagent grade

EPR spectroscopy: X-band (9.86 GHz) EPR measurements were performed by BRUKER EMX spectrometer with the aid of a rectangular TE102 resonator from Bruker. The offset in the magnetic field and the exact g-factors in X-band measurements were determined with a polycrystalline DPPH (2-diphenyl-1-picrylhydrazyl) reference sample of well-known g-factor ($g = 2.0036$). The EPR spectral analysis has been performed using the WINEPR program from Bruker. The following EPR experimental parameters were used: microwave power: 1 mW; modulation amplitude: 0.5 G; time constant: 163.84 ms; receiver gain: 2×10^4 .

PL spectroscopy: Three samples of ZnO NPs, GO-ZnO, and TrGO-ZnO were prepared in parallel in the same procedure as following: 10 mg of each above material was dispersed in 10 ml DMF by sonication for 10 min forming homogeneous dispersion. The dispersion was then drop-cast on a microscope slide, DMF solvent was then evaporated by heating the slide on a hotplate at 100 °C for ca. 5 min. Afterwards, the as-prepared three samples were measured PL spectra by utilizing a J&M FL3095 spectrometer (J&M, Germany) with excitation at 320 nm, entrance slit: 5 nm bandpass, exit slit: 5 nm, integration time 0.1 s.

TEM imaging: For TEM measurement, the two samples were prepared by dip-coating holey structured carbon coated-copper grids (Quantifoil Micro Tools GmbH, Germany) into a solution of TrGO-ZnO and GO-ZnO in DMF, respectively and measured by a LEO 912 OMEGA (Zeiss) transmission electron microscope.

REFERENCES

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- (2) Pham, C. V.; Eck, M.; Krueger, M., *Chem. Eng. J.*, **231** (2013) 146–154.