

# Synthesis and optical properties of CdSe nanoparticles in PVK semiconducting polymer

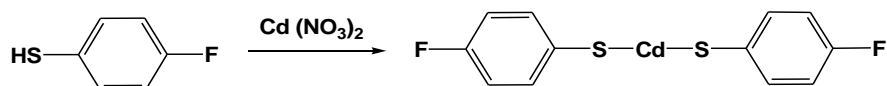
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## Abstract

Semiconducting nanocrystals, or quantum dots, exhibit interesting properties like size-dependent photoemission wavelength over a wide spectral range and high photoluminescence quantum yields [1]. Blends of polymer solutions and nanocrystals in colloidal suspension are very attractive from the point of view of device fabrication since the resulting nanocomposite material combines the optical properties and robustness of inorganic particles with the ease of processing and flexibility of polymers [2,3]. Poly(N-vinylcarbazole) (PVK) is a hole transport polymer exhibiting an emission spectrum that, owing to the properties of carbazole groups, covers the entire blue region. CdSe is an II-VI semiconductor with a 1.74 eV bandgap which is suitable for integration in optoelectronic devices operating in the visible wavelength range.

Based on the method reported in [4] we have performed the synthesis of CdSe nanocrystals capped with Fluorothiophenol (ShPhF) introducing several variations in the procedure. 640  $\mu$ l of SHPhF were dissolved in 10 ml of methanol and 308 mg of  $\text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  were dissolved in 2 ml of water and 8 ml of methanol. The  $\text{Cd}(\text{NO}_3)_2$  solution was added to the SHPhF solution resulting in a white precipitate according to the following reaction:



The precipitate was washed with methanol and centrifuged three times. The washed precipitate was vacuum dried and the resulting powder was analyzed by X-ray photoelectron spectroscopy with a Phi 5500 ESCA system, which confirmed the chemical composition of the powder. The  $\text{Cd}(\text{FC}_6\text{H}_5\text{S})_2$  complex contains both the cadmium atoms for the subsequent CdS synthesis and the organic molecule for the capping.

52 mg of the  $\text{Cd}(\text{FC}_6\text{H}_5\text{S})_2$  powder was dissolved in 20 ml of dimethyl sulfoxide (DMSO) and 0.1 ml of a elemental Se 0.1% solution in toluene were added to the  $\text{Cd}(\text{FC}_6\text{H}_4\text{S})_2$  resulting in an optically clear yellow solution indicating the formation of CdSe quantum dots. Bright yellow fluorescence of this solution could be observed under UV light ( $\lambda=365\text{nm}$ ) illumination. The nanocrystals remained stable during months showing no change in luminescence intensity and wavelength. The synthesis of the CdS nanocrystals using the  $\text{Cd}(\text{FC}_6\text{H}_4\text{S})_2$  complex has a major advantage compared to other cadmium salts: the molecule contains both the cadmium atoms and the organic radical for the capping leaving no residual after reaction with elemental selenium.

Three blends of CdSe quantum dots and PVK 0.3% in toluene were obtained by mixing different volumes of the respective solutions according to the following proportions: 25% vol. PVK : 75% vol. CdSe, 50% vol. PVK : 50% CdSe and 75% vol. PVK : 25% vol. CdSe (samples 1:3, 1:1, 3:1 respectively). An aliquot of the starting CdSe nanocrystal and PVK solutions were kept for reference purposes (samples 0:1 and 1:0 respectively).

Transmission electron microscopy (TEM) images were obtained with a Philips CM30 microscope operating at 300 kV. The absorbance spectra were recorded with a Shimadzu UV-1603 spectrometer. TEM images of the quantum dots prior to the mixing with the polymer were obtained in order to determine the size and the quality of the nanoparticles. The images show isolated nanoparticles with an average size about 4 nm. Since the Bohr radius of CdSe is about 5 nm [1], we expect to observe the effects of the quantum confinement in the optical characterization measurements. Photoluminescence (PL) spectra were obtained by means of a Photon Technology International fluorimeter.

The optical absorption of the nanocomposite solution as well as the reference samples is presented in fig. 1. The spectrum of the pure quantum dot solution (sample 0:1) shows an excitonic peak at an energy  $E = 3.06\text{ eV}$  ( $\lambda = 406\text{ nm}$ ) which is far from the bandgap energy of bulk CdSe (1.74eV). This shift indicates that strong quantum confinement has been achieved, as expected from the TEM observations.

The absorption spectrum of the bare PVK solution (sample 4:0), depicted in the same figure, shows an absorption edge located at 3.7 eV ( $\lambda = 335$  nm). The spectra of the blends of the two solutions show an increasing absorbance of the excitonic peak related to the quantum dots as the amount of CdSe is increased (samples 1:3, 2:2, 3:1).

Photoluminescence (PL) measurements of the reference samples and blends were performed using an excitation wavelength at 370 nm. The recorded spectra are presented in fig.3. The luminescence spectrum of the pure PVK solution (sample 4:0) is dominated by a peak located at 3.1 eV (400 nm) while the pure quantum dot solution sample (0:4) shows a broad peak found at 2.42 eV (513nm). The PL spectra of the blends display the characteristics of the emission from the two species. Note that although the PVK intensity decreases gradually as the PVK amount is reduced, the intensity change of the CdSe peak is weaker compared to that of PVK. This observation could be related to a Förster-type energy transfer from PVK to CdSe [5]. This kind of energy transfer requires an overlap between the emission spectrum of donor and the absorption spectrum of the acceptor. In our case, the overlap is evident since the PL peak of the polymer is located at 3.1 eV and the excitonic peak of the nanocrystals has a maximum at 3.06eV. Thus, this diluted nanocomposite shows the potential to be used as active layer for optoelectronic devices.

## References

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## Figures

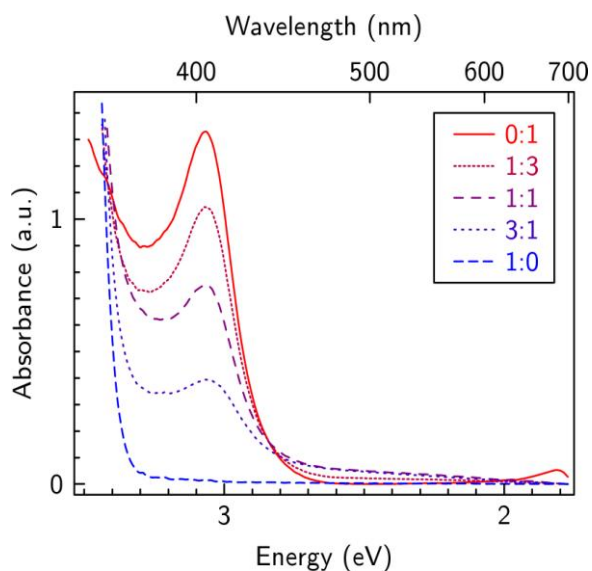


Fig. 1. Optical absorption spectra of pure CdSe nanocrystal (0:4), pure PVK (4:0) and blends of 25% PVK:75% CdSe (1:3), 50% PVK:50% CdSe (1:1) and 75% PVK:25% CdSe (3:1).

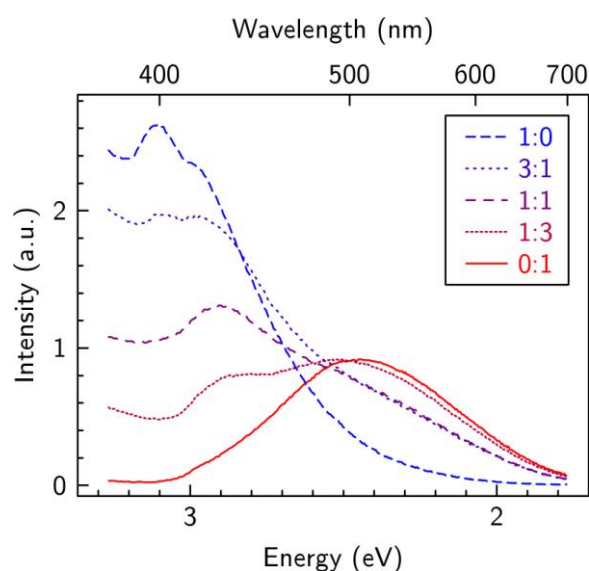


Fig. 2. PL spectra of pure CdSe nanocrystal (0:4), pure PVK (4:0) and blends of 25% PVK:75% CdSe (1:3), 50% PVK:50% CdSe (1:1) and 75% PVK:25% CdSe (3:1).