"Firecracker-shaped" ZnO/Polyimide Hybrid Nanofibers

via Electrospinning and Hydrothermal Process

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Materials

Pyromellitic dianhydride (PMDA, 99%) and 4,4'-oxydianiline (ODA, 99%) were of chemical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. PMDA was recrystallized from acetic anhydride and dried at 150 °C in vacuo. ODA was purified by sublimation under reduced pressure. Zinc acetate dihydrate $(C_4H_6O_4Zn\cdot 2H_2O)$, zinc nitrate hexahydrate $(Zn(NO_3)_2\cdot 6H_2O)$, hexamethylenetetramine $(C_6H_{12}N_4)$, and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received.

Experimental section

Preparation of polyimide (PI) nanofibers

The PI nanofibers were prepared according to our previous work.¹ The poly(amic acid) (PAA) solution, a precursor of PI, was synthesized by polycondensation. In a typical example, 6.54 g (30 mmol) of PMDA, 6.00 g (30 mmol) of ODA, and 70 g of DMAc were added to a 150 mL flask. The system was equipped with a nitrogen inlet and mechanical stirrer. The mixture was stirred at 0 °C under nitrogen for about 5 h. The synthesized PAA solution was electrospun into PAA nanofibers onto aluminum foil. Electrospinning was carried out using a syringe and a high voltage from a DC power supply of 30 kV over a 15 cm gap between the spinneret and collector. A microinfusion pump was set to deliver the PAA solution at a flow rate of 10 mL h⁻¹ using a 1 mL syringe. The PAA nanofiber mat that was removed from the substrate was then converted into a PI nanofiber mat via thermal imidization with several different oxidation steps in a high-temperature furnace.²

Preparation of ZnO/PI hybrid nanofibres

ZnO/PI hybrid nanofibers were prepared via immobilization of ZnO seeds onto PI nanofiers, followed a hydrothermal process. First, the PI nanofibers were coated with ZnO nanoparticles as seeds by a dip-coating technique, according Yang's report.³ In a typical example, the PI nanofibers were immersed into a solution of 0.005 M C₄H₆O₄Zn·2H₂O in ethanol, followed by rinsed with clean ethanol after 10 s, and finally dried with Ar blow. This process is repeated five times. The PI nanofibers covered with C₄H₆O₄Zn·2H₂O were heated to 300 °C in air for 30 min to yield layers of ZnO seeds. Subsequently, the PI nanofibers coated with ZnO seeds were immersed into a 50 mL aqueous solution of equimolar Zn(NO₃)₂·6H₂O (0.025 M) and C₆H₁₂N₄ (0.025 M). The hydrothermal process was conducted at 90 °C for 6 h. After the reaction, the hybrid nanofibers were removed from the solution, washed exhaustively with excess amounts of deionized water and ethanol, and dried with Ar blow.

Characterization

The morphology of the ZnO/PI hybrid nanofibers, which were C-sputtered prior to observation, was observed with a JSM-6700F field emission scanning electron microscope (FE-SEM). X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using Cu Ka radiation. Pristine and modified PI nanofiber surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS HIS spectrometer and a monochromatized Al K α X-ray source (1486.6 eV photons). The pressure in the analysis chamber was maintained at 10⁻⁶ Pa or less during each measurement. Surface elemental stoichiometries were determined from the sensitivity-factor-corrected spectral area ratios and were reliable within ±10%. The photoluminescence (PL) spectrum was recorded at room temperature using a Xe lamp with an excitation wavelength of 325 nm by a Hitachi F-4500 fluorescence spectrometer. The photocatalytic activity was investigated using an aqueous RhB as a probe and a self-made vessel as the photoreactor according to Zhang's report.⁴ The photocatalytic degradation process was monitored by UV-vis spectrophotometer (CARY Bio-100) to measure the

absorption of RhB at the wavelength of 553 nm. The humidity of the laboratory was about 60%.



Fig. 1S FE-SEM image of interface from ZnO nanorods and PI nanofiber.

Photoluminescence property

Room temperature photoluminescence (PL) spectrum was recorded with an excitation wavelength of 325nm (Fig. 2S). It can be observed that a weak peak located at 386 nm, which was attributed to the recombination of photogenerated electrons and holes.⁵ The low emission intensity at 386 nm indicates that the rate of the recombination between photogenerated holes and electrons might be lower, which is beneficial for the photocatalytic process. In addition, the PL spectrum shows a strong intense peak around ~530 nm and ~583 nm. The green emission peak around 530 nm can be related to singly ionized oxygen vacancy, and this emission results from the recombination of a photogenerated hole with a singly ionized charge state of the specific defect. It is well-known that oxygen vacancies participate in photocatalytic reactions as electron traps, charge transfer sites, and adsorption sites of oxygen, which is beneficial for the photocatalytic process further.⁶⁻⁸ The yellow emission peak at about 583 nm can be likely attributed interstitial oxygen.^{5.9}



Fig. 2S PL spectrum of the ZnO/PI hybrid nanofibers.

Notes and references

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