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Electrochemical synthesis of CdTe nanocrystal/polypyrrole composites for optoelectronic applications

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Electrochemical polymerisation has been found to be a convenient method for the synthesis of a thin film composite of a conducting polymer (polypyrrole) and strongly luminescent CdTe semiconductor nanocrystals. Optimal conditions (relatively low anodic potential, neutral pH, aqueous solution) for the synthesis of uniform high-quality films combining the mechanical, electrical and optical properties of the polymer with the luminescence properties of the semiconductor nanocrystals have been established. It has been shown that insertion of the CdTe nanoparticles into the polypyrrole matrix leads to a significant increase in their electroluminescence quantum efficiency.

Introduction

Conducting polymers have been extensively investigated because of their potential applications in advanced electronic devices.[1] Among them, polyaniline, polypyrrole, polythiophene and their derivatives are of particular importance because they may be obtained through electrochemical polymerisation. Electrochemical polymerisation opens up an opportunity for the one-step formation of polymer thin films with controllable morphology, thickness, doping level (*i.e.* conductivity) *etc.*, which is convenient for a number of applications.[1–3] Since electropolymerisation can be applied to micro- and nanoarea patterning,[3,4] this technique is particularly useful for building up microdevices. Conducting polymers are also known as uniform, transparent, relatively highly conducting matrices for inorganic micro- and nanoparticles.[2,5,6] Composites based on polymers and strongly luminescent semiconductor nanocrystals are considered to be promising materials for optoelectronic applications as light-emitting diodes (LEDs).[2,6–9]

In this paper, CdTe nanocrystal/polypyrrole composites have been produced *via* the electrochemical polymerisation of pyrrole in the presence of CdTe nanocrystals. The conditions leading to the controllable formation of a nanocrystal/polymer composite which combines the mechanical and charge-transport properties of the polymer with the size-dependent luminescence properties of nanocrystalline semiconductors have been established. Polypyrrole (PPy) has been chosen as a hole-conducting material[10] which can be electrochemically polymerised from aqueous solution under conditions that are suitable for nanoparticle stability (neutral pH value and relatively low anodic potential).

Experimental

Aqueous colloidal solutions of CdTe nanocrystals were prepared by the method of Rogach *et al.* reported previously.[11] As stabilisers, either 3-mercapto-1,2-propanediol (thioglycerol, TG), thioglycolic acid (TGA) or a mixture of thioglycerol with 2,3-dimercapto-1-propanol (dithioglycerol, DTG) in the molar ratio 2 : 1 were used. CdTe nanoparticles with sizes from 2.5 to *ca.* 5 nm were found to grow continuously during the prolonged refluxing. There were hints that the thiols, which are initially covalently bound to the particle surface, were decomposed by prolonged heating and became a sulfide source, so the formation of mixed CdTe(S) crystals cannot be excluded.[12] After preparation, the CdTe nanocrystals were subjected to size-selective fractionation[11] to narrow down their size distribution. The resulting sols of 2.5–5 nm particles show pronounced 1s–1s electronic transitions in the absorption spectra (Fig. 1), a relatively narrow FWHM (35–50 nm) and reasonably strong "excitonic" luminescence (up to 20% room temperature quantum efficiency, as measured in comparison with Rhodamine 6G[13]). The luminescence is tunable with particle size due to the quantum confinement effect (Fig. 1). In this paper, CdTe nanocrystals of 3.0 nm average size stabilized by a mixture of TG–DTG were used for the preparation of CdTe/PPy composites. Details of the structural and optical characterization of CdTe nanocrystals can be found elsewhere.[11–15]

Electrochemical measurements were carried out with a Solartron 1286 potentiostat. The electrochemical cell had a standard three-electrode configuration: a glass slide covered by an F-doped tin oxide film (SnO_2–F) with a sheet resistance of *ca.* 10 Ω □$^{-1}$ as the working electrode, Ag/AgCl,Cl$^-$(sat.) reference electrode (0.201 V *vs.* NHE), and a Pt counter-electrode. A 0.5 M aqueous solution of $LiClO_4$ was used as the electrolyte. Polypyrrole was obtained by anodic oxidation of pyrrole monomers in aqueous electrolyte solution, containing 0.1 M pyrrole, under galvanostatic control conditions (1 mA cm^{-2}).

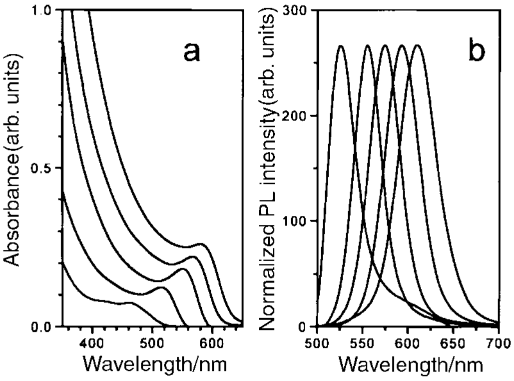

Fig. 1 Absorption (a) and PL ($\lambda_{ex} = 360$ nm) (b) spectra of thiol-capped CdTe nanocrystals of different sizes (2.5–4 nm) in aqueous solutions.

Photoluminescence (PL) and electroluminescence (EL) spectra were measured at room temperature using a Fluoro-Max-2 spectrofluorimeter (SA Instruments). For the EL and electrical measurements, the samples were covered with an aluminium layer of *ca.* 50 nm thickness by the vacuum evaporation technique and inserted into an electric circuit with the positive pole of the voltage source connected to the SnO$_2$–F electrode and the negative one to the Al electrode.

Results and discussion

In order to compare the properties of thin films made from CdTe nanocrystals with those of the CdTe/PPy composites, aqueous colloidal solutions of CdTe nanocrystals were cast onto the surface of SnO$_2$–F or quartz slides by a spray technique. This structure was subsequently dried in air at 70 °C for 1 h. Their UV-Vis and PL spectra were compared to those of CdTe nanoparticles in aqueous solutions. The absorption spectra of the CdTe nanocrystals in solid layers and in solution remained unaltered, whereas the maximum in the PL spectrum of the CdTe film is considerably red-shifted as compared to the PL spectrum of the solution (Fig. 2). The latter spectroscopic phenomenon can be explained in terms of an energy transfer from smaller to larger particles in close-packed nanocrystal layers, as was shown for CdSe nanocrystals.[16] The colloidal solution obtained by re-dispersion of the dried CdTe layer in water shows exactly the same absorption and PL spectra as the initial solution.

In order to establish conditions for the electrodeposition of PPy films in the presence of CdTe nanocrystals, the chemical and electrochemical behaviour of both CdTe nanocrystals and PPy in electrolyte solutions were studied. The nanocrystals studied were found to be reasonably stable in aqueous solutions at pH values no less than 4.5. Shifting the pH to the more acidic region led to irreversible loss of luminescence and to the precipitation of the colloids. At the same time, PPy can successfully be electrodeposited from acidic or neutral aqueous electrolyte solutions. Increasing the pH value leads to overoxidation of the polymer backbone, which gives rise to a decrease in the conjugation length and, hence, to a loss of polymer conductivity.[17] Therefore, neutral aqueous electrolyte solutions seemed to be the most appropriate media for CdTe/PPy composite formation. The stability of the CdTe nanocrystals against electrochemical oxidation was found to be strongly dependent on the nature of the stabiliser used in their synthesis. CdTe nanocrystals stabilised by a mixture of TG–DTG were found to be most stable against electrochemical oxidation in neutral aqueous electrolyte solutions. The onset potential of the pyrrole electropolymerisation was found to be slightly below the region where electrooxidation of TG–DTG-stabilised CdTe nanocrystals, in the form of both colloidal particles in solution and thin solid films, took place (Fig. 3).

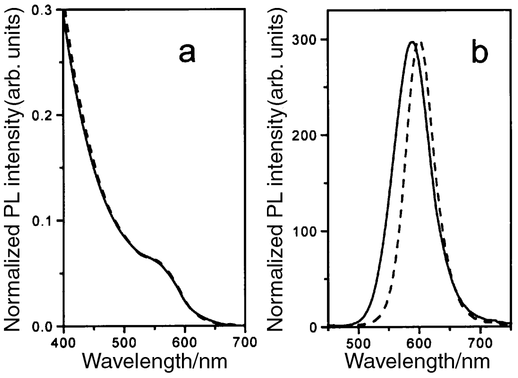

Fig. 2 Absorption (a) and PL ($\lambda_{ex} = 360$ nm) (b) spectra of CdTe nanocrystals in aqueous colloidal solution (solid line) and as a thin solid film on a quartz substrate (dashed line).

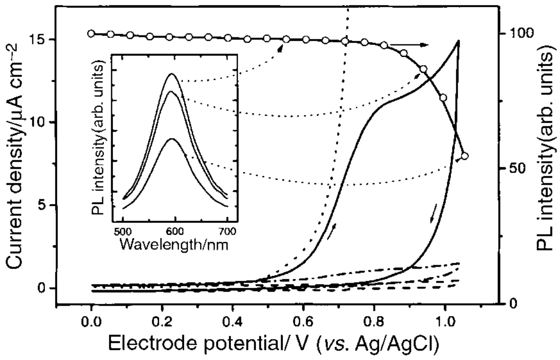

Fig. 3 Polarization characteristics of a SnO$_2$–F electrode covered by a thin film of CdTe nanocrystals in 0.5 M LiClO$_4$ (solid line), a SnO$_2$–F electrode in 0.5 M LiClO$_4$, (dashed line), in a 0.5 M LiClO$_4$ + 10^{-4} M CdTe colloidal solution (dash dot line) and in a 0.5 M LiClO$_4$ = 0.1 M pyrrole solution (dotted line). For the CdTe thin film, the measured *in situ* PL peak intensity at 595 nm (–○–○–) and photoluminescence spectra (insert) are shown. The electrode potential scan rate was 20 mV s^{-1}.

The PL intensity of the TG–DTG-stabilised CdTe nanocrystals deposited on the SnO$_2$–F electrode was only slightly diminished during the anodic polarisation, even when the potential was sufficient for carrying out the pyrrole electropolymerisation, *i.e.* in the 0.6–0.8 V potential region (Fig. 3).

The galvanostatic deposition technique was used for the formation of the CdTe/PPy composite because it is known to be a convenient way of synthesising uniform thin films of conducting polymers with controllable thickness and morphology. However, immediately after the potential was applied to the SnO$_2$–F electrode in the electrolyte solution containing pyrrole, a spike in the potential was observed (Fig. 4). This could be due to the relatively low rate of the initial step, involving a nucleation process in the polymerisation reaction on the surface of the SnO$_2$–F electrode. This spike was found to be as large as 0.95 V, which results in the oxidation of the nanocrystals. The voltage spike was absent when the electrode was precovered with an ultrathin layer of PPy (Fig. 4), due to the autocatalytic nature of the electropolymerisation process of pyrrole,[18,19] which includes the formation of oligomers at the electrode/solution interface.

Based on the results described above, the formation of the CdTe/PPy composite was carried out as follows. The SnO$_2$–F electrode was precovered with an ultrathin film of PPy by applying an anodic current (1 mA cm^{-2}) for 5 s in aqueous solution containing 0.1 M pyrrole and 0.1 M HClO$_4$ (pH 1.04). The thickness of the film, estimated from the charge value,[20] was *ca.* 20 nm. Immediately after electropolymerisation, the film was washed thoroughly with water to remove the excess acid. On the SnO$_2$–F/PPy surface, a thin film of CdTe nanocrystals was formed by spraying the colloidal solution

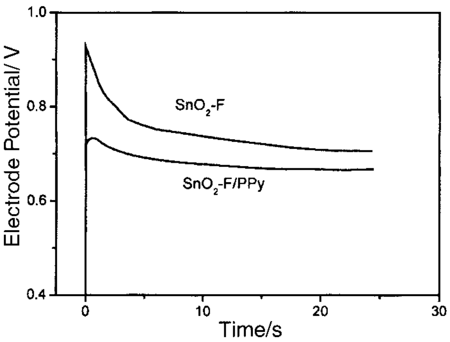

Fig. 4 Potential–time dependence measured with the SnO$_2$–F electrode and a SnO$_2$–F electrode precovered with an ultrathin PPy layer following a current step from 0 to 1 mA cm^{-2} in a 0.5 M LiClO$_4$ + 0.1 M pyrrole solution.

with subsequent drying at 70 °C in air for 1 h. The CdTe film thickness, estimated from its absorption spectrum, was in the range 30–50 nm. Finally, the SnO_2–F/PPy electrode covered with the layer of CdTe nanocrystals was put back into the electrochemical cell, where the polymerisation was continued under 1 mA cm^{-2} for 20 s in an aqueous solution containing 0.1 M pyrrole and 0.5 M $LiClO_4$.

The composites obtained in this way were stable against the dissolution of the CdTe nanocrystals in aqueous media: even 1 h of soaking in water did not result in any evident changes in their PL properties. After completing the polymerisation, the samples were washed with water, dried in air and characterised by UV-Vis (Fig. 5a), PL and EL spectroscopy. In contrast to the PL behaviour of the CdTe nanocrystals in the compact layer (Fig. 2b), a red shift of the PL peak of the CdTe nanocrystals in the composite, compared to the nanoparticles in solution, was not observed (Fig. 5b). One possible explanation might be that the nanoparticles in the composite cannot be considered as closely packed. Under this assumption, the polymerisation of pyrrole most probably occurs in such a way that the CdTe particles become separated from each other as a result of the polymer growth during electrochemical deposition. This should lead to a structure in which all, or almost all, nanocrystals are surrounded (and connected) by conducting polymer, which is an important condition for optoelectronic applications, *e.g.* in LEDs.

Some characteristics of LEDs based on CdTe/PPy composites biased between SnO_2 and Al electrodes are shown in Fig. 6. EL spectra of composites can be recorded at relatively low voltages (*ca.* 3 V), similar to LEDs based on polyaniline (PAni) soaked in colloidal solutions of CdTe nanocrystals.[6] The combination of electron-conducting nanoparticles with hole-conducting polymers into a single composite provides effective charge transport and allows the expansion of the recombination zone over the composite layer. At the same time, the relative value of the EL quantum efficiency (estimated as the integrated EL intensity-to-current ratio) is about twice as high in the new structure. In the CdTe/PPy composites, the fraction of nanocrystals being involved in radioactive recombination processes is obviously higher. Probably, charge transport through the nanocrystals/polymer boundaries is more efficient in the present case because of the closer contact between the individual nanocrystals and the PPy matrix compared to the CdTe/PAni composites studied previously, which were prepared using a polymer casting procedure.[6] The current–voltage and EL–voltage characteristics of the CdTe/PPy composites (Fig. 6a) show features which are typical for LEDs based on nanocrystal/conductive polymer composites.[6,7,9] The possibility of recording EL spectra at low voltages allowed us to observe a pronounced reversible blue shift of the EL emission maximum depending on the electric field applied (Fig. 6b). At voltages more positive than 5.5 V, the shift achieves its largest value. This blue shift of the EL maximum, which was also observed for LEDs based on both CdTe compact layers[12] and CdSe/PPV composites,[7] can be explained in terms of trap filling by carriers injected into the emitting layer[7] or by an electric field influence on the emitting state dipole.

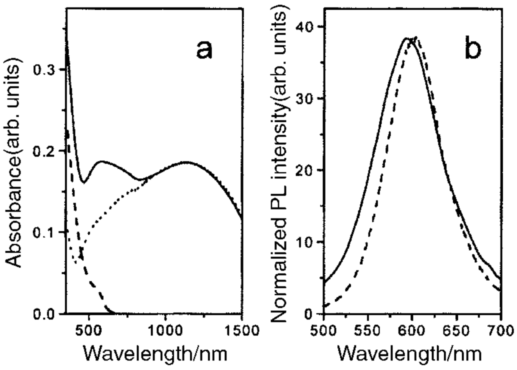

Fig. 5 (a) Absorption spectra of the composite thin film structure (solid line), the thin solid film of CdTe nanocrystals (dashed line) and polypyrrole (dotted line). (b) PL spectra (λ_{ex} = 360 nm) of the composite film (solid line), and the thin solid film of CdTe nanocrystals (dashed line).

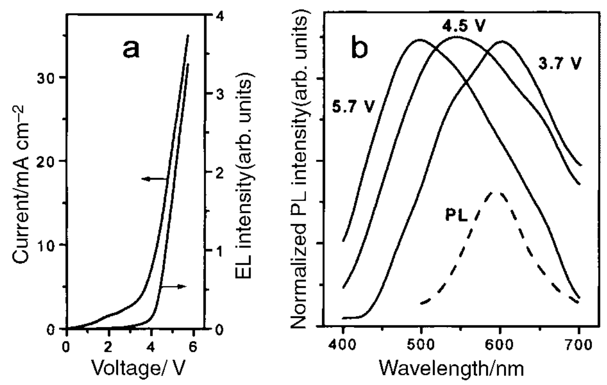

Fig. 6 (a) Voltage dependences of current and integrated EL intensity of a light-emitting structure based on the CdTe/PPy thin film composite. (b) EL spectra (solid lines) of the same structure recorded at different voltages. For comparison, the PL spectrum (λ_{ex} = 360 nm) is shown (dashed line).

In conclusion, the electropolymerisation technique has been shown to be convenient for the fabrication of CdTe nanocrystal/polypyrrole thin film composites combining the mechanical, electrical and optical properties of the polymer with the luminescence properties of semiconductor nanocrystals. The luminescent properties of the composite, in general, can be tuned by using CdTe nanocrystals of different sizes, which is promising for optoelectronic applications. Investigations into micropatterning of the CdTe/PPy composites with differently-sized CdTe particles are currently under way.

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