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Effect of some industrial dyes on the self-assembly of polymeric opals based on core-shell nanoparticles

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ABSTRACT

Opals are photonic structures with applications varying from coatings and pigments to photonics and optical devices. Colloidal self-assembly of polymer-based nanoparticles is a cheap and green method to create opals over large areas: recently, procedures combining co-deposition of crosslinker precursors and other additives with nanoparticle self-assembly have emerged as routes to large-area efficient deposition. We investigate how the presence of some common organic dyes and pigments affects the properties and self assembling behavior of core shell polystyrene particles with a poly(methacrylic acid) shell during horizontal deposition (casting) from water, studying both the variation of particles properties in solution and the structure and properties of the resulting films. The study further includes the effects of a precursor of silica crosslinking (Tetraethoxysilane), and its combination with the same dyes, and we are able to show how interactions starting in the nanoparticles dispersion affect the structure and properties of the crystals.

1. Introduction

Photonic crystals (PC) have interesting properties both as model systems and for industrial applications [1,2]. A particularly interesting class of these are the simple 3D systems based on the ordered packing of monodisperse spheres, i.e. opals.

Due to the limited range of optical properties of simple opals many modifications have been proposed to increase their efficiency, such as precise engineering of defects and the inclusion of dyes and other dopants [3,4].

Doped opals, crosslinked or not, can have a variety of optical effects and can be a cheap polymeric system with a complete bandgap. Examples include the addition of carbon black [5] for enhanced color, and specific additives for safety inks [6], fluorescent systems [3] solar concentrators [7] and more. The application of opals as filming active layers (e.g. in the coating field) may require complex formulations to give structured materials that control optical and surface properties (wettability, roughness) simultaneously [8].

Self-assembly of charged monodisperse nanospheres based on polystyrene (PS) [9] has been widely used to create stable opal films with or without crosslinking [10,11]. A key passage is the optimization of their self-assembly step, to build the ordered crystal: this process is complex, depending on a number of steps and forces, (such as convective forces, capillarity, and the interplay of electrostatic charges) whose relative importance depends on particle structure, deposition technique and filming conditions [9].

In a previous paper [12] we have described intrinsically functional core-shell nanoparticles made of polystyrene core and methacrylic acid shell (PS-MAA Nps) that can self-assemble into opals with different degrees of order according to their structure and their intrinsic surface charge (zeta potential). The methacrylic acid rich shell facilitates water stability and allows efficient self-assembly by simple casting from water without the need for more volatile solvents. This shell-controlled self-assembly step, however, is known to be sensitive to external factors, especially the local solution characteristics, such as ionic strength or pH in a manner similar to hydrogels or micelles [13].

Abbreviations: TEOS, tetraethoxy silane; PC, photonic crystal; PS, polystyrene; MAA, polymethacrylic acid; PS-MAA, polystyrene-polymethacrylic acid; Np, nanoparticle; NpA, nanoparticles A; NpB, nanoparticles B; PDI, Polydispersity Index from DLS; B1, FD&C Blue 1 dye; BFe, black iron oxide pigment; RFe, red iron oxide pigment; R6, FD&C Red 6 dye; R30, FD&C Red 30 dye.

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Vertical deposition of rigid spheres has been the preparative method of choice for opal preparations where a small area of high quality crystal is needed, but a number of other methods are reported which require less time and open the possibility of larger scale preparation [14] such as horizontal deposition [15]. This procedure has received more and more interest during recent years as a greener and more upscalable method, especially when water is used as the casting solvent: among the details reported in the literature, the effect of solvent composition and zeta potential on the self-assembly procedure have been studied. Solvent properties, especially volatility, have been shown to affect the degree of self ordering of rigid Nps, i.e. alcoholic solvents increase the quality of crystals in some cases [16]; drying speed (i.e. the drying temperature) of the film was also found to influence the quality of the opal, especially when water is used as casting medium. However, water casting of charged particles is a complex and delicate process [17].

High zeta potentials seem to favor the formation of more regular crystals and the same does high solvent polarity, while unexpectedly a high ionic strength has been found to favor close packing by shielding particle repulsive interactions [18]. The effect of pH and ionic strength on the packing of charged spheres has been studied in the literature for simple model compounds (such as NaCl) especially for rigid silica particles [19], and also the progressive neutralization with NaOH for PS-MAA particles modulating their aggregation behavior [13].

In the case of rigid silica particles, pH between 1.5 and 3.5 (small fraction of ionized silanol groups) or the presence of solvated ions screening the excess of charge at low pH or at pH around 9–10 are known to help the opal formation while high electrostatic repulsion and an excess of solvated ions disturb the surface tension and the capillary forces causing sedimentation to a disordered solid [18].

Co-deposition of TEOS with charged spheres has been shown to yield a better and faster film formation than a deposition/infiltration process using vertical deposition [16,20] with less cracking and wider crystalline areas.

All of these results indicate that it is possible to influence the degree and geometry of self ordering by varying the environmental conditions of the particles in the film preparation.

The complex interactions between core-shell particles and organic dyes, which would be most important in view of real life applications (e.g. as optical materials) have never been studied in depth. The behavior of core-shell particles is very sensitive to additives: a packing strictly resembling an fcc arrangement in the presence of ions has been reported [21] and this effect was attributed to the long-range interaction of the respective ionic layers. In apparent contrast to this, carbon black has also been reported to improve the degree of order [5], which was attributed to the formation of hydrogen bonds between ionic impurities of carbon black defects and the surface of the particles. In Ref. [21] the adsorption of Rhodamin B was used to prepare a model sensor, exploiting a shift in reflectivity in the presence of solvent vapors, but the effect of the dye itself on the structural packing was not studied.

In this paper we investigate how the presence of some commonly used organic and inorganic dyes may affect the properties and self-assembling behavior of core-shell PS particles with an acidic MAA shell during horizontal deposition (casting) alone or in the presence of TEOS. In this latter case dye inclusion and crosslinking take place simultaneously.

2. Materials and methods

2.1. Chemicals

All chemicals were purchased from Sigma–Aldrich and used without further purification except styrene. Styrene was washed twice with a 1 M KOH solution to eliminate the stabilizer (4-*tert*-butyl catechol) and then with water until neutrality. Dyes (cosmetic grade) were a gift from Intercos SpA, and used as received except R30 (extracted with ethanol) and B1, obtained from FD&C Blue1 lake. This was suspended in water, filtered to yield the free dye; the solution was then treated with concentrated HCl, dried, redissolved in methanol, filtered and re-dried to obtain the free acidic compound. Doubly distilled water was used in the synthesis and where not specified. MilliQ water was used for purification and DLS/Zeta potential measurements.

2.2. Methods

2.2.1. Synthesis procedure

Core-shell nanoparticles were prepared as reported in the literature [12] by surfactant free emulsion radical polymerization at 100 °C under stirring. As an example, the synthesis of nanoparticles A is described here. In a two-necked flask equipped with a condenser, magnetic stirring and heating bath, 6 ml (5.454 g, 0.524 mol) of styrene were mixed with 0.2 ml (0.203 g, 2.358 mmol) of methacrylic acid and suspended in water (20 ml) under vigorous stirring. The mixture was heated at reflux for 10 min before adding the initiator, potassium persulfate (25 mg), and allowed to react for 90 min. The resulting white latex was cooled to RT and purified by tangential flow filtration using MilliQ water in a Millipore Pellicon XL Biomax 1000 cassette with 1 million cutoff.

Nanoparticles B were obtained using the same procedure but suspending the monomer mixture in 25 ml water.

2.2.2. Np/dye suspension

2 mg of the appropriate dye were dissolved in 100 μL of water and added to 0.5 ml of the nanoparticles solution (20% wt in water, 100 mg polymer content) under stirring. The mixture was sonicated for 20 min before use.

2.2.3. Np/dye/TEOS suspension

To a solution prepared as described above, 35 mg of TEOS (resulting in 10 mg SiO_2 after sol-gel reaction and drying) were added. The mixture was then sonicated for 20 min before use.

2.2.4. DLS/Zeta potential

Mixtures prepared as described above were diluted to 0.01 mg/ml solid content with MilliQ water for DLS and zeta potential measurements. Measurements were performed 24 h after preparation.

2.2.5. Film casting

We applied a silicone rubber ring on a cleansed glass slide to create a mold. The mold was filled with the nanoparticle dispersion (about 500 μl) and the liquid was left to evaporate at room pressure and temperature to allow the formation of a thin vivid iridescent colloidal crystal with a thickness of some micrometers.

2.2.6. Characterization

Polymer nanoparticles were characterized by Zeta potential, Dynamic Light Scattering, Atomic Force Microscopy and optical measurements. Dynamic Light Scattering and Zeta potential were measured in diluted MilliQ water solutions (0.01 mg/ml), at room temperature using a Brookhaven 90 Plus size analyzer. The apparatus was equipped with an He–Ne laser emitting light at $\lambda = 632.8$ nm and a detector recording intensity at a fixed scattering angle $\theta = 90°$. Zeta potentials were recorded on the same instrument equipped with AQ- 809 electrode. Data were processed by Zeta Plus Software.