

Electronic supplementary information (EIS)

Quantum dots embedded N-doped functionalized multiwall carbon nanotubes boost short-circuit current of Ru(II) based dye-sensitized solar cells

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2. Experimental

2.2 Formation of N-doped *f*-MWCNTs

The N-doped functionalized multiwall carbon nanotubes (N-*f*-MWCNTs) were synthesized by the hydrothermal method. [1] In brief, *f*-MWCNTs (0.2 g) were dispersed in deionized water (60 mL) with sonication to form a uniform dispersion solution. Then, the solution was placed inside the pre-heated water at 25 °C and added 10 mL of ammonia solution (NH₄OH) dropwise with the stirring process, obtained a dark black solution. Then the mixture was hydrothermally treated at 180 °C for 12 h, and the solid products were separated by centrifugation and washed with distilled water. Finally, the residue was dried at -75 °C for 22 h in vacuum freeze dryer by lyophilization.

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2.3. Acidification and functionalization of multiwall carbon nanotubes

Normally, 300 mg pristine MWCNTs were added to 250 ml beaker containing 100 ml of HCL (con.36.5 %) and then shifted to 250 ml three-neck flask after 30 minutes of sonication. After being refluxed at 80-90 °C for 4h, the suspension was cooled down at normal temperature and successively centrifuged. The resulting residue was removed by the decantation process. After that, the black residue solution was separated with 0.22 µm thin filter paper and washed with D.I. water through "SHB-III water circulating vacuum pump" 3 to 4 times until the pH value reached to neutral. Finally, the product was dried at -75 °C for 24 h in a vacuum freeze dryer.

Furthermore, Carboxylated attached MWCNTs were prepared by the same refluxing method. Briefly, 200 mg of acid-treated MWCNTs were added to 250 ml of a beaker containing 100 ml of HNO₃ (con.63%) and was placed for 30 minutes ultrasonication. After that, the suspension was poured into the three-necked round bottom flask with a capacity of 250 ml and refluxed at 120 °C for 6 h under magnetic stirring. The resulting residue was separated by the decantation process. Finally, the COOH-MWCNTs were dried at -75 °C for 24 h in a vacuum freeze dryer and stored in a vial for subsequent use. Such an acid purification and functionalization of the multiwall carbon nanotubes is very vital and essential for the synthesis of SnS₂ (NFs) on the walls of the MWCNTs since it acts as sites for nucleation of SnS₂ (NFs) as oxygen-containing groups.

2.4. Fabrication of graphene oxide (GO)

Initially, H₂SO₄ (180 mL, 98%) and H₃PO₄ (20 mL, 85%) were mixed in (500 mL) beaker, and subsequently (1.5 g) graphite powder was placed into another (500 mL) beaker. The acid mixed solution was poured into the graphite powder slowly and was placed for a water bath at 50 °C pre-heated water under magnetic stirring. Furthermore, 9g of KMnO₄ added into the

above solution with an insensible rate under magnetic stirring to keep the temperature was maintaining at about 50 °C for 6 h. During the stirring process the diluted (200 mL) H₂O₂ was added into the above solution without trouble to avoid bubbles, just with changed color of solution from black to purple, and finally turned to bright yellow color. Subsequently, the above solution was further stirred for 3h at 50 °C and then cooled at normal temperature until the pH value of the product was closed to neutral. After the age of 22 h, it was collected through centrifugation process and washed with D.I. water and (C₂H₅OH) 3-4 times. Finally, the residue was dried at -75 °C for 24 h in vacuum freeze dryer for subsequent use. Additionally, graphene oxide (GO) was changed into reduced graphene oxide (RGO) at 160 °C for 8 h by hydrothermal reduction method.

2.6. Fabrication of counter electrodes (CEs) and dye-sensitized solar cells (DSSCs)

The prepared sample was used as a raw material for the fabrication of counter electrodes. Normally we used a 4:1 ratio. Briefly, 0.04 g of the composite material was milled with 0.01 g reagent polyethylene glycol (C₂H₆O₂) and 2 ml of ethanol solution grind with mortar to form thin gelatin. In this purpose, "Fluorine-doped tin oxide (FTO)" layered glass substrates "NSG, 13 Ωsq⁻¹, 1×2 cm²" were used. After cutting the FTO, washed with absolute water and sonication with ethanol for further 30 minutes three to four times and finally dried in an oven to remove the impurities at 80 °C for 30 min. After rinsing and drying the FTO, first check the conductive side of the FTO with digital multimeter (DMM) and pasted the adhesive tape (3M) on the each edge of the conductive side of the FTO.

Furthermore, the prepared gelatin was pasted on the center of the FTO is an area (0.5×0.5 cm²) by using the doctor blade method and left for several minutes to disappear the ethanol from the FTO surface. After drying the deposited film, the adhesive tape was removed from the edges

of the CE. Finally, the counter electrodes were positioned into the quartz boat and put into the oven at 400 °C for 1 h in the presence of the Argon (Ar) gas.

The fabrication of the sandwich like DSSCs was constructed typically by assembling a TiO₂ photoanode (sensitized by dye), and as-prepared CEs escorted by the addition of redox electrolytes. Initially, the purchased TiO₂ (Yingkou OPV Tech. New Energy Co., Ltd. Liaoning (Yingkou) China) photoanodes whose active surface area is 0.16 cm² (0.4 cm×0.4 cm) and thickness is (10 μm) were sensitized by dipping in “N719” dye solution for 20 h at normal temperature in dark place. The dye solution consists of (0.15 mM) ethanol solution. After that, the sensitized TiO₂ photoanodes were washed with ethanol and dried in the flow of hot air. The TiO₂ photoanodes were divided off from the CE by a scotch tape. Now the acetonitrile electrolyte solution (Yingkou OPV Tech. New Energy Co., Ltd. Liaoning (Yingkou) China) consist of “(0.6 M 1-propyl-2,3-dimethyl-imidazolium iodide, 0.5 M LiI, 0.05 M I₂ and 0.5 M 4-tert-butylpyridine)” was injected into the gap between TiO₂ photoanode and the counter electrode.

2.7. Materials Characterization

In this research, the following characterizations were used to characterize the prepared samples. Rigaku/Max-3A, Japan X-ray diffractometer is used to the crystallographic characterization with the source of "Cu K_α radiation (λ=1.54056 Å)" was used as the evidence of X-ray diffractometer pattern for the given sample. To study the chemical states we used the Smart Lab 9 kW polycrystalline X-ray diffractometer. The Raman spectra were examined by using Laser Confocal micro-“Raman Spectrometer (Model: Renishaw Via-Reflex),” with three lasers were equipped, with the wavelength of 325 nm, 532 nm, 785 nm with resolution 2 cm⁻¹. “X-ray photoelectron spectra (XPS)” were carried out on an (ESCALAB250Xi) spectrometer with a monochromatic Al K_α radiation. Morphologies and size of the material particles we checked with “Transmission Electron Microscopy (TEM)”, “High-Resolution Transmission

Electron Microscopy (HR-TEM)" and corresponding "Selected Area Electron Diffraction (SAED)", (Hitachi S-4800 microscope and JEOL JEM-2010SX, JAPAN), with an operating voltage of 200 kV is used to study the microstructure of the materials. The specific surface area and pore size of the as-prepared samples were calculated by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH), respectively. The instrument used based on N₂ adsorption and desorption isotherms measured at 77 K using the gas adsorption apparatus (Autosorb-iQ, Quantachrome Instruments, U.S.).

A workstation "Electrochemical Impedance Spectroscopy (EIS)" with a 100 Hz frequency; 200 mA AC amplitude was used to examine the impedance of the replica cell "CE/719/CE" in a 0.1~10⁶ Hz frequency with 10 mV AC voltage amplitude. Tafel curves kept quasi-stationary conditions with the voltage range (-1 to 1 V) at 50 mV/s scan rate. Cyclic Voltammetry (CV) tests, (ZAHNER ZENNIUM CIMPS-1, Germany), an electrochemical workstation was used which consist of the three electrodes system, "Pt sheet used as (CE)", "Ag/AgCl saturated with KCl solution or Saturated calomel electrode as the simulated reference electrode (RE)", and the "Sample electrode used as working electrode (WE)" in an anhydrous acetonitrile solution of "(100 mM LiClO₄, 10 mM LiI, and 1 mM I₂)" in range from -0.4 to 1.1 V at scan rate of 25 mVs⁻¹. A workstation "Keithley 2410, 1100V" was used for the "Photocurrent density-Voltage (J-V)" test attached by the digital source indicator lower AM 1.5 illumination stable solar simulator for PV cells, by using a (SAN-EI ELECTRIC CO., LTD, XES-402S-CE, Japan), solar light simulator having light intensity 100 mW·cm⁻² which was then standardized by a Silicon as reference cell earlier. All the above tests were performed at a normal temperature.

3. Results and discussion

3.1. Morphological and Crystallographic investigation

$$D = \frac{k\lambda}{\beta \cos(\theta)} \text{----- (1)}$$

In Eq. 1, k is the shape factor which is (0.89) or 1, wavelength (λ) of CuK α with 0.154 nm radiation, expanding of diffraction line (β) estimated at half maximum intensity in radian or ' β ' is the full-width half-maximum (FWHM) of the particular diffraction peak, ' θ ' is the Bragg's angle and 'D' is the grain diameter.

Table: Comparison of the electrocatalytic performance of the hybrid materials reported before and in this work for DSSCs.

Samples	Synthesis Method	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	References
MoS ₂ /CNT	Hydrothermal	12.43	0.62	0.4	3.08	[46]
CNTs	Chemical method	13.25	0.80	0.65	7.0	[19]
3% Ag-doped CoS	Hydrothermal	15.48	0.716	0.711	7.89	[91]
NCNT-Co	Thermal treatment	16.03	0.74	0.65	7.75	[61]
graphene/carbon	Facile approach	15.07	0.70	0.57	5.99	[90]
MWCNTs/PPy	Electrochemical polymerization route	14.83	0.77	0.65	7.42	[89]
Ni _{0.95} Mo _{0.05} S	Electrochemical deposition method	17.21	0.65	0.64	7.15	[47]
ZnS@N,f-MWCNTs	Hydrothermal	17.55	0.73	66.0	8.5	present work
ZnS@N,f-MWCNTs@rGO	Hydrothermal	18.12	0.78	66.5	9.4	present work

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