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Simultaneous patterning of two different types of nanoparticles into alternating domains of a striped array of a polymer blend in a single spin-casting step

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ABSTRACT

A fast and convenient method is developed for simultaneously patterning inorganic nanoparticles with different optical, electronic or magnetic functionality to specific surface regions, by spin-casting onto microcontact printed substrates blend solutions in which the two nanoparticle types are functionalized with surface polymer brush layers of different surface energies. The process is based on phase separation of different nanoparticles based on their immiscible brush layers during spin-casting, with the underlying surface energy heterogeneity of the patterned substrate directing the different NP types to domains of different surface energies. Here, we specifically demonstrate the simultaneous localization of cadmium sulfide quantum dots (CdS QDs), addressed with a surface layer of polystyrene (PS), and silver nanoparticles (Ag NPs), addressed with a surface layer of poly(methyl methacrylate) (PMMA), onto the non-polar and polar surface domains, respectively, of hydrophilic glass patterned with hydrophobic octadecyltrichlorosilane (OTS) stripe arrays with micron-scale periodicities. In order to prevent gelation of solvent-swollen polymer-brush coated NPs during spin casting, which effects strong kinetic constraints on phase separation and localization, PS, PMMA or PS/PMMA homopolymer blends of sufficiently high M_w were added to the NP blends to increase the free volume between approaching NPs. The process parameters were fine-tuned to obtain control over defects in the obtained patterns.

1. Introduction

Organizing nanoparticles (NPs) into micro- and nanoscale structures on surfaces have various applications in medical diagnostics [1,2], sensing [3,4], nano- and optoelectronic devices [5,6], light emitting diodes [7], and photovoltaics [8]. A variety of techniques have been applied to this challenge including scanning probe-related patterning techniques [8–14], the use of optical tweezers to position NPs on surfaces [15,16], microcontact printing [7,17–21], layer-by-layer assembly techniques [22,23] and various other lithographic approaches [24–28].

The ability to fabricate patterned structures of multiple NP types with different functionalities (such as optical properties) opens up many new routes to design micro and nanodevices. Hua et al. employed a layer-by-layer assembly approach combined with lithography to obtain a pattern of two types of NPs, where each one is directed to the desired location on the surface to form striped pattern of NPs [29]; although this technique results in high precision patterning, it is a labor-intensive multistep process. Jamshidi et al. developed an elaborate technique termed “nanopen” to pattern multiple NPs using optoelectronic tweezers to collect and immobilize them into patterned structures via electrokinetic forces [30]. Vossmeyer et al. reported a selective deposition technique for patterning multiple NP types through selective deposition of each NP type onto chemically distinct interaction sites of a substrate, which was prepared by lithographic masking [31]. However, there is still the need for a fast, simple and efficient approach to patterning structurally- and compositionally-complex NP containing films.

Microcontact printing (μCP) is a convenient technique for patterning colloids, polymers and NPs [32–36]. Here, we develop a versatile technique based on μCP for simultaneous patterning of multiple NP types to discrete surface locations using a facile single-step spin-casting process. Our method is based on directed phase separation of polystyrene/poly(methyl methacrylate) (PS/PMMA) blend films [37–49] via spin-casting onto pre-patterned octadecyltrichlorosilane (OTS) on glass, as developed previously

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in our group [36]. Also in that work, the methodology was extended to patterning of CdS quantum dots (QDs), by replacing PS homopolymer within the spin-cast solution with PS-coated CdS QDs (PS-CdS); the QDs possessed similar surface energy to the PS homopolymer and therefore localized selectively above the OTS lines. In this paper, this technology is further extended to include the simultaneous patterning of PS-CdS QDs–that should be directed to the lower-surface energy OTS lines of the substrate–and PMMA-coated Ag NPs (PMMA-Ag), which should be directed to the higher-surface energy regions between the OTS lines. Our main interest in polymer-supported patterns of Ag NPs and CdS QDs is to provide a suitable proof-of-concept system for simultaneous creation of patterns containing multiple NPs. However, this specific combination of NPs also exhibits interesting optical behavior as a result of QD-surface plasmon interactions, which will be discussed in a forthcoming publication.

2. Experimental

2.1. Materials

Three different PS homopolymer samples with molecular weights (M_w) of 131,000 g/mol (previously synthesized in our group by anionic polymerization), 33,000 g/mol (Polymer Source Inc.) and 6000 g/mol (Polymer Source Inc.) were used for mixing with the NP blends; they are denoted in the text as PS 131 k, 33 k and 6 k, respectively. PMMA homopolymer with M_w = 120,000 g/mol (denoted as PMMA 120 k) was also used as received from Aldrich.

2.2. Synthesis of PS-coated CdS quantum dots (PS-CdS)

The polystyrene-coated CdS QDs (PS-CdS) used in this work is similar to that described in previous work from our group [50–53]. In summary, QDs were synthesized via templated growth of CdS in the cores of reverse micelles consisting of polystyrene-*block*-poly (acrylic acid) copolymer PS(226)-*b*-PAA(22), where numbers in brackets indicate number-average degrees of polymerization for each block. The core of each PS-CdS contains a ~5 nm CdS nanoparticle (determined from UV–vis and using Henglein's empirical relationship) [54,55], with a poly(cadmium acrylate) (PACd) layer at the CdS surface, covalently-attached to a solubilized external PS brush layer.

2.3. Synthesis of PMMA-coated silver nanoparticles (PMMA-Ag)

For the synthesis of poly (methyl methacrylate)-coated silver nanoparticles (PMMA-Ag), poly (methyl methacrylate)-*block*-poly (acrylic acid) copolymer, PMMA(170)-*b*-PAA(28), where numbers in brackets indicate number-average degrees of polymerization for each block, was purchased from Polymer Source Inc. Silver acetate 99.99%, sodium borohydride ($NaBH_4$) and methanol (99.8+%) were purchased from Aldrich. Reagent grade THF was purchased from Anachemia. In order to prepare PMMA-Ag, first a 2 wt% solution of PMMA(170)-*b*-PAA(28) was prepared in reagent grade THF and stirred for 3 h. In the meantime, a 0.25 M suspension of silver acetate in deionized (DI) water was prepared and a stoichiometric amount (measured as 1 Ag^+ to 1 acrylic acid repeat unit) was added quickly in a single shot from a volumetric pipette to the copolymer solution with constant and rapid stirring. The reason for adding silver acetate from a concentrated suspension was to keep the amount of water in the reaction solution at a minimum, in order to avoid precipitation of copolymer from the THF solution. The reaction solution immediately turned from clear and colorless to turbid bluish indicating the formation of micelles. After 1 h stirring, the reducing agent, which is 0.50 M aqueous solution of $NaBH_4$, was added to the solution in variable excess amounts relative to the molar amount of added silver acetate. Reduction of Ag^+ to Ag results in a color change of the solution to dark yellow. The solution was stirred overnight and then precipitated into cold methanol. The collected precipitate was washed with methanol several times and dried overnight under vacuum. This procedure is illustrated by the schematic depiction in Fig. 1.

2.4. Preparation of polydimethylsiloxane (PDMS) stamps for microcontact printing

Masters with microscale periodic stripe patterns were obtained using commercial compact disks (CDs). Top layers on a CD were removed revealing the underlying polycarbonate layer with the desired topographic features. The polycarbonate was used as the master, and a 10:1 (v/v) ratio of prepolymer to curing agent for polydimethylsiloxane (PDMS) (Dow Corning: Sylgard 184 DC-184 A and DC 184-B) were mixed and poured over the polycarbonate master. The PDMS was cured for 4 h at 80 °C. The topology of the resulting PDMS stamp consisted of periodic raised stripes corresponding to the troughs of the polycarbonate masters. The PDMS stamps were sonicated in a 1:2 (v:v) solution of ethanol/deionized water immediately prior to use.

2.5. Microcontact printing of glass substrates with octadecyltrichlorosilane (OTS)

Glass cover slips (VWR scientific, 18 × 18 mm) were cleaned by sonication for 10 min in 95% ethanol, followed by 10 min sonication in deionized water. To introduce a layer of hydroxyl groups on the glass surface, the coverslips were submerged in a piranha solution at 70 °C for 30 min. Piranha solution consists of a 3:1 (v/v) mixture of concentrated H_2SO_4 and 30% H_2O_2. (*Warning: piranha solution is a strong oxidizing agent, so extreme care is necessary when using it.*) Following piranha treatment, the coverslips were sonicated in DI water for 10 min and then rinsed with methanol, followed by two further repetitions of the sonication/rinsing process. The resulting hydrophilic glass substrates were dried with a UHP N_2 (g) stream and used immediately for μCP. The ink for μCP was prepared by dissolving octadecyltrichlorosilane (OTS, Aldrich) in anhydrous hexane (⩾99%, Aldrich) under UHP N_2 (g) to obtain a 5 mM silane solution. For inking the PDMS stamp, an unpatterned smooth block of PDMS was used as an ink pad. One drop of the ink solution was spin-cast onto the pad at 3000 rpm for 30 s followed by 20 s drying under a stream of UHP N_2 (g). Then a PDMS stamp was brought into contact with the inked pad for 10 s. The inked PDMS stamp was then used to transfer the OTS molecules to the surface of a hydrophilic glass cover slip by a conformal contact for 30 s under a 200-g weight. The OTS-patterned glass substrates were used immediately for spin-casting the NP polymer blends.

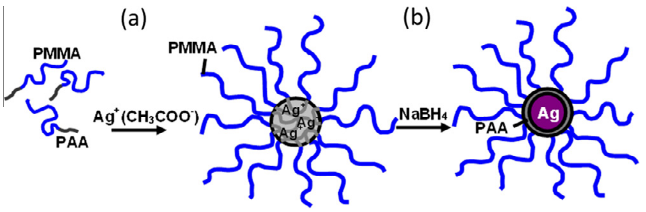

Fig. 1. Synthesis of PMMA-Ag NPs: (a) micelle formation by the addition of silver acetate to the solution of PMMA-*b*-PAA in THF with soluble PMMA brush layer and insoluble Ag^+-containing PAA core; (b) Ag NP formation by reduction in Ag^+ in the core to Ag^0 using $NaBH_4$ as the reducing agent, forming the final PMMA-Ag nanoparticles.