

Effect of Surfactant on the Morphology of Nanocrystal – Polymer Composite Films

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Introduction

Organic solar cells offer the possibility of inexpensive and efficient energy conversion, and one design currently being investigated is the nanoparticle bulk heterojunction cell. In this type of cell, inorganic semiconductor nanoparticles are dispersed in a semiconducting conjugated polymer to create the cell's active layer. One challenge limiting the efficiency of bulk heterojunction cells is the film morphology. For the device to be efficient, percolation must be achieved for both the nanoparticle and the polymer phases. This is accomplished with a uniform dispersion of nanoparticles in the film.

A popular method for fabricating nanoparticles is the hot injection method, which produces particles capped with a surfactant layer, typically TOPO. However, this capping molecule can be changed through surface exchange reactions, allowing for control of the surfactant groups present in the film. In this work, the effect of two different capping molecules on surface morphology is studied for cadmium selenide nanoparticles dispersed in P₃HT polymer.

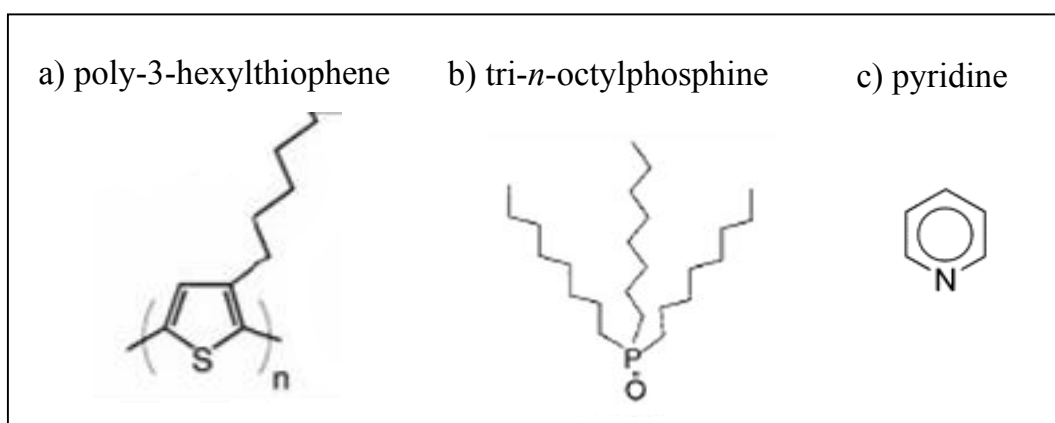


Figure 1. Chemical structures.

Experimental

The organic materials investigated in this work are shown in Figure 1. P₃HT is commercially

available from Aldrich. Selenium, tri-*n*-octylphosphine (TOP), and TOPO were purchased from Aldrich. The synthesis of TOPO-capped CdSe nanoparticles has been reported elsewhere in detail [1]. After growth, the nanoparticles were recovered through centrifugation and washed with methanol to remove excess surfactant. The surface exchange reaction was performed by dissolving the nanoparticles in pyridine and precipitating in hexane. Repeating this process several times effectively replaces the TOPO on the nanoparticle surface with pyridine [2]. The nanocrystals were characterized by TEM (Philips CM 200,200V) and photoluminescence. Thin films of CdSe:P₃HT were made by spin casting a solution of CdSe nanocrystals and P₃HT (60:40 weight ratio) in a pyridine-chloroform binary solvent mixture onto an indium tin oxide (ITO) coated glass substrate. The morphology of the blend films was characterized via AFM using a Nanoscope IIIa from Digital Instruments.

Results and Discussions

As shown in Figure 2 a), the surface roughness of composite films fabricated with TOPO-capped nanocrystals decreases as the percentage of pyridine in the solvent mixture increases. This is believed to occur due to surface exchange taking place in the composite solution prior to film deposition. This exchange happens to a higher degree with a higher pyridine concentration in the solution. However, an increase of pyridine content beyond 50% results in poor solutions and films, as P₃HT is poorly soluble in pyridine, resulting in polymer precipitation from the solution. Representative AFM images of these films are shown in Figure 3 a-c.

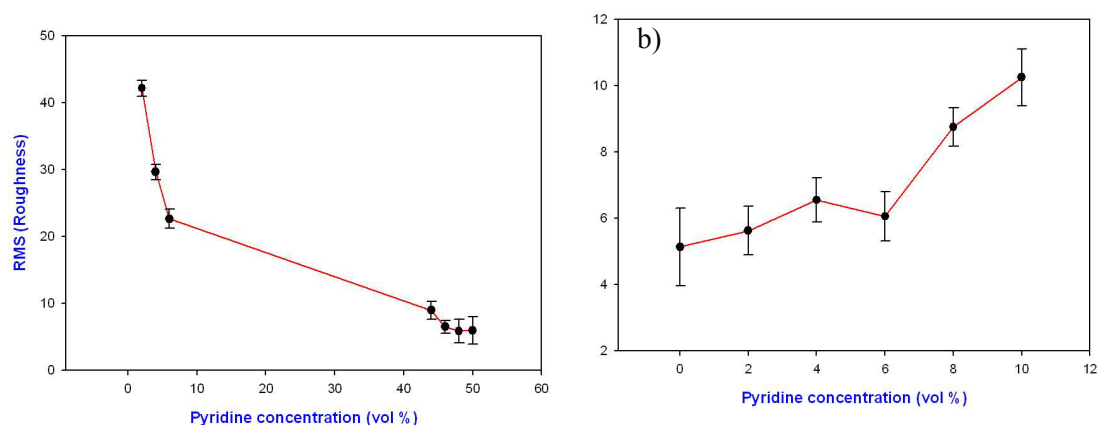


Figure 2. Surface roughness of CdSe:P₃HT composite films in pyridine:chloroform solvent with varying pyridine concentration. a) TOPO-coated CdSe, b) pyridine-coated CdSe.

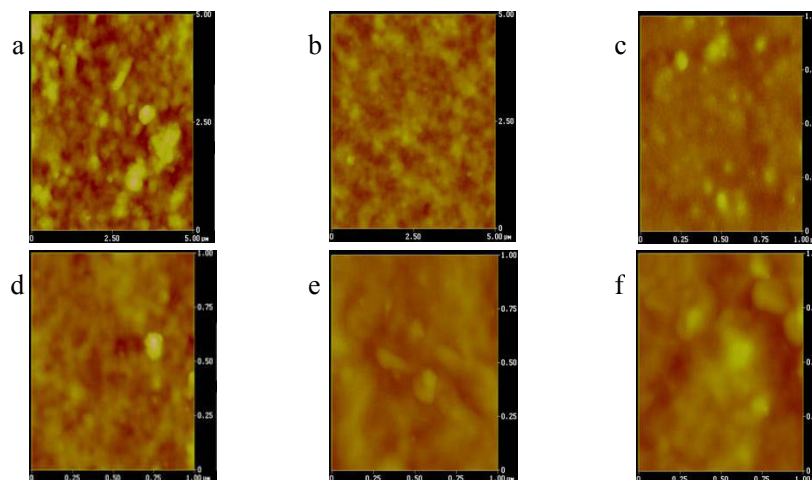


Figure 3. AFM images of composite films of CdSe:P₃HT in pyridine:chloroform solvent with varying pyridine volume fraction. Images a)-c) are TOPO-coated nanoparticles, images d)-f) are pyridine-coated nanoparticles. Pyridine volume percentages are a) 2%, b) 6%, c) 50%, d) 2%, e) 6%, f) 10%.

Composite films spin-coated from mixtures of pyridine-coated nanocrystals and polymer showed lower surface roughness with a smaller amount of pyridine present in the solvent mixture, as shown in Figure 2 b). Because the pyridine surface exchange process was performed prior to mixing the composite solution, an excess of pyridine in the solution is no longer needed. In fact, even films spin-coated from 100% chloroform solvent show surface roughness of below 10 nm. For these films, shown in Figure 3 d-f, an increase in pyridine concentration results in an increase in surface roughness. As previously noted, this is due to the poor solubility of P₃HT in pyridine.

Photoluminescence measurements on nanoparticle powders showed significant quenching in the case of pyridine-coated particles, shown in Figure 5. This quenching is due to a charge-transfer pathway being established to allow separation of electrons and holes generated by laser excitation [3]. This demonstrates that pyridine provides a more efficient charge-transfer pathway to and from the particles as compared to TOPO.

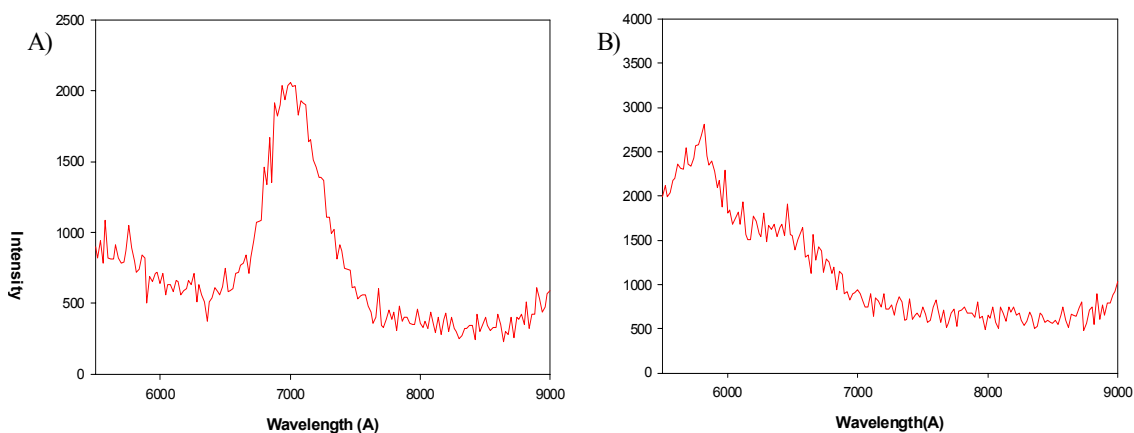


Figure 5. Photoluminescence spectra from nanoparticle powders. A) TOPO-coated nanoparticles. B) Pyridine-coated nanoparticles.

Conclusions

Investigation of the surface roughness of bulk heterojunction films has been performed. It has been shown that for TOPO-coated CdSe nanoparticles in P₃HT surface roughness of less than 10 nm can be achieved using a 1:1 solvent mixture of chloroform and pyridine. Using pyridine-coated CdSe nanoparticles, sub-10 nm roughness is achieved using a pyridine concentration of less than 10% in the solvent. In addition to being compatible with low pyridine content solvents, the pyridine-coated particles provide charge transfer pathways to allow efficient transport between the nanoparticle and polymer.

Acknowledgements

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References

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