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A New Approach to Hybrid Nanocomposite Materials with Periodic Structures

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There is an immense interest in the use of submicrometer core−shell particles as functional building blocks in fabrication of materials with periodic structure and composition.[1] Such materials can have the properties of photonic crystals, with potential applications in chemical sensors, in optical data storage devices, and in optical limiters and switches.[2] In particular, enhancement in optical limiting and photoluminescence properties is expected for periodically structured hybrid materials doped with semiconductor nanoparticles (quantum dots). Substantial progress has been achieved in synthesis of core−shell microbeads bearing metal, metal oxide, and semiconductor nanoparticles (NPs).[3] However, fabrication of macrosopic nanostructured materials using self-organization of these hybrid core−shell particles is impeded by the difficulty in their incorporation in suitable matrices while preserving the periodicity of the ultimate material. Infiltration of polymers in ordered 3D arrays of colloid spheres[4] does not provide good control over material structure, for example, over the distance between the particles; whereas polymer shells of hybrid core−shell particles prepared via layer-by-layer polyelectrolyte deposition are not sufficiently thick to form a void-free matrix phase.

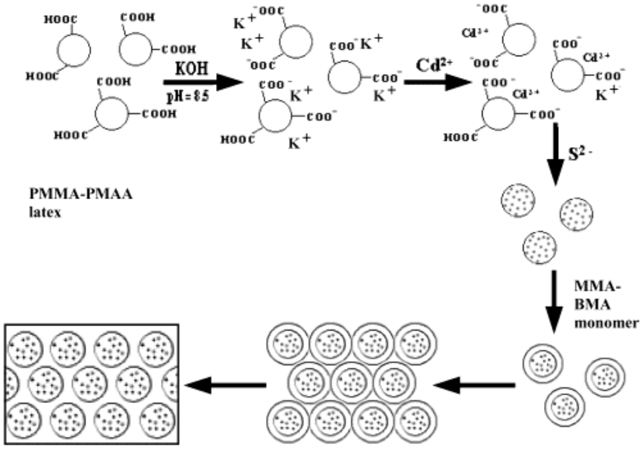
Herein, we report on the new strategy for production of hybrid periodically structured nanocomposites containing semiconductor or metal NPs. The proposed approach has two essential features: (a) in situ synthesis of NPs on the surface of polymer microspheres by employing ion exchange of counterions in the electrical double layer of latex beads and (b) the use of *three-layer* hybrid core−shell particles as the structural units of the nanocomposite material.

Scheme 1 presents an overview of our approach. Monodisperse poly(methyl methacrylate)−poly(methacrylic acid) (PMMA−PMAA) latex particles were synthesized via emulsion polymerization with a PMMA/PMAA weight ratio varying from 10 to 4 and the particle diameters varying from 150 to 600 nm. The particles were treated with 1 equiv of 0.1 M KOH, dialyzed to pH = 8.5, and then treated with a solution of $Cd(ClO_4)_2$ to initiate ion exchange between the K^+ counterions in the electrical double layer and the Cd^{2+} ions bearing a higher charge.[5] The mole ratio of Cd^{2+} ions to surface COOH-groups was 2:1. After removing excess of free Cd^{2+} ions via dialysis, a solution of Na_2S was slowly introduced into the dispersion. The color of the dispersion instantly became yellow, indicating the formation of CdS. The dispersion of the composite CdS−latex particles was stable, and the polydispersity index (PDI) determined by image analysis of the SEM images of the latex microbeads increased from 1.05 to 1.1.

A similar strategy was used to synthesize hybrid microspheres coated with Ag NPs. Following addition of KOH and dialysis, the PMMA−PMAA latex dispersion was treated with a solution of $AgNO_3$. The mole ratio of Ag^+ ions to surface COOH groups was 2:1. Then $NaBH_4$ was added as a reducing agent at 0 °C.

The PMMA−PMAA beads coated with CdS or Ag NPs could be readily assembled in ordered arrays using evaporative assembly,[6] electrodeposition,[7] or the assistance of oscillatory shear,[8] as confirmed by optical diffraction experiments.

Scheme 1. Schematic of the Preparation of Hybrid Polymer-Based Material with Periodic Structure



The TEM micrographs of hybrid microspheres imaged under different magnification are shown in Figure 1. Figure 1a shows a highly periodic array of 580-nm-sized interconnected PMMA−PMAA microbeads (black domains) coated with CdS NPs. The trend to formation of thin necks between these hybrid spheres appeared stronger when water evaporation rate from the particle array was decreased. In Figure 1b TEM images of the surface of polymer beads taken under higher magnification featured random distribution of well-isolated CdS NPs on the polymer surface.

The average diameter of CdS NPs was ca. 6 nm, consistent with their absorption spectrum. In principle, the size of CdS NPs could be varied from ca. 3 to 8 nm by changing the density of surface COO^- groups through the variation of MMA/MAA weight ratio in the copolymerization process. The inset to Figure 2b shows a fragment of the latex surface uniformly covered with Ag NPs with average size 5 nm. The composition of CdS and Ag NPs was confirmed by elemental analysis carried out in energy-dispersion X-ray experiments. Within the sensitivity of this method no presence of potassium was noticed on the microsphere surface. Figure 1c shows a typical high-resolution TEM image of the highly crystalline individual 5-nm-sized CdS nanoparticle.

In situ synthesis of semiconductor and metal NPs on the surface of latex spheres provided a route to creation of macroscopic nanostructured materials with a periodic structure and composition. The realization of such materials was accomplished by interfacial polymerization of a polymeric shell on the surface of PMMA−PMAA/CdS or PMMA−PMAA/Ag microbeads, as shown in Scheme 1. The main requirement to the shell-forming polymer (SFP) was that its glass transition temperature, T_g, was substantially lower than T_g of the PMMA−PMMA core, which varied from 112 to 130 °C. To obtain a void-free material the ratio between the core radius and the polymer shell thickness was at least 5:1. The

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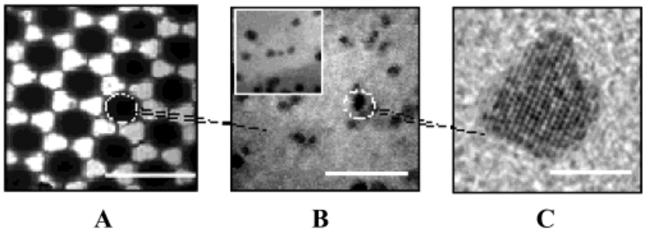

Figure 1. TEM micrographs of PMMA−PMAA beads covered with CdS and Ag NPs obtained under different magnification. The concentration of the surface carboxyl groups is ∼4.8 mol %. (A) Periodic array of 580-nm-sized PMMA/PMAA/CdS particles. Scale bar is 1.3 μm. (B) Fragment of the PMMA−PMAA surface coated with CdS NPs. Scale bar is 30 nm. (Inset) Fragment of the latex surface coated with ca. 5 nm Ag NPs; (C) High-resolution image of an individual CdS particle. The periodic dot pattern arises from the coherent imaging of Cd and S atoms making up the NP. Scale bar is 5 nm. Weight ratio PMMA/PMAA = 5.

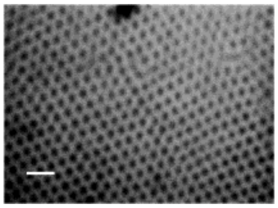

Figure 2. LCFM image of the CdS−polymer nanocomposite prepared from ca. 800-nm-sized PMMA−PMAA/CdS/PMMA−PBMA particles. The image is taken 10 μm below the surface of the film. CdS was excited at 364 nm. Scale bar is 2 μm.

SFP with $T_g = 70$ °C was synthesized from poly(methyl methacrylate)−poly(butyl acrylate) (PMMA−PBMA) copolymer in the weight ratio 1:1. The thickness of the polymeric shell varied from 80 to 300 nm, and it could be further increased using a multistage polymerization process.[9] The three-layer particles had PDI = 1.14 ± 0.05.

Hybrid microbeads were assembled in 3D periodic arrays on polished Teflon or on hydrophobized glass substrates, dried and annealed at T_{ann}= 90 °C, that is, $T_{g,PMMA-PMAA} < T_{ann} < T_{g,PMMA-PBMA}$. Under these conditions, the outer shells softened, filled the interstitial space between the two-layer particles, and ultimately formed a matrix, whereas the PMMA−PMAA/CdS or PMMA−PMAA/Ag two-layer cores remained intact. In this manner, a macroscopic nanocomposite material with a periodic structure was obtained, in which hybrid 150−600 nm rigid spheres formed an ordered array. Cracking and distortion of the periodic array structure due to ca. 26% contraction of the polymer during annealing was verified using SEM and laser confocal fluorescent microscopy (LCFM), respectively. The resulting free-standing films were free of cracks and transparent, and the dimensions of the CdS and Ag NPs did not change during polymerization of the SFP and the annealing process.

Figure 2 shows the morphology of a hybrid film studied by LCFM. The morphology of the film appears as an inverse of the structure anticipated in the final stage in Scheme 1. The difference arises from the fact that in Figure 2 the dark domains correspond to the nonfluorescent cross-sections of the PMMA−PMAA latex cores, whereas, the bright background corresponds to the PMMA−PBMA matrix doped with fluorescent CdS NPs. The uniform mixing of the CdS NPs with the SFP (presumably accomplished during interfacial polymerization of the latex shell or during annealing) was confirmed by imaging different planes of the material with steps of 0.2 μm. To the best of the resolution of LCFM no distortion in the structure (z vs x-y planes) was observed.

Our strategy has several features, which are very important in the fabrication of hybrid materials with periodic structures. While synthesis of semiconductor and metal NPs in highly polar microdomains of block copolymers has been reported,[10] attachment of NPs to the surface of submicrometer spheres makes this method particularly important in producing photonic crystals. The advantages of the described synthesis of NPs over attachment of preformed semiconductor or metal NPs are manyfold. Our approach provides higher stability of the latex dispersion and better monodipersity of the polymer microbeads. Good control over the size and amount of the NPs incorporated in hybrid two-layer composite particles (and ultimately, in the nanocomposite material) allows for quantum confinement. Finally, the surface of hybrid two-layer particles is sufficiently smooth to allow for colloid crystal growth. The proposed method can be applied to synthesis of other NPs, using neutralization of surface COO^- groups localized at the latex surface with metal ions.

The proposed approach gives a new avenue for producing optically responsive materials with periodicity commensurable with the wavelength of light, an intrinsic property of photonic crystals. For example, in films containing CdS NPs, good control of photoluminescence and optical limiting properties can be achieved by combining structurally and angularly dependent electromagnetic resonances (arising from periodicity of the material) and optical properties of the NPs (providing spectral control through the quantum-size effect). The variation in NP dimensions enables the spectral position of absorption peak to be changed, which would, in turn, change the nonlinear properties of the material. Moreover, since the NPs are spatially localized in the periodic array, the material enables tunable nonlinear diffraction. Using our approach, nanocomposite materials with periodically modulated magnetic and electric properties can be produced by incorporating metal NPs in three-layer microbeads. Furthermore, nanostructured materials with *several* functions can be fabricated by employing hybrid particles with multilayer structures, in which the cores and the shells are doped with *different* nanoparticles.

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