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Enhanced photocurrent gain by CdTe quantum dot modified ZnO nanowire

Lei Li[a,b], Shuming Yang[a,b,*], Weixuan Jing[a,b], Zhuangde Jiang[a,b], Feng Han[a,b]

[a] Collaborative Innovation Center of High-End Manufacturing Equipment, Xi'an Jiaotong University, Xi'an 710049, PR China
[b] State Key Laboratory for Manufacturing Systems Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China

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ABSTRACT

In this paper, a zinc oxide (ZnO) nanowire (NW) photodetector was fabricated using dielectrophoresis technique. The ZnO NW was synthesized by chemical vapor deposition (CVD) method, and characterized by SEM, XRD and photoluminescence (PL) spectrum. The photodetector showed obvious photoresponse to 365 nm UV light. By decorating the ZnO NWs with CdTe quantum dots (QDs), the photocurrent (PC) gain was enhanced from 199 to 2896, when the light intensity was 5.3 mW/cm^2. The response spectrum was also extended to the visible light region. The underlying mechanism of the enhancement was assigned to the high-efficiency charge transfer caused by the type-II band structure between ZnO NWs and CdTe QDs. The greatly quenched PL intensity of CdTe QDs/ZnO NWs composites provided further evidence for the high efficiency charge transfer.

1. Introduction

Zinc oxide (ZnO) nanowire (NW) has been considered as ideal building blocks for the nano-scale ultraviolet (UV) optoelectronic devices due to its wide direct band gap, large excitation banding energy and surface-to-volume ratio etc. [1]. ZnO NWs reported so far have been used for lasers [1], solar cells [2,3] and photodetectors etc. [4–8]. Since Kind et al. [6] reported the single ZnO NW UV photodetector in 2002, there have been many reports about NW photodetectors [7,8]. Due to the large surface-to-volume ratio, the surface of the NW influences the photodetector performance significantly [9,10], and many methods based on the NW surface modification have been introduced to improve the performance of the ZnO NW photodetector. For example, some metal nanoparticles, such as Au, Ag and Ti modified ZnO NWs have been used to enhance the photocurrent because of the surface plasmon resonance or nano heterojunction effect [11–13]. Organic polymer was also introduced to passivate the NW surface states and enhance the photocurrent [14,15]. Compared with the aforementioned methods, quantum dot (QD) modified NWs is a promising method for the QD's unique optical properties, such as tunable emission and absorption band, good photostability, and high light absorption coefficient etc. [16]. However, most of the QDs/NWs composites were used in photovoltaic cells devices to enhance the light-converting efficiency, there were rare reports using QDs/NW composites to fabricate the photodetectors. Recently, CdSe and I–III–VI ($CuInS_2$, $CuInSe_2$) QDs have been proved to enhance the photocurrent gain of SnO_2 NW, and an enhancement factor of up to 700% was realized [16,17]. For ZnO NW based photodetector, only Aga et al. [28] reported the cadmium telluride (CdTe) decorated ZnO nanowire for enhancing the photocurrent gain. But the photocurrent gain was still very low, even enhanced after CdTe QDs decoration.

In this paper, a ZnO NW photodetector with large photocurrent gain was fabricated using alternating current (AC) dielectrophoresis (DEP) technique, which was much easier than electron beam lithography (EBL) and focused ion beam (FIB) techniques [4,5]. CdTe QDs were used to increase the photocurrent gain of the photodetector. The CdTe QDs were deposited on the ZnO NWs surface by a simple drop casting method [17]. After deposition of CdTe QDs, the photocurrent (PC) gain was enhanced more than 10 times. The large enhancement was attributed to the high-efficiency charge transfer between QDs and NWs caused by the type-II band structure. The photoluminescence results also proved the high efficiency charge transfer at the interface of NWs and QDs.

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* Corresponding author. Fax: +86 29 8266 8616.
E-mail address: shuming.yang@mail.xjtu.edu.cn (S. Yang).

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2. Experiments

2.1. Synthesis of CdTe QDs

The Mercaptosuccinic acid (MSA, 99.0%) capped CdTe QDs were synthesized via a modified procedure [18]. Typically, $CdCl_2$ (0.04 mol/L, 4 mL) was diluted to 50 mL in a three-necked flask, and tri-sodium citrate dihydrate (400 mg). Na_2TeO_3 (0.01 mol/L, 4 mL), MSA (100 mg) and $NaBH_4$ (50 mg) were added successively, under vigorous stirring. When the solution became transparent and the color changed to green, the flask was attached to a condenser and refluxed at 100 °C for 9 h in N_2 atmosphere, and then the CdTe QDs were synthesized.

2.2. ZnO NW growth

The ZnO NW growth was conducted using a horizontal tube furnace by chemical vapor deposition (CVD) process [19]. Before NW growth, 8 nm Au thin film was deposited on the Si substrate by magnetron sputtering, served as the NW growth catalyst. The mixture of ZnO and C powder (1:1 weight ratio) was used as the source material for NW growth, and placed at the center of the heating zone. The Au coated Si substrate was placed downstream about 3 cm away from the source material. 200 sccm Argon/Oxygen ($Ar:O_2 = 9:1$, volume ratio) was introduced into the tube furnace as carrier gas, and the pressure was maintained at 2000 Pa. The furnace was heated from room temperature to 950 °C at a rate of 40 °C/min, and held at 950 °C for 40 min. Then the furnace was cooled down to room temperature naturally, and the ZnO NW was obtained. Before the dielectrophoresis (DEP) experiments, the ZnO NW was immersed into 5 mL ethanol solution and ultrasonicated for 15 min to detach and disperse the ZnO NWs into the ethanol and form ZnO NW-ethanol suspension.

2.3. Preparation of photodetector

The metal-ZnO NW-metal (MSM) photodetector was fabricated by DEP method [4]. The DEP electrode was prepared on the Si substrate coated with 300 nm SiO_2 using UV photolithography and lift-off techniques. The Pd/Ti (200 nm/50 nm) electrode was deposited using DC magnetron sputtering technique. The electrode interval was 10 μm and the length was 110 μm. Before DEP experiment, a drop of the NW solution was dripped on the electrode interval. Then an AC electric field ($f = 20$ MHz, $V_{pp} = 20$ V) was applied on the electrodes. The DEP experiment was executed for 3 min. After DEP assembling, the sample was rinsed several times to remove the NWs that did not steadily contact with the electrode. Finally, the sample was dried on a hot plate at 100 °C for 5 min to remove organic residue.

For CdTe QDs decoration experiment, the CdTe QDs were firstly diluted to 20% of its initial concentration. And then the diluted CdTe QDs was deposited on the NW surface by drop casting method [16]. Finally, the sample was baked at 100 °C for 5 min to evaporate the residual solution in order to achieve high coupling strength between the CdTe QDs and ZnO NWs.

2.4. Apparatus

The ZnO NW and the device were investigated by FE-SEM (SU 8010, Hitachi, Japan). The NW crystal structure was characterized by X-ray diffractometer (XRD, XPert Pro, PANalytical, Netherlands). The photoluminescence (PL) spectra of ZnO NW, CdTe QDs and the NW/QD composite were measured by fluorescence spectrometer (PTI-40, PTI, USA) with the excitation light of 325 nm. The absorption spectrum of the CdTe QDs solution was measured by UV–vis spectrophotometer (UV3600, Shimadzu, Japan). The QDs and the ZnO NW/CdTe QDs composite were characterized by TEM (JEM-2100F, JEOL, Japan) at 200 kV. For photoresponse measurement, the sample was illuminated by a 365 nm UV light. The photocurrent was recorded by a Source Meter system (Keithley 2611A).

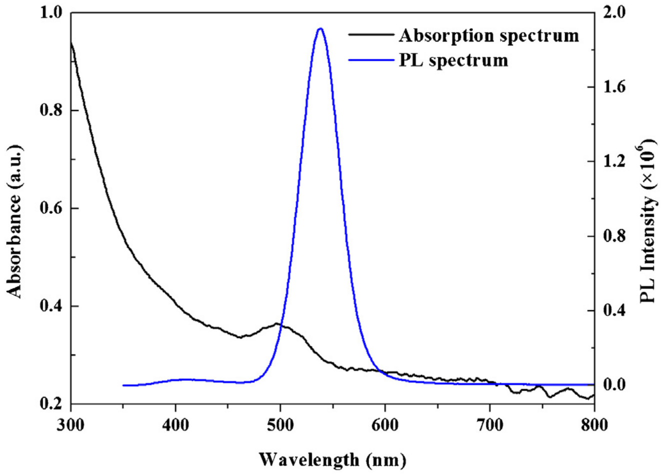

Fig. 1. The absorption and photoluminescence spectra of the as synthesized CdTe QDs.

3. Results and discussion

3.1. CdTe QDs

The QDs showed obviously green fluorescence light under the UV lamp. The photoluminescence (PL) and UV/Vis absorption spectra of CdTe QDs solution were shown in Fig. 1. Compared with the bulk materials, the absorption and the emission peaks of the CdTe QDs were blue shifted to 500 nm and 540 nm, respectively, because of the quantum size effect [20]. The QDs exhibited very strong PL intensity, indicating that the QDs had high quantum yield [21].

3.2. ZnO NWs

Fig. 2 showed the typical SEM images of the as grown ZnO NWs. The diameter of the ZnO NWs ranged from 50 nm to 200 nm, and the length was several tens of micrometers. Fig. 3a was the XRD pattern of ZnO NWs, all of the diffraction peaks can be indexed to the typical hexagonal wurtzite structure of ZnO (JCPDS No. 36-1451), the calculated lattice constants were $a = 0.326$ nm and $c = 0.521$ nm which were consistent with the standard values. The sharp diffraction peaks indicated that the ZnO NWs were highly crystallized. Two weak diffraction peaks of cubic phase Au (1 1 1) and (2 0 0) were also detected (JCPDS No. 65-8601), which come from the Au catalyst thin film. The PL spectrum of ZnO NWs was shown in Fig. 2b, the NWs presented strong near band edge (NBE) emission centered at 383 nm. A wide visible light spectrum was also investigated, which was because of the oxygen vacancies defects [22].

3.3. Device fabrication and CdTe QDs modification

The results of DEP experiment are shown in Fig. 4a–c. Since most of the NWs were longer than the electrode interval, the NW can directly span across the electrodes. The following current–voltage measurement indicated that the ZnO NWs contacted well with the Pd electrodes. The TEM image of CdTe QDs decorated ZnO NWs was shown in Fig. 4d, the black dots was CdTe QDs, the diameter was