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Controlled placement of polystyrene-grafted CdSe nanoparticles in self-assembled block copolymers

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ABSTRACT

Surface functionalization of semiconductor CdSe nanoparticles has been achieved with polystyrene (PS) brushes by “grafting from” technique for further addition to a polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymer in order to obtain self-assembled composites. For modification of nanoparticle surface 3-

glycidoxypropyltrimethoxysilane (GPS) was used at first for the later attachment of the 4,4'-azobis(4-cyanopentanoic acid) (ACP) azo initiator. Fourier transform infrared spectroscopy (FTIR) confirmed the presence of GPS and PS on the surface of nanoparticles. Atomic force microscopy (AFM) was used for morphological characterization of SBS/CdSe nanocomposites. Modification of nanoparticles with PS brushes by radical polymerization improved their affinity with PS block and the dispersion of nanoparticles avoiding agglomeration. CdSe nanoparticle size was measured to be around 2 nm by the use of X-ray diffraction (XRD) and UV-vis techniques. Optical properties were characterized using fluorescence measurements.

1. INTRODUCTION

Semiconductor nanoparticles have unique optical and electronic properties due to the quantum confinement of the exciton to a distance shorter than the Bohr radius [1]. These nanoparticles are interesting in research fields ranging from biotechnology to microelectronics [2-4]. However, in order to take advantage of these properties, the most useful problem lies in controlling the size, spacing and size distribution of the nanoparticles.

Engineering the self-assembly of inorganic nanoparticles within block copolymer nanodomains is useful for the design of periodic structures to form materials with enhanced mechanical strength as well as to achieve unique optical, electronic and magnetic properties on the nanometer scale. Block copolymers are a versatile platform material because they can self-assemble into various periodic structures for proper compositions and under adequate conditions, owing to the microphase separation between dissimilar blocks [5-7]. To overcome the problem of the nanoparticles tendency to aggregate because of their high surface area and surface energy and to facilitate their dispersion in a selected block of a block copolymer and avoid macrophase separation different routes have been used [5, 7-9]. Peponi et al. [5] used surfactants to disperse conductive silver nanoparticles in the desired domains of polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymers. Emrick et al [7-9] used different strategies to disperse CdSe nanoparticles in block copolymers. In one hand, they controlled the surface hydrophobicity by using different surfactants in order to disperse CdSe nanoparticles in polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP)

block copolymer, creating hierarchically ordered patterns with CdSe nanoparticles located in PS or P2VP domains depending on the surfactant used [7, 8]. On the other hand, they used electrophoretic deposition [9] to place CdSe nanoparticles in diblock copolymer templates.

Among different strategies used to modify particles with polymers one of the most effective ones is the grafting of polymers either through physical adsorption [10-11] or by covalent bonding of the polymer chain. Non-covalent interaction, physisorption, makes the processing of particles difficult and hence, covalent bonding is preferable in many cases [12].

There are essentially two techniques to chemically graft polymers on a solid surface. One is “grafting to” method where suitable end-functionalized polymers are covalently attached to appropriate nanoparticle surface sites [13] and the other is the “grafting from” technique which consists of *in situ* growth of polymer chains from initiators immobilized on the surface of the nanoparticles [14]. The “grafting to” technique has the disadvantage of the difficult diffusion of reactive chain-ends to the surface at high graft densities while in “grafting from” technique the compounds that have to diffuse have low mass.

The aim of this work is to confine semiconductive CdSe nanoparticles in PS domains of self-assembled SBS block copolymer. Our group has previously confined conductive Ag nanoparticles in PS domains of SBS copolymer by using surfactants [5], so that was the first route used with benzyldimethylhexadecylammonium chloride and trimethylhexadecylammonium chloride as surfactants (the dodecanethiol surfactant used in the previous work was immiscible with water, the solvent used in the synthesis) but no confinement was obtained and aggregates were found to form. To overcome this problem the followed route has been the synthesis of semiconductive CdSe nanoparticles functionalized with PS chains polymerized by “grafting from” technique (CdSe-PS) in order to improve the affinity between nanoparticles and PS block. Once CdSe-PS nanoparticles have been obtained they have been confined in PS domains of SBS copolymer, as shown by atomic force microscopy (AFM).

2. EXPERIMENTAL SECTION

2.1. Materials

2-Mercaptoethanol (ME), cadmium sulfate hydrate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$), selenium metal powder (Se), sodium sulfite (Na_2SO_3) and N,N-dimethylformamide (DMF) were purchased from Panreac and used without further purification. 3-glycidoxypropyltrimethoxysilane (GPS), 4,4'-azobis(4-cyanopentanoic acid) (ACP), α -picoline and styrene monomer (St) were supplied by Aldrich. Styrene monomer (99%) was distilled under reduced pressure over CaH_2 before use. Polystyrene-block-polybutadiene-block-polystyrene (SBS) linear triblock copolymer (Dynasol C540), that contains 40 wt % polystyrene, was kindly supplied by Repsol-YPF. M_n of PS and PB blocks was around 30,000 and 45,000 g/mol respectively

2.2.Synthesis of ME capped CdSe nanoparticles

Mercaptoethanol stabilized CdSe nanoparticles were prepared in aqueous solution [15]. Typically, freshly prepared Na_2SeSO_3 solution was added to nitrogen saturated CdSO_4 solution at pH 9.0 in the presence of mercaptoethanol as stabilizing agent to achieve CdSe precursor. The precursor was maintained at the desired temperature in reflux to control the growth of nanoparticles.

2.3.Introduction of azo groups onto CdSe nanoparticles

The introduction of the azo initiator onto surface of CdSe nanoparticles was performed according to the method described by Tsubokawa et al [16]. In the first step, the surface of CdSe nanoparticles was treated by GPS from 5% solution in DMF for 8 h. CdSe nanoparticles were washed with methanol. After this surface treatment ACP was introduced on the surface of the nanoparticles. The particles were dispersed in a 2% solution of ACP in DMF with α -picoline, which was used as catalyst, at 50 °C for 5 h. The resulting CdSe nanoparticles with the azo initiator bound to the surface were washed with THF.

2.4.Polystyrene graft polymerization

DMF suspension of CdSe nanoparticles with initiator attached to the surface was kept in a glass reactor under nitrogen atmosphere with a magnetic stirrer. St monomer was added to the reactor and stirred vigorously at 72 °C for different times.

2.5.Nanocomposite preparation

The samples for AFM were prepared by casting toluene solutions of a mixture of 5 wt % SBS and different percentages of CdSe-PS nanoparticles, in this case 0.5 and 3 wt % CdSe-PS nanoparticles, and solutions of neat block copolymer onto glass substrates. The samples were annealed for 24 h at 102 °C under vacuum after 24 h at room temperature for solvent removal. Previous rheological and morphological studies of SBS block copolymer set this annealing treatment as adequate in order to obtain a self-ordered structure [17].

2.6. Characterization

Fourier transform infrared spectroscopy spectra were carried out in a Nicolet Magna IR system 750 spectrometer. Spectra were taken with a 2 cm⁻¹ resolution in a wavenumber range from 4000 to 400 cm⁻¹. Nanoparticles were pressed together with KBr to form pellets and before measurements they were dried under vacuum.

UV-vis measurements were taken using a Jasco V-630 spectrophotometer in a scan range from 275 to 700 nm. Optical absorption studies were carried out by dispersing nanoparticle powder in different solvents and using the respective solvent as the reference.

Photoluminescence spectra (PL) were measured using a Felix32 spectrophotometer of Photon Technology International (PTI). Spectra were obtained from CdSe nanoparticles dispersed in different solvents in standard quartz cuvettes.

Thermogravimetric analysis (TGA) was performed with a TGA/SDTA851 (Mettler Toledo) under nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 600 °C. Samples were prepared by drying under vacuum oven for solvent removal.

X-ray powder diffraction (XRD) patterns were collected by using a Philips X-Pert automatic diffractometer operating at 40 kV and 40 mA, in theta-theta configuration, secondary monochromator with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a PIXcel solid state detector. Samples were mounted on a zero background silicon wafer fixed in a generic sample holder. Data were collected from 10 to 70° 2 θ (step size = 0.026 and time per step = 30 s) at room temperature. A fixed divergence and antiscattering slit giving a constant volume of sample illumination were used. Removal of the instrumental broadening was done collecting a pattern LaB₆ standard. The X-ray

powder pattern of LaB6 standard was collected in the same diffractometer conditions, the obtained data were fitted with the Rietveld method using the FULLPROF program [18, 19].

Atomic force microscopy images were obtained in tapping mode with a scanning probe microscope (Nanoscope IIIa Multimode, Digital Instruments) equipped with an integrated phosphorous doped tip/cantilever having a resonance frequency of approximately 75 kHz and a spring constant of about 3 N/m; the tip radius was lower than 10 nm. Images show in the left part the surface morphology and in the right part the simultaneously taken phase image.

3. RESULTS AND DISCUSSION

The synthesis scheme of ACP functionalized CdSe nanoparticles is shown in scheme 1. CdSe nanoparticles capped with mercaptoethanol stabilizing agent on the surface were synthesized in water following previous synthesis methods [15]. Glycidoxy groups were attached to the surface of CdSe nanoparticles by the reaction of surface hydroxyl groups with GPS. The introduction of the initiator azo groups onto the surface of the nanoparticles was achieved by reaction of the glycidoxy groups with ACP.

XRD and UV-vis measurements were used to characterize mercaptoethanol capped CdSe nanoparticle crystalline structure and size respectively. The obtained sizes for CdSe nanoparticles were orientative but these techniques had been widely used in recent researches obtaining good agreement with more accurate techniques as TEM [15,20]. XRD spectrum is shown in Fig. 1. Cubic crystalline structure was set for CdSe nanoparticles as was observed in previous works [21]. An average size of around 2 nm was obtained for ME-capped CdSe nanoparticles using Scherrer formula [22]. A very small nanoparticle size, as the broad width of the (111) plane peak suggested.

As it can be seen in UV-vis measurements, Fig. 2, the three samples (ME-capped nanoparticles, GPS functionalized nanoparticles and nanoparticles with polystyrene brushes) showed an absorption at about 365 nm. The almost same location of the absorption band indicated that the size of CdSe nanoparticles remained nearly constant during the synthetic process in a distinct way than that for previous functionalization with other silane [21]. However, a small blue shift was observed, which could be produced because of the elimination of the biggest CdSe nanoparticles by centrifugation

in the different cleaning processes. In addition it was seen that through the different functionalisation reactions the second transition shown at first was lost, probably due to the fact that nanoparticles lost part of their structure during functionalisation. The size of the particles was obtained from the peak positions. One can estimate the average size of CdSe nanoparticles from equation 1 [23].

$$D = (1.6122 \times 10^{-9}) \lambda^4 - (2.6575 \times 10^{-6}) \lambda^3 + (1.6242 \times 10^{-3}) \lambda^2 - (0.4277) \lambda + (41.57) \quad (1)$$

where D is the average diameter of CdSe quantum dots and λ is the wavelength of the absorption peak. The diameter of the obtained CdSe nanoparticles was around 2 nm, which agrees with the size estimated from XRD diffractograms.

FTIR was used to confirm the functionalization of nanoparticles with the different organic ligands used. Fig. 3 shows FTIR spectra of ME-capped nanoparticles, CdSe nanoparticles functionalized with GPS and PS grafted CdSe nanoparticles. The absence of S-H stretching band at around 2560 cm^{-1} confirmed the bonding between Cd^{2+} and ME and breaking of -SH bond in the case of ME-CdSe. -OH group stretching (3400 cm^{-1}), -CH₂ bending vibrations (1419 cm^{-1}) and C-O primary stretching (1050 cm^{-1} and 1000 cm^{-1}) were the observed characteristic peaks for mercaptoethanol. The disappearance of the -OH stretching band at 3400 cm^{-1} is a confirmation of the condensation reaction between the hydroxyl groups of ME and the glycidoxy groups of GPS. The strong absorption peak at around 1087 cm^{-1} which corresponds to the overlapping of asymmetric stretching vibration of Si-O-Si and Si-O-C bands from the trimethoxysilane groups of GPS certified the presence of the silane on the surface of CdSe nanoparticles [24].

Furthermore, PS-CdSe nanoparticle FTIR spectrum showed strong absorption bands indicative of the grafted polystyrene aromatic rings as C-H aromatic stretching vibration ($3030\text{-}3000 \text{ cm}^{-1}$), C-C stretching frequency of ring in plane (1600 cm^{-1}), stretching vibration of ring in plane (1500 cm^{-1}) and C-H out-of-plane bending vibration of ring (700 cm^{-1}), thus confirming the presence of the polymer on the surface of the nanoparticles [25].

Photoluminescence measurements were made to analyze optical properties of PS-CdSe nanoparticles. Fig. 4 shows PL emission spectra of ME-CdSe and PS-CdSe nanoparticles. In both cases strong emission peaks were observed with maxima located around 560 nm and 530 nm, respectively. As shown above, this blue shift of the

emission maxima could be due to loss of the bigger nanoparticles of the solution. An increase in the emission peak strength and width occurred for CdSe nanoparticles with PS brushes compared with ME-capped nanoparticles. This increase of the intensity and width are probably due to changes in the surface of CdSe nanoparticles, with the presence of polystyrene brushes [26].

Grafting density was obtained using Sun et al [25] method. PS polymer chains molecular weight was obtained by GPC analysis, which was calculated to be of 20,000 g/mol. The weight loss of the PS attached to the surface of CdSe nanoparticles was calculated by the use of thermogravimetric analysis, shown in Fig. 5. For comparison it can be also seen the thermogram of CdSe nanoparticles modified with the silane group. The graft density of PS on the surface of CdSe nanoparticles was 0.17 PS chains per nm^2 . Due to the low grafting density and the lower molecular weight of the brushes comparing with the molecular weight of the PS block of the copolymer it is supposed that the matrix PS block could wet well the nanoparticle brushes [27].

Fig. 6 shows AFM height and phase images of annealed neat SBS film. A self-ordered structure due to microphase separation can be seen. A lamellar self-assembled structure of SBS perpendicular to the substrate, with a lamellar periodicity of around 30 nm where dark regions are PB blocks and light regions PS block domain (PS block is harder at room temperature) was observed. It can be seen that the value of the phase profile kept almost constant. As a first attempt, neat nanoparticles, only stabilised with mercaptoethanol, were added to the block copolymer. As the nanoparticles were not soluble in toluene a good mixture was not obtained, being nanoparticles placed at the bottom of the flask and making the proper preparation of the composite impossible.

As commented previously, the first route followed to modify the surface and disperse the CdSe nanoparticles through the polystyrene phase of the block copolymer was the use of surfactants. To functionalise the nanoparticles with ammonium salts as surfactants the method used by Zhao et al [28] was followed. As can be seen in Fig. 7, dispersion of nanoparticles was poor, with the presence of big agglomerates.

To improve these results CdSe-PS nanoparticles were used. For 0.5 wt % SBS/CdSe-PS nanocomposites (Fig. 8a), the morphology of SBS matrix was not significantly altered compared with that of neat SBS film. Small bright CdSe-PS nanoparticles can be observed in both phase and height images. As can be seen in the magnification of the

AFM image (Fig. 8b) the bright points were all located in the PS phase. While in the case of the lamellas the value of the phase intensity was of around 15, the value for the bright points was of around 40, thus indicating that the places where the bright points were located were harder than the copolymer. This could be probably due to the presence of the nanoparticles, which could allow to conclude that nanoparticles were selectively confined in the PS block of the copolymer. Taking into account CdSe nanoparticle size calculations by UV-vis and XRD measurements, the diameter is too small to achieve such big bright points. The aggregation of various nanoparticles into PS domains would be the explanation for this phenomenon. Nevertheless, lamellar nanostructuring of SBS block copolymer was not disturbed despite the dispersion of PS-CdSe nanoparticles and their agglomeration.

In the case of 3 wt % SBS/PS-CdSe nanocomposite (Fig. 9), the morphology of neat SBS block copolymer was still kept with lamellar nanostructure. An increase in the number of bright PS-CdSe nanoparticles can be seen in the PS block domains with respect to 0.5 % SBS/PS-CdSe composite. In the phase profile could be seen that the value of the phase intensity increased up to the double when there was a nanoparticle agglomeration. While the size of the point was not big enough the width of the lamellas kept constant but when it was big enough the lamella of the polybutadiene had to make a curve surrounding the point instead of following the straight line as can be seen in the magnification of the AFM image in Fig. 10.

4. CONCLUSIONS

An efficient method for obtaining nanocomposites based in semiconductive CdSe nanoparticles has been developed. After failing in the attempt of using surfactants to confine the nanoparticles in PS domains, the route of grafting polystyrene to the surface was followed. To improve the affinity of nanoparticles for one of the blocks of SBS, brushes of PS with a graft density of 0.17 chain/nm² were anchored onto CdSe nanoparticles via “grafting from” technique by radical polymerization. Fluorescence measurements showed that PS-CdSe nanoparticles had good optical properties. Constant maintenance of nanoparticle size during different surface functionalization steps was confirmed by UV-vis absorption spectra. An SBS copolymer able to nanostructure in a lamellar morphology was used as matrix. Polymerization of PS brushes on the surface of the nanoparticles improved the affinity of CdSe nanoparticles

for PS domains and facilitated their segregation in PS block of the copolymer without breaking the lamellar nanostructure of the neat block copolymer. AFM studies showed the location of PS-CdSe nanoparticles on the PS block lamellas. A higher phase intensity was detected in the areas where the nanoparticles were located, up to the double of the copolymer phase value. Local widening or disruption of the nanostructure was seen due to the presence of some agglomerates bigger than PS lamella width.

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REFERENCES

1. Alivisatos AP (1996) Semiconductor clusters, nanocrystals, and Quantum Dots. *Science* 271: 933-937
2. Weiss EA, Chiechi RC, Geyer SM, Porter VJ, Bell DC, Bawendi MG, Whitesides (2008) GM. Size-dependent charge collection in junctions containing single-size and multi-size arrays of colloidal CdSe Quantum dots. *J Am Chem Soc* 130: 74-82
3. Klimov VI. (2007) Spectral and dynamical properties of multiexcitons in semiconductor nanocrystals. *Annu Rev Phys Chem* 58: 635-673
4. Chen X, Hutchinson JL, Dobson PJ, Wakefield G (2008) A one-step aqueous synthetic route to extremely small CdSe nanoparticles. *J Colloid Interf Sci* 319: 140-143
5. Peponi L, Tercjak A, Gutierrez J, Stadler H, Torre L, Kenny JM, Mondragon I (2008) Self assembling of SBS block copolymers as templates for conductive silver nanocomposites. *Macromol Mat Eng* 293: 568-573
6. Lo CT, Lee B, Winans RE, Thiyagarajan P (2006) Effect of dispersion of inorganic nanoparticles on the phase behavior of block copolymers in a selective solvent. *Macromolecules* 39: 6318-6320
7. Lin Y, Böker A, He J, Sill K, Xiang H, Abetz C, Li X, Wang J, Balazs A, Russell TP (2005) Self-directed self-assembly of nanoparticle/copolymer mixtures. *Nature (London)* 434: 55-59
8. Zou S, Hong R, Emrick T, Walker GC (2007) Ordered CdSe nanoparticles within self-assembled block copolymer domains on surfaces. *Langmuir* 23:1612-1614
9. Zhang Q, Xu T, Butterfield D, Misner MJ, Ryu DY, Emrick T, Russel TP (2005) Controlled placement of CdSe nanoparticles in diblock copolymer templates by electrophoretic deposition. *Nano Lett* 5: 357-361
10. Hadziioannou G, Patel S, Granik S, Tirrell M (1986) Forces between surfaces of block copolymers adsorbed on mica. *J Am Chem Soc* 108: 2869-2876
11. Saleh N, Phenrat T, Sirk K, Dufour B, Ok J, Sarbu T, Matyjaszewski K, Tilton RD, Lowry GV (2005) Adsorbed triblock copolymers deliver reactive iron nanoparticles to the oil/water interface. *Nano Lett* 5: 2489-2494

12. Ladmiral V, Morinaga T, Ohno K, Fukuda T, Tsujii Y (2009) Synthesis of monodisperse zinc sulfide particles grafted with concentrated polystyrene brush by surface-initiated nitroxide-mediated polymerization. *Eur Polym J* 45: 2788-2796
13. Synytska A, Ionov L, Minko S, Motornov M, Elchorn K, Stamm M, Grundke K (2004) Tuning wettability by controlled roughness and surface modification using core-shell particles. *Polym Mater Sci Eng* 90, 624-625
14. Wang TL, Yang CH, Shieh YT, Yeh AC (2009) Synthesis of CdSe–Poly(N-vinylcarbazole) nanocomposite by atom transfer radical polymerization for potential optoelectronic applications. *Macromol Rapid Commun* 30: 1679-1683
15. Rogach AL, Kornowski A, Gao M, Eychmüller A, Weller H (1999) Synthesis and characterization of a size series of extremely small thiol-stabilized CdSe nanocrystals. *J Phys Chem B* 103: 3065-3069
16. Tsubokawa N, Kogure A, Maruyama K, Sone Y, Shimomura M (1990) Graft polymerization of Vinyl Monomers from inorganic ultrafine particles initiated by azo groups introduced onto the surface. *Polym J* 22: 827-833
17. Garcia I, Tercjak A, Zafeiropoulos NE, Stamm M, Mondragon I (2007) Self-Assembling nanomaterials using magnetic nanoparticles modified with polystyrene brushes. *Macromol Rapid Commun* 28: 2361-2365
18. Rietveld H.M., (1969) A profile refinement method for nuclear and magnetic structures. *J Appl Crystallogr* 2: 65-71
19. Rodriguez-Carvajal (1993) Recent advances in magnetic structure determination by neutron powder diffraction. *J Physica B* 192: 55-69
20. William Yu W, Lianhua Q, Wenzhuo G, Peng X (2003) Experimental determination of the extinction coefficient of CdTe, CdSe and CdS nanocrystals. *Chem Mater* 15, 2854-2860
21. Etxeberria H., Zalakain I, Tercjak A, Kortaberria G, Mondragon I Functionalisation of semiconductor nanoparticles with polystyrene brushes by radical polymerization. (Sent for publishing)
22. Shyju TS, Anandhi S, Indirajith R, Gopalakrishnan R (2010) Effects of annealing on cadmium selenide nanocrystalline thin films prepared by chemical bath deposition. *J Alloys Compounds* 506: 892-897

23. Nguyen HQ (2010) Synthesis and optical properties of CdSe nanocrystals and CdSe/ZnS/core/shell nanostructures in non-coordinating solvents *Adv Nat Sci: Nanosci Nanotechnol* doi:10.1088/2043-6254/1/2/025004
24. Liu J, Li T, Hu K, Shao G (2009) Preparation and adsorption performances of novel negatively charged hybrid materials. *J Appl Polym Sci* 112: 2179-2184
25. Sun Y, Ding X, Zheng Z, Cheng X, Hu X, Peng Y (2007) Surface initiated ATRP in the synthesis of iron oxide/polystyrene core/shell nanoparticles. *Eur Polym J* 43: 762-772
26. Guo L, Chen S, Chen L (2007) Controllable synthesis of ZnS/PMMA nanocomposite hybrids generated from functionalized ZnS quantum dots nanocrystals. *Colloid Polym Sci* 285: 1593-1600
27. Xu C, Ohno K, Ladmiral, V, Composto, RJ (2008) Dispersion of polymer-grafted magnetic nanoparticles in homopolymers and block copolymers. *Polymer* 49: 3568-3577
28. H. Zhang, Z. Cui, Y. Wang, K. Zhang, X. Ji, C. Lü, B. Yang, M. Gao (2003) From water-soluble CdTe nanocrystals to fluorescent nanocrystal-polymer transparent composites using polymerizable surfactants. *Adv. Mater.* 15: 777-780

Scheme captions

Scheme 1 Synthesis of ACP functionalized CdSe nanoparticles

Figure captions

Fig. 1 XRD spectrum for ME-CdSe nanoparticles

Fig. 2 UV-vis spectra for a) ME-CdSe, b) GPS-CdSe and c) PS-CdSe

Fig. 3 FTIR spectrura of a) ME-CdSe b) GPS-CdSe and c) PS-CdSe

Fig 4 Fluorescence emission spectra for ME-CdSe and PS-CdSe

Fig. 5 TGA diagram of PS-CdSe and GPS-CdSe nanoparticles

Fig. 6 AFM images (left/center/right: height/phase/profile) for: SBS neat copolymer

Fig. 7 AFM images (left/right: height/phase) for 3 wt % SBS/BDHA-CdSe composite

Fig. 8 AFM images for a) (left right: height/phase) 0.5 wt % SBS/PS-CdSe composite and b) magnification of image a)

Fig. 9 AFM images for (left/center/right: height/phase/profile) for: 3 wt% SBS/PS-CdSe composite

Fig. 10 AFM image of magnification of image 9