Investigation of electroluminescence properties of CdTe@CdS core-shell nanocrystals (NCs)

M MOLAEI* and S POURJAFARI†

Department of Physics, Faculty of Science, Vali-e-asr University, Rafsanjan, Iran

†Department of Physics, Faculty of Science, Tarbiat Modares University, Tehran, Iran

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Abstract. In this work, CdTe@CdS NCs were synthesized using a thermochemical approach and synthesized NCs were used as an emissive layer, a light emitting device, with ITO/MoO₃/PVK/CdTe@CdS(core-shell)/Mg:Ag structure. Structural and optical properties of synthesized NCs were investigated by means of XRD, UV-Vis and photoluminescence (PL) analyses. Fabricated device was characterized by electroluminescence spectra. XRD analysis demonstrated cubic phase NCs. Photoluminescence spectra showed a narrow band emission with a peak centred at about 600 nm. Fabricated device showed an emission at 600 nm, which is related to CdTe@CdS NCs. Turn on voltage of fabricated device is about 8 V and brightness is 53.7 Cd/m² at a working voltage of about 14.57 V.

Keywords. CdTe@CdS nanocrystals; photoluminescence; electroluminescence.

1. Introduction

In recent years, semiconductor nanocrystals (NCs) have attracted great attention because of their unique optical and electrical properties, arising from quantum confinement effects (Dabbousi *et al* 1995; Schlamp *et al* 1997; Mattoussi *et al* 1998; Colvin *et al* 2004). As it is reported in several articles, semiconductor NCs demonstrate a large electron affinity, size tunable emission and high thermal and electrical stability (Gao *et al* 2000; Colvin *et al* 2004; Sun *et al* 2007; Rogach *et al* 2008; Molaei *et al* 2012). For these reasons, they are well suited for use in light emitting devices (Colvin *et al* 2004; Dabbousi *et al* 1995). Quantum dot light emitting devices (QD-LEDs) are a new generation of LEDs, which have attracted a great deal of attention in recent years (Colvin *et al* 2004; Dabbousi *et al* 1995). This hybrid organic-inorganic LEDs are taking main advantages of organic LEDs like fabrication ease and flexibility together with the exceptional luminescence properties of the inorganic NCs (Dabbousi *et al* 1995; Colvin *et al* 2004). They also represent a narrow band emission (about 18–30 nm) compared to the polymer and organic light emitting materials (Sun *et al* 2007). Although the efficiency of QD-LEDs is still about one order of magnitude lower than that of purely organic LEDs (around 0.0005–1.0% (Dabbousi *et al* 1995; Schlamp *et al* 1997; Mattoussi *et al* 1998; Gao *et al* 2000; Colvin *et al* 2004; Sun *et al* 2007; Rogach *et al* 2008; Molaei *et al* 2012)), but there are some advantages which merit the future researches in this field. The main ones are spectrally pure emission colour and thermal and electrical stabilities of these structures (Dabbousi *et al* 1995; Schlamp *et al* 1997;

Mattoussi *et al* 1998; Gao *et al* 2000; Colvin *et al* 2004; Sun *et al* 2007; Rogach *et al* 2008; Molaei *et al* 2012).

In this work, CdTe@CdS NCs were synthesized by a new thermochemical method using thioglycolic acid as capping agent molecule. In this method, CdS shell was formed around CdTe shell by a thermochemical reaction between CdSO₄ and Na₂S₂O₃, as we have synthesized CdS using this method previously (Molaei *et al* 2011). After synthesis, photoluminescence properties of synthesized NCs were investigated and these NCs were used as emissive layer in a hybrid light emitting device with ITO/MoO₃/PVK/CdTe@CdS (core-shell)/Mg:Ag structure using MoO₃ as hole injection layer. Electroluminescence properties of fabricated device was investigated and the role of MoO₃ as a hole transport layer was investigated.

2. Experimental

2.1 Materials

NaBH₄ (Merck, 99%), tellurium powder (Merck, 99%), 3CdSO₄·8H₂O (Merck, 99%), thioglycolic acid (Merck, 98%) and Na₂S₂O₃ were prepared from Merck Co., polyvinylcarbazole (PVK) and MoO₃ powder were bought from Sigma-Aldrich. High quality ITO coated glasses were purchased from precision glass and optics (PGO).

2.2 Synthesis of CdTe@CdS NCs

Synthesis of CdTe@CdS core/shell NCs includes two stages.

2.2a Synthesis of CdTe core: Aqueous growth of CdTe NCs results from the reaction of CdSO₄ and NaHTe in presence of thioligands. A solution of CdSO₄ and thioglycolic acid

*Author for correspondence (m.molaei@vru.ac.ir)

(TGA) was prepared, 1 molar solution of NaOH was used to adjust pH value of the solution to 9. NaH₂Te solution was prepared using a reaction between NaBH₄ and Te powder as reported in Liu *et al* (2006). NaH₂Te solution was injected slowly into CdSO₄ solution in presence of Ar gas. The molar ratio between Cd:thiol:Te was 1:2.4:0.5 (He *et al* 2007; Wang *et al* 2007). Prepared solution was heated at 100 °C in silicon oil bath. After the synthesis of CdTe core, CdTe NCs were separated from solution by adding methanol and 3 times centrifugation was carried out at 5000 rpm for 5 min, the precipitated NCs were dispersed in 3 mL of deionized water as CdTe core solution.

2.2b Growth of CdS shell around CdTe core: We have used a new method for growth of CdS shell around CdTe core. Na₂S₂O₃ is a UV and heat sensitive material releasing S species and free electron needed for CdS formation reaction (Sedaghat *et al* 2006). A solution of CdSO₄, TGA and Na₂S₂O₃ was prepared and the concentration of CdSO₄, TGA and Na₂S₂O₃ was 6, 28 and 60 mM, respectively. NaOH was used to adjust pH value of the solution to 9. CdTe core solution was added to this solution. After 1 h refluxing at 100°C, CdTe@CdS core/shell NCs were prepared. Synthesis of NCs with different CdS shell thicknesses is possible only by change of CdSO₄ concentration in this step.

2.3 Fabrication of light emitting device

CdTe@CdS core-shell NCs were used as an emissive layer in a light emitting device with ITO/MoO₃/PVK/CdTe@CdS-(core-shell)/Mg:Ag structure. MoO₃ layer with thickness of 50 nm was deposited using thermal evaporation of MoO₃ powder having a pressure of 2×10^{-4} Pa. PVK layer was subsequently spin-coated on MoO₃ layer and was heated at 100 °C for 1 h. The spin coating parameters were set to result in 80 nm thickness for PVK layer. CdTe@CdS NCs were centrifuged for two times in 6000 rpm, then NCs were dispersed in a solution of methanol:water (2:1) and were spin-coated on PVK layer, the thickness of coated layer was 40 nm. Mg:Ag layer was deposited using thermal evaporation having a pressure of 2×10^{-4} Pa, the corresponding thickness of the coated layer was 200 nm.

2.4 Characterization

X-ray diffraction (XRD) was performed on the centrifuged and extracted particles using a Philips MRD X'pert Pro system. Transmission electron microscope (TEM) images were taken using a Philips CM200 system. Optical transmissions were measured using a Perkin-Elmer Lambda 25 spectrophotometer. Photoluminescence measurements were performed using an Avantes spectrometer (AvaSpec-2048 TEC). Electroluminescence and *I-V* features of devices were measured using a spectraScan 650 system.

Figure 1. XRD patterns of synthesized CdTe and CdTe@CdS NCs.

Figure 2. TEM image of synthesized CdTe@CdS core-shell NCs.

3. Results and discussion

3.1 XRD and TEM analyses

Figure 1 shows XRD patterns of CdTe and CdTe@CdS core/shell NCs. The positions of the three main peaks at 24.55, 40.82 and 47.69° correspond to (111), (220) and (311) crystalline planes of the cubic phase CdTe, respectively which is well matched with the standard card (JCPDS No. 5-0566).

It can be seen that the broad diffractive peaks are typical for NCs. With the growth of CdS shell, the peak positions shift slightly toward larger angles as compared with CdTe core, while the pattern of peak's width and shape remain almost unchanged, which further demonstrates the formation of a core/shell structure rather than an alloyed structure (Talapin *et al* 2004; He *et al* 2008). Additionally, no separate

Figure 3. Absorbance (a) and PL (b) spectra of CdTe and CdTe@CdS NCs (Shell thickness is increased by increase of CdSO_4 concentration).

Figure 4. Energy diagram of fabricated device.

Figure 5. Electroluminescence spectra of fabricated device.

CdS peaks are observed. These results confirm formation of the heterostructure of CdTe/CdS.

Figure 2 indicates TEM image of CdTe/CdS NCs. There is clearly a CdS shell around CdTe cores. According to the inset of figure 2, the core size is about 6 nm and 2 nm CdS shell surrounded the CdTe cores.

3.2 PL and UV-Vis analyses

Figure 3 shows absorbance (a) and photoluminescence (b) spectra of synthesized CdTe@CdS NCs with different CdS shell thicknesses after 1 h refluxing. It can be seen that both the absorption and emission peaks of CdTe/CdS NCs continuously shift to higher wavelengths. This phenomenon can be caused by the increase in size of particles due to the growth of CdS shell. The red shift upon shell growth is the result of decrease in the kinetic energy of the excited electrons and holes in NCs due to the spreading of their wave functions into the shell (Peng *et al* 1997). This red shift also indicates that obtained particles are of a core-shell structure rather than $\text{CdTe}_x\text{S}_{1-x}$ alloyed structure, since the formation of $\text{CdTe}_x\text{S}_{1-x}$ alloyed NCs would lead to a blue shift

in the absorption and PL spectra due to the larger bandgap energy of $\text{CdTe}_x\text{S}_{1-x}$ alloyed NCs compared to pure CdTe NCs (Mekis *et al* 2003; Steckel *et al* 2006). According to PL spectra, PL intensity significantly increased because, the surface traps of CdTe NCs were effectively eliminated by the growth of CdS shell (Peng *et al* 1997). PL intensity reached a maximum value when the thickness of CdS shell increased to a critical threshold. Afterwards, PL intensity started to decrease, possibly due to dislocations and new defects that were formed with further growth of CdS shell resulting from the intrinsic strains due to the lattice mismatch (11.5%) between CdTe and CdS (Peng *et al* 1997). PL full width at half maximum (FWHM) height is increased by the growth of CdS shell which also confirms formation of core-shell structure.

3.3 Investigation on electroluminescence of fabricated device

The electron affinity of CdTe in bulk case is 4.28 eV and the bandgap energy is 1.56 eV (Sharma and Purohit 1974). As a result, the energy level corresponding to the top of valence band is set on 5.84 eV compared to the vacuum level. The effective mass ratio of hole to electron (m^*_h/m^*_e) for CdTe is 4.0 as it was reported in the literature (Sharma and Purohit 1974), therefore, according to the effective mass approximation the change in energy state of electrons in NCs is much higher than that of holes (Brus 1983, 1984). Consequently, the energy level corresponding to the top of valence band would not considerably change. Nevertheless, the energy level corresponding to the bottom of conduction band will shift up. Here, NCs with 2.19 eV bandgap was used for fabrication of light emitting device. Therefore, energy diagram of fabricated device is shown in figure 4. According to the energy diagram, using MoO₃ will decrease the energy barrier for injection of holes from ITO to HOMO energy state of PVK. Energy barrier of the electron injection from the conduction band of CdTe@CdS NCs to LUMO energy state of PVK is 1.35 eV. On the other hand, energy barrier is about 0.04 eV for injection of the holes from HOMO energy states of PVK to the valence band of CdTe@CdS NCs, in this case, the emission should be dominantly belonging to CdTe@CdS NCs. Figure 5 shows electroluminescence spectra of fabricated device at different working voltages. There is a very weak peak at about 410 nm that can be attributed to the emission from PVK (Molaei *et al* 2012) and the strong peak at 600 nm is related to CdTe@CdS NCs. As it is clear, the EL intensity is increased by increasing the working voltage. In figure 6, current density–brightness–voltage (I – B – V) of the fabricated device is shown. Turn on voltage is about 8 V and brightness is 53.7 Cd/m² at working voltage of about 14.57 V.

For investigation of the effect of MoO₃ layer, two devices with and without MoO₃ layer was fabricated. Figure 7 shows current density–voltage features of fabricated devices. Turn on voltage of device without MoO₃ layer is higher than that

Figure 6. Current–brightness–voltage characteristic of fabricated device.

Figure 7. Current density–voltage feature of fabricated devices with and without MoO₃ layer.

for device with MoO₃ layer. It is reasonable, because without MoO₃, the barrier for injection of holes will be increased and therefore, turn on voltage of fabricated device should be increased.

4. Conclusions

CdTe@CdS NCs were synthesized using a thermochemical approach. Photoluminescence spectra showed a narrow band emission with a peak centred at about 600 nm. A light emitting device fabricated using MoO₃ as hole injection layer and CdTe@CdS NCs as emissive layer, fabricated device showed an electroluminescence spectra related to CdTe@CdS NCs and a very weak emission of PVK. Fabricated device showed an emission at 600 nm, which is related to CdTe@CdS NCs. Turn on voltage of fabricated device is about 8 V and brightness is 53.7 Cd/m² at a working voltage of about 14.57 V. Our results showed that without MoO₃ turn on voltage of fabricated device was increased considerably.

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