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Sorption of CdTe and Au nanoparticles by microporous isotactic polypropylene

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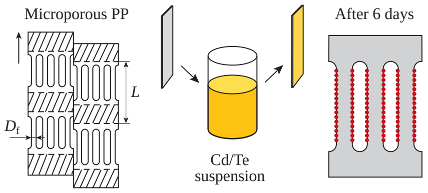
Porous polypropylene films effectively absorb CdTe and Au nanoparticles from aqueous solutions.



The microporous polymer materials are of interest as templates for the synthesis and stabilization of different nanoparticles.[1–3] Polymeric films (coatings) with functional nanosized inclusions are promising for producing the elements of optical and electronic devices, catalytic and microanalytical systems, alternative energy sources, *etc*.[4–10] Porous polymers can form films and fibers and provide good mechanical properties; therefore, they are promising matrices for the incorporation of functional compounds.[10–12] In this case, porous crazed polymers are of particular interest.[13] Crazing involves the development of a highly dispersed fibrillar-porous structure; the typical dimensions of pores and craze fibrils are about 10 nm.[14] Such systems may be promising for the stabilization of different nanoparticles (NPs) and the preparation of polymer-based nanocomposites. One could obtain nanocomposites in the form of polymeric films and filaments possessing, on the one hand, good mechanical characteristics and, on the other, valuable properties (conductance, incombustibility, electrostatic properties, *etc*.) imparted by target additives.[15] Recent research has been focused on the development of new nanoparticle–polymer composite materials, in particular, those containing quantum dots (QDs). QDs reveal unique properties and have a number of advantages over conventional organic fluorescent dyes; however, in most cases, methods for the incorporation of QDs into a polymer matrix are complicated and labor-intensive, and the premodification of QDs is also needed.[16,17] Here, we describe a simple method for the preparation of fluorescent QD-containing composites.

We studied the sorption of QDs, CdTe and Au NPs from aqueous solutions by porous isotactic polypropylene (PP). We used microporous films of hard-elastic isotactic PP as a matrix, which could be prepared in several steps.[14] At the first step, upon the annealing of pre-oriented PP samples near the melting point, a system of folded lamellar crystals is formed. The lamellas are arranged in parallel to each other and perpendicular to the axis of orientation. The uniaxial deformation of PP at room temperature (the second step) is accompanied by the formation of many crazes localized in the interlamellar regions of the crystalline polymer and filled with highly disperse fibrillated matter. At the third step of thermal fixation (isometric annealing at 100–120 °C), the porous structure of crazed PP is stabilized. Figure 1 schematically shows the microporous PP structure.

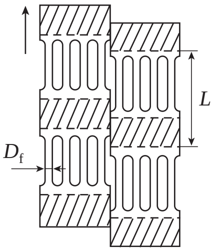


Figure 1 Structure of the microporous PP.

We used PP samples doubly stretched at room temperature and then annealed under isometric conditions at 120 °C for 30 min. As follows from our previous investigations, the porosity of PP films was 0.3 cm^3 g^{-1}; according to small-angle X-ray scattering data, the distance between crazes (*L*) was ~100 nm; the diameter of fibrils (D_f) was 20 nm; the fibril surface area was 30 m^2 g^{-1}, and the transverse dimension of pores between fibrils was 15 nm.[14] Note that porous PP films demonstrate good mechanical properties (tensile strength, 150 MPa; elongation at break, ~100%) and high thermal stability.

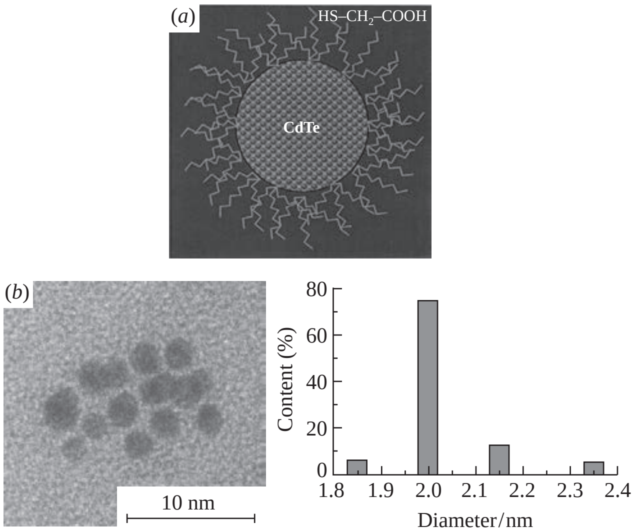


Figure 2 (*a*) Schematic view of CdTe NPs 2 mm in diameter stabilized with thioglycolic acid. (*b*) Typical TEM image of CdTe NPs 2 nm in diameter and a size distribution histogram.

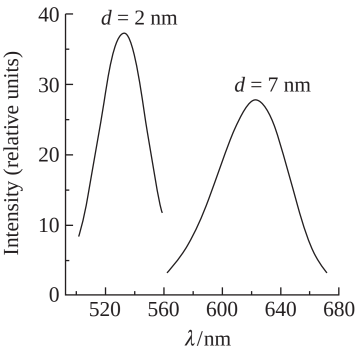


Figure 3 Luminescence spectra of the aqueous solutions of CdTe NPs 2 and 7 nm in diameter. Excitation wavelength, 360 nm.

In our study, PP samples containing water in micropores were used. First, these ‘dry’ microporous PP films were impregnated with ethanol. Then, the wetted samples were transferred to cuvettes with water to replace ethanol with water in crazes.

We used aqueous dispersions of CdTe NPs 2–2.5 and 7 nm in diameter stabilized with thioglycolic acid [Figure 2(*a*)]. These particles were negatively charged due to the ionization of acid groups. We evaluated the net charge of CdTe nanoparticles at –2.2±0.4 in aqueous dispersions according to a published procedure.[18]

The particle diameter was determined by transmission and atomic force microscopy [Figure 2(*b*)]. The CdTe NPs were synthesized by the addition of a freshly prepared aqueous solution of NaHTe to an alkaline solution of $Cd(ClO_4)_2 \cdot 6H_2O$ as described earlier.[19]

Figure 3 shows the luminescence spectra of the aqueous solutions of CdTe NPs. Note that the colloidal solutions of CdTe NPs have a strong fluorescence: the quantum yield is 15–20%. The position of a luminescence spectrum maximum depends on the size of NPs. For CdTe NPs of sizes 2 and 7 nm, the maxima are observed at 530 and 620 nm, respectively. This result is consistent with published data, and it reflects the fact that the position of a luminescence maximum of chalcogenide NPs (1–10 nm in diameter) is shifted towards longer wavelengths with increasing particle size.[20]

We also used the aqueous dispersions of Au NPs 5 nm in diameter from Sigma. We carried out the adsorption of the NPs at 20 °C. The PP film thickness was 150 μm. The value of adsorption was estimated from difference in the concentrations of colloidal solutions before and after adsorption determined from the UV absorption spectra. The calibration curves of the optical density of the colloidal solutions at 300–350 (for CdTe dispersions) and 490–530 nm (for Au dispersions) *versus* particle concentration were plotted.

The specific adsorption G (g g^{-1}) was calculated as follows: $G = V(c_0 - c)/m$, where c_0 is the initial concentration, c is the solution concentration after adsorption (g ml^{-1}), m is the adsorbent weight (g), and V is the solution volume (ml) (Table 1).

The porous PP films effectively absorbed CdTe nanoparticles 2 nm in diameter from aqueous solutions with relatively low NPs concentrations. After five days, the relative concentration of the nanoparticles Q reached 9 wt%. We found that the concentration of CdTe (2 nm) in microporous PP was higher by approximately three orders of magnitude than the concentration of CdTe in aqueous solution. It means that the most part of CdTe NPs in PP pores is in adsorbed state and appears to be localized in the surface layers of the fibrils connecting walls of crazes. The specific adsorption values were determined for CdTe NPs (2 nm in diameter) at the initial concentrations of 7.8×10^{-5}, 3.9×10^{-4} and 7.8×10^{-4} g cm^{-3}. After five days, the specific adsorption values changed insignificantly with the initial concentration of NPs, and they were 0.085, 0.09 and 0.094 g g^{-1}, respectively.

Table 1 Sorption of NPs by microporous PP.

NPs	Time of sorption/days)	$C_0{}^a/10^{-4}$ g cm^{-3}	G/g g^{-1}
CdTe (d = 2 nm)	2	3.9	0.065
CdTe (d = 2 nm)	3	3.9	0.08
CdTe (d = 2 nm)	5	3.9	0.09
CdTe (d = 7 nm)	5	3.9	0
Au (d = 5 nm)	5	1	0.01

[a] C_0 is the initial concentration of NPs in water.

The absorption was irreversible: nanoparticles were not removed from the films after multiple rinsing with water.

We calculated the maximum specific adsorption (G') corresponding to the formation of an NP monolayer on the surface of fibrillar elements connecting the walls of crazes in microporous PP according to the formula $G' = M_{NPs}S_f/S_{NPs}N_A$, where M_{NPs} is the molar mass of a nanoparticle, S_f is the specific fibril surface area, S_{NPs} is the landing area of NPs, and N_A is the Avogadro number.

We suggested that the landing area of a CdTe particle is d^2, where d is the particle diameter of 4–6 nm^2. For the microporous PP samples, the specific fibril surface (S_f) was found to be 30 m^2 g^{-1}.[14] According to ref. 21, 2 nm CdTe particles contain 54 Cd atoms and have the formula $Cd_{54}Te_{32}(SR)_{52}$. Therefore, the molar mass of a CdTe particle 2 nm in diameter is 14969 g mol^{-1}.

The calculated maximum specific adsorption (G') was 0.150–0.187 g g^{-1}. For CdTe (2 nm in diameter), G' was close to the experimental equilibrium value of G (Table 1). This allows us to conclude that nanoparticles form a thick monolayer on the surface of fibrillar elements connecting the walls of crazes in microporous PP.

After the adsorption of NPs, polymer films were colored in yellow and demonstrated luminescent properties. The luminescence spectrum of a polypropylene–CdTe film (particle diameter, 2 nm) has a broad band at 530 nm (Figure 4). The position of the spectrum maximum of the composite roughly coincides with that of a colloidal solution of CdTe NPs 2 nm in diameter in water (see Figure 3).

However, it is well known that there is a strong relationship between the wavelength of excitation and the chalcogenide particle diameter.[20] Therefore, we assumed that the diameter of the NPs in the PP film coincides with the size of NPs in aqueous solution. The results make it possible to conclude that the particles in the pores (crazes) do not aggregate.

The efficiency of adsorption decreases sharply with increasing the size of NPs. For 5 nm nanoparticles, Q was 1 wt%, 7 nm nanoparticles were not absorbed at all. Apparently, as soon as the NP size becomes comparable with the pore size in the PP, the rate of diffusion of colloid particles in the adsorbent decreases.

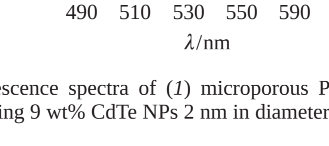


Figure 4 Luminescence spectra of (*1*) microporous PP and (*2*) microporous PP containing 9 wt% CdTe NPs 2 nm in diameter. Excitation wavelength, 360 nm.

Thus, the incorporation of CdTe and Au NPs into a PP matrix results in highly fluorescent materials with good mechanical properties and large pore surface areas. The results are of great interest for the development of new composites that can be applied in photonics and to the design of sensors, photovoltaic devices and detectors.

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