

Controllable Synthesis and Electroluminescence Property of Water-Sol ZnCdTe Alloy for Light-emitting Diodes

Yan Wang, Yanbing Hou, Haixin Cui, Changjiao Sun, and Yunzhang Lu

Abstract—By changing the stabilizer system and synthesis temperature, ZnCdTe alloy have been controllably synthesized in aqueous solution using a simple route. A high synthesis temperature leads to nanoparticles growth using thioglycolic acid (TGA) as the stabilizer, whereas a low synthesis temperature promotes the form of nanorods using TGA and L-Cysteine(L-Cys) as the stabilizer. The different morphologies of samples have been characterized by transmission electron microscopy (TEM). The optical properties of the obtained ZnCdTe nanorods and nanoparticles have been investigated by photoluminescence (PL) spectroscopy with different refluxing times. We have also demonstrated electroluminescence (EL) property from heterostructure device fabricated with the prepolymer of Poly(p-phenylenevinylene) (PPV) and ZnCdTe alloyed nanocrystals. Current density of device with ZnCdTe alloy in emitting layer is obviously increased.

Index Terms—Optical properties, electroluminescence, ZnCdTe, alloy.

I. INTRODUCTION

Nanostructured materials, especially one-dimensional (1D) materials such as nanowires, nanorods and nanotubes have been the focus of intensive research[1], [2]. The ability to rationally tune the shape of colloidal nanocrystals from spheres to rods/wires has been actively sought during the last several years. Up to now, many methods have been developed to achieve 1D growth, including metal particle-initiated 1D uniaxial growth [3], [4], and template-directed 1D growth [5], [6]. Besides these important methods, exploring new and simple wet synthetic routes without using metal seeds and templates for achieving 1D growth of semiconductor nanomaterials is also one of the focuses of intensive research.

Among various II - VI semiconductor materials, CdTe have attracted much attention of the scientists because such material has shown significant potentials to be used in biological labeling [7], light-emitting devices[8], and solar cells[9]. Size-tunable properties of CdTe nanocrystals have been investigated by many world-wide research groups [10], [11]. However, the tuning of physical and chemical properties of binary nanocrystals is limited by only changing the particle size, which causes problems in many applications such as biological labeling, superlattice structures, and

nanoelectronics[12], [13]. This is because very small nanocrystals is hard to passivate and exhibit unstable optical properties. Recent advances in ternary composition-tunable semiconductor nanocrystals have attracted attention of scientists[12]-[16]. As has been clarified in our previous studies[17], ternary $Zn_xCd_{1-x}Te$ nanocrystals can be synthesized successfully. Currently, some interesting results have been obtained in further research, and we found the shape of ZnCdTe nanocrystals can be controlled by changing the stabilizer system and synthesis temperature. Ternary ZnCdTe nanorods and nanoparticles can be shape-controllable synthesized in aqueous media by a simple route. Our method is of particular interest due to the controllability of compositions, low temperature, simple facilities, low cost, good homogenization, better water-soluble, shape-controllable and bio-compatible. Furthermore, we investigated the electroluminescence property of heterostructure devices fabricated with ZnCdTe alloy and prepolymer PPV, which were used as an emitting layer.

II. SYNTHESIS OF ZNCDTE NANOPARTICLES AND NANORODS

Mixed precursor solutions were prepared firstly by mixing $Cd(CH_3COO)_2 \cdot 2H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$ solution. Then the stabilizers were added to the mixed precursor solutions under N_2 flow. The precursor solutions were adjusted to pH 9 by NaOH solution. Then, oxygen-free NaHTe solution, which was freshly prepared from tellurium powder and $NaBH_4$ in water, was injected into the above solution under vigorous stirring. The resulting mixture solution was refluxed in fixed temperature for different times. We found ZnCdTe nanoparticles were produced with using TGA as the stabilizer when the refluxed temperature is above $80^\circ C$, and ZnCdTe nanorods were produced with using TGA and L-Cys mixed stabilizer system in lower temperature. It is a simple route to achieve shape-controlled synthesis of ZnCdTe nanoparticles and nanorods.

III. DEVICE FABRICATION

ITO-coated glass substrate was first cleaned for sample preparation by detergent and distilled water in an ultrasonic bath, respectively. A hole injection layer of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spin-coated onto a cleaned ITO glass substrates and the layer then was heated to $80^\circ C$ for about 10min. The PEDOT:PSS layer was used to improve the holes transport. The ZnCdTe alloyed nanocrystals and prepolymer PPV were dissolved in distilled water, and then the blend was

Manuscript received November 10, 2011; revised November 20, 2011.

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spin-coated onto the top of PEDOT:PSS layer with a thickness of about 50nm. The organic films of BCP (11nm) and Alq3 (9nm) was vapor-deposited onto the nanocomposite layer as the hole-blocking layer and the electron-transporting layer by the thermal evaporation method, respectively.

IV. CHARACTERIZATION

Transmission electron microscopy (TEM) images were performed on a HITACHI H-700 transmission electron microscope. X-ray diffraction (XRD) pattern was measured by Philips APD-10 X-ray diffractometer with graphite monochromatized Cu K α radiation ($\lambda=0.154178$ nm). PL spectra were performed by a SPEX Fluorolog-3 Spectrofluorimeter. All the measurements were performed at room temperature under ambient atmosphere. Cyclic voltammetry (CV) measurement was performed on a CHI660A electrochemical workstation. Current-voltage curves of the devices were measured using a Keithley 2410 source meter.

V. RESULTS AND DISCUSSION

TEM images of TGA-stabilized ZnCdTe nanoparticles reacted for 30min were shown in Fig.1, TEM image shows clearly that the morphology of ZnCdTe nanoparticles using TGA as the stabilizer is close to spherical. As shown in Fig. 1, the ZnCdTe nanoparticles is small obtained for refluxing 30min and the average particle size is about 3.8 nm in diameter. The average particle size of samples increases to about 5.4nm with continually increasing time from 30min to 120min. There is not obvious size difference for ZnCdTe nanoparticles reacted for more than 120min, which may due to dominant growth of ZnCdTe nanoparticles occurred in the early stages.

TEM images of ZnCdTe nanorods stabilized by TGA and L-Cys mixed stabilizers in the lower growth temperature with different refluxing times (30min and 60min) were shown in Fig.2a-b. We can observe the formation of ZnCdTe nanorods under this experimental condition. The diameters of the short and the long axis of the samples remained at about 20-40 and 30-100 nm, respectively (in Fig.2).

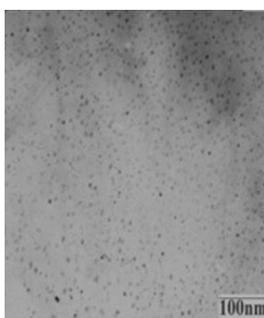


Fig. 1. TEM images of ZnCdTe nanoparticles stabilized by TGA reacted for 30min.

In the TGA and L-Cys mixed system, partial removal of stabilizer (TGA) can decrease the mutual electrostatic repulsion of the products. As a result, the dipole attraction is favorable for 1D growth with $-NH_2$ and $-COO_2$ of L-Cys

acting as a pair of binding sites for metallic ions[18]. Once the small ZnCdTe nanocrystals formed in the reaction system, the nanocrystals have a chance of combining with each other through the chelate function between the stabilizers and metallic ions. TGA and L-Cys mixed system made the growth orientation more restricted, suppressing other growth directions[2]. In addition, if OR which is a diffusion-limited process is suppressed properly, it should favor anisotropic growth of nanocrystals. In the aqueous process of growth of ZnCdTe nanorods, the nucleation occurs at low temperature. OR process may be suppressed at lower growth temperature, which leads to the formation of ZnCdTe nanorods[11]. As shown in Fig.2, the average size of ZnCdTe nanorods becomes bigger with increasing the refluxing time from 30min to 60min, which dues to the continuous growth of ZnCdTe nanorods with rased time.

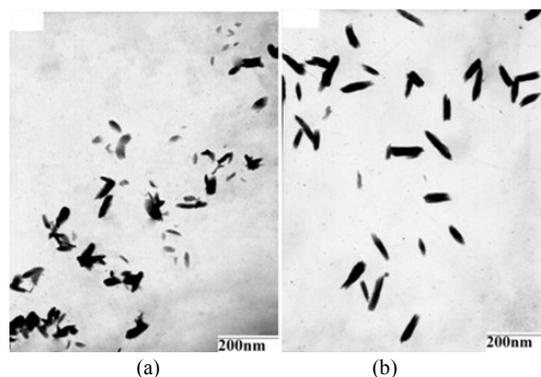


Fig. 2. TEM images of ZnCdTe nanorods stabilized by TGA and L-Cys with different refluxing times (a) 30min (b) 60min.

The crystallographic properties of the as-synthesized ZnCdTe nanocrystals were determined using powder X-ray diffraction (XRD). As an example, the XRD pattern of the as-synthesized ZnCdTe nanocrystals was shown in Fig.3. The crystal structures can be assigned as cubic structures with the presence of characteristic (1 1 1), (2 2 0), and (3 1 1) peaks in the XRD patterns. XRD spectra show obvious broadening phenomena, which indicates the small size of the alloyed nanocrystals.

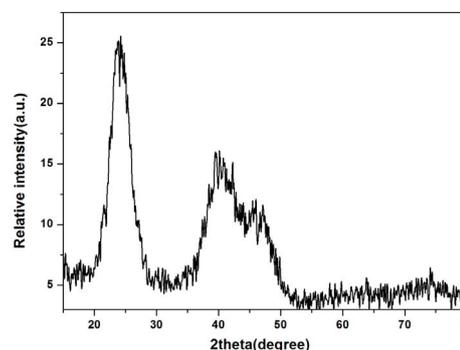


Fig. 3. XRD spectra of as-synthesized ZnCdTe nanocrystals.

As shown in Fig. 4, the photoluminescence (PL) spectra of ZnCdTe nanoparticles and nanorods were investigated with different refluxed times (30min, 60min, 120min). All obtained ZnCdTe nanoparticles and nanorods show strong luminescence. The PL peaks of ZnCdTe nanoparticles appeared at 513, 520 and 522 nm, respectively. The full

width half maxima (FWHM) of ZnCdTe nanoparticles is 40-44nm, indicating a relative narrow size distribution (Fig.4a). As mentioned above, the nanoparticles growth was accompanied by a red shift in the luminescence peaks. Fig.4b shows the PL spectra of ZnCdTe nanorods stabilized by L-Cys and TGA with different refluxing times. The full width half maxima (FWHM) of ZnCdTe nanorods is 50-58 nm. Nanorod sample has green PL (peak: 540 nm) with refluxing for 30 min. With increasing refluxing time, ZnCdTe nanorods show the longer wavelength emission (peak: 560nm) with larger size due to quantum confinement effect. The red shift of nanorods with increased refluxing time may due to the elongation of two axes and the decrease of confinement in two dimensions [2].

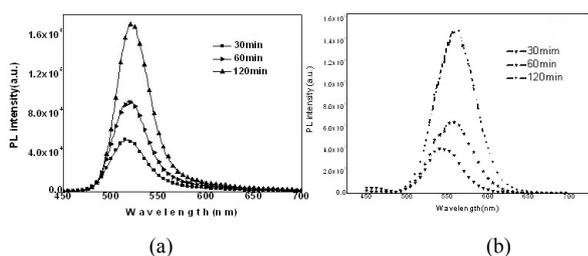


Fig. 4. (a)Photoluminescence spectra of TGA-stabilized ZnCdTe nanoparticles; (b)Photoluminescence spectra of TGA and L-Cys stabilized ZnCdTe nanorods.

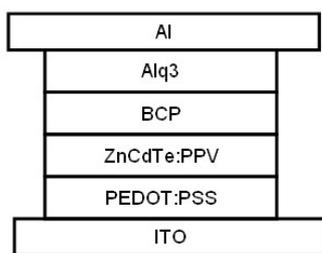


Fig. 5. Device configuration of the device.

Next we fabricated the heterostructure device by adding ZnCdTe alloyed nanocrystals into the prepolymer of Poly(p-phenylenevinylene) (PPV) as emitting layer. The schematic diagram of the device is shown in Fig. 5 In order to clarify the energy level of PPV prepolymer, a typical CV curve of PPV prepolymer solid film is first measured. As shown in Fig. 6, the oxidation peak and reduction peak were observed with good reproducibility, which corresponds to HOMO level of 5.44 eV and LUMO level of 3.44 eV calculated by formulas, respectively. The energy values were referenced against ferrocene as an internal standard where acetonitrile was used as a solvent [19], [20].

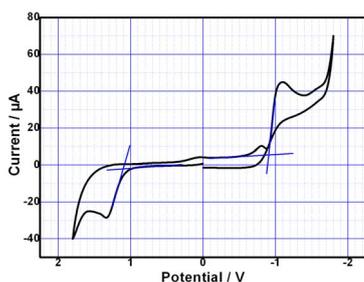


Fig. 6. Cyclic voltammogram of a PPV prepolymer film on top of the Pt work electrode in a 0.1M solution of tetrabutylammonium perchlorate in acetonitrile.

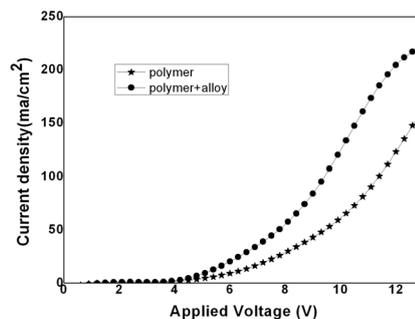


Fig. 7. Current versus voltage characteristic for devices with and without ZnCdTe alloy as the emitting layer.

Fig.7 shows the performance of the devices with and without ZnCdTe alloy as the emitting layer. As the result shown, current density of device with adding ZnCdTe is obviously increased comparing with that without adding ZnCdTe alloy. For PPV prepolymer, the carrier mobility is lower, which could result in lower electroluminescence efficiency of device. It favors to improve injection and transport of carrier and decrease the loss of combination process with a certain amount of ZnCdTe alloy in the nanocomposite, resulting in the increase of current density of device.

VI. CONCLUSION

In conclusion, we have successfully synthesized ZnCdTe nanorods and nanoparticles in aqueous solution with changing the stabilizers and synthesis temperature using a facile route. The measurements of PL show the obtained samples have relative narrow photoluminescence FWHM and display few electronic defect PL properties. This new method for synthesizing ZnCdTe nanoparticles and nanorods in aqueous solutions is simple and environmentally friendly compared to organometallic approaches. We investigated the heterostructure device using the prepolymer PPV and ZnCdTe alloy as the emitting layer. The results showed that ZnCdTe alloy could improve the current intensity of the device.

ACKNOWLEDGMENT

We thank the Basic Scientific Research Fund of National Nonprofit Institutes (BSRF 201108) and Beijing Municipal Science & Technology Commission (Nos. 4102046) for the financial support of this work. We thank Beijing Jiaotong University for help with optical property analysis.

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