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Nanoparticle separation by mesoporous molecular sieves

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A separation technique based on the size-selective adsorption of nanoparticles by mesoporous silica sieves is proposed, which provides a narrow size distribution of PbSe nanocrystals incorporated into the pores.

Recently, semiconductor quantum dots have received a great deal of attention due to their unique electronic and optical properties, which give rise to their high potential for a wide range of applications such as solar cells, laser sources, electroluminescence devices, tunnel diodes and biological luminescent labels.[1–3] The ability to prepare quantum dots with a narrow size distribution is a prerequisite to implement many technological applications such as line emitters, sensing self-assembled arrays, *etc*. Traditionally, the tuning of size distribution is performed by a size-selective precipitation procedure,[4] which is based on size-dependent solubility of nanocrystalline particles in nonpolar solvents. Solvent/nonsolvent pairs, such as hexane/acetone, toluene/ethanol and others, can be used to separate nanocrystals by size. However, this technique necessitates large quantities of samples and usually requires a number of repeatable cycles to provide a sufficiently high monodispersity of particles for the formation of self-assembled arrays.

Here, we propose an alternative separation technique based on the size-selective adsorption of nanoparticles by mesoporous silica sieves. Mesoporous silica exhibits a highly ordered uniform pore structure with a very sharp pore size distribution.[5] The pore diameter of the molecular sieves can be controllably varied from ~2 to 50 nm. One could expect that the size of nanoparticles incorporated into the mesoporous silica matrix to be consistent with the dimensions of the porous framework. Therefore, in this work, we tested the possibility of separating PbSe nanoparticles by mesoporous silica sieves.

The synthetic procedure for the preparation of PbSe quantum dots is based on the method reported by Murray *et. al*.[6] The particles of oleic acid-capped lead selenide were synthesised by the reaction of lead oleate (0.1 M) and trioctylphosphine selenide (1 M) in diphenyl ether at 120 °C. A PbSe colloid was precipitated by ethanol and redispersed in hexane. The size of the prepared nanoparticles capped with oleic acid (PbSe sample) was found in the range 3–7 nm [Figure 1(*a*)] with the optical bandgap of 3.8 eV (Figure 2). The diffraction pattern for a sample deposited by sol drop drying on carbon mesh confirms the formation of PbSe nanocrystals [see inset in Figure 1(*a*)].

The mesoporous silica sieve (sample MS) was prepared by the polycondensation of a silica source [tetraethyl orthosilicate (TEOS), 98%, Aldrich] in an aqueous template solution [octadecyltrimethylammonium bromide (OTAB), 99%, Aldrich] with a basic catalyst (pH ≈ 12, NH_3).[7] For the additional widening of the pores, an auxiliary organic agent [mesitylene (MES), 99.5%, Aldrich] was added to the solution. The final molar ratio was $1\text{TEOS}:0.152\text{OTAB}:1\text{MES}:2.8\text{NH}_3:141.2\text{H}_2\text{O}$. The

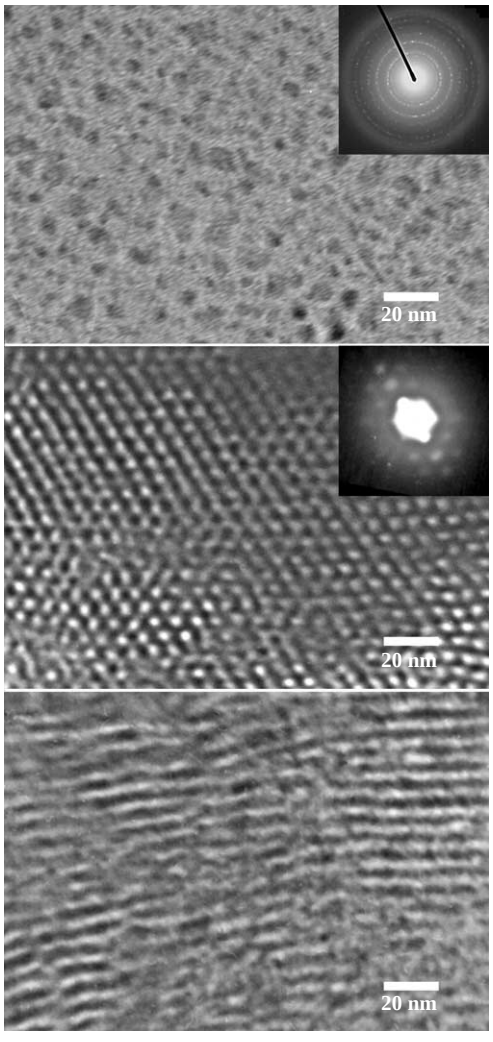

Figure 1 (*a*) Transmission electron micrograph and electron diffraction pattern of PbSe nanoparticles, (*b*) a cross-sectional image of mesoporous structure (MS sample) representing the ordered hexagonal arrangement of mesopores and (*c*) a longitudinal section of MS_PbSe composite indicating the intercalation of PbSe nanoparticles (dark regions) into mesoporous silica channels and partial destruction of an ordered system of pores.

precipitate was filtered off, washed with deionised water to pH 7 and dried at 363 K for 12 h. The parameters of the porous structure of the resulting molecular sieve were determined using the capillary adsorption of nitrogen at 77 K and small angle X-ray scattering. The sample was characterised by hexagonal pore ordering with a pore diameter of 5.0±0.1 nm and an interpore distance of 6.5±0.1 nm [Figure 1(*b*)].

The separation of PbSe nanoparticles was carried out by vigorous stirring of MS sample in a lead selenide colloidal solution for 5 h. The resulting russet-coloured sample (MS_PbSe) was filtered off and repeatedly washed with hexane in order to get rid of the particles absorbed on the external surface. According to the chemical analysis, the total quantity of lead selenide in MS_PbSe sample corresponds to the molar ratio Pb:Si = 1:16. The microphotograph of the sample after impregnation indicates the intercalation of particles into the porous structure. Note that a comparison between the microstructures of a pure mesoporous silica matrix and a matrix filled with PbSe nanoparticles shows partial destruction of the pores [Figures 1(*b*),(*c*)]. Obviously, it is related to the intercalation of PbSe particles with diameters exceeding pore diameters. In our opinion, this could be explained by high capillary forces in the mesoporous silica channels, which draw up particles into the pores even if it requires stretching of amorphous silica walls.

The optical properties of the prepared composite show a blue shift of the bandgap value to 4.0 eV, which corresponds to the particle size of PbSe nanocrystals below 2.4 nm (*e.g.*, only a low-diameter fraction was absorbed). Actually, it is in good agreement with the inner diameter of the mesopores: semiconductor PbSe particles in the colloidal solution are capped with oleic acid giving an organic shell thickness of about 1.3 nm. At the same time, the increase of the light absorption of PbSe nanoparticles at the edge of the adsorption band becomes sharper after intercalation into the porous matrix indicating the narrowing of the particle size distribution of PbSe nanocrystals (Figure 2).

Thus, the proposed method results in the size-selective adsorption of PbSe nanoparticles; therefore, it could be extended to the separation of nanoparticles with different sizes and chemical compositions.

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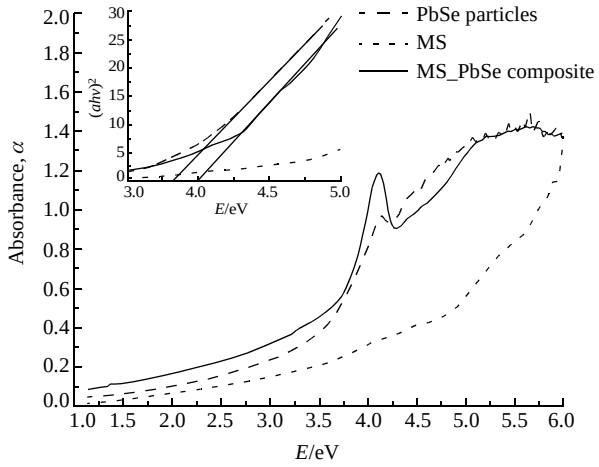

Figure 2 Optical absorption spectra of a colloidal solution of PbSe nanoparticles (band gap, E_g = 3.8 eV), pure mesoporous molecular sieve and MS_PbSe composite (E_g = 4.0 eV) indicating the narrowing of the particle size distribution of PbSe nanocrystals. The band gap values were calculated from the plot of transformed Kubelka–Munk function *vs.* the energy of the light absorbed (see inset).

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