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Responsive polymer/gold nanoparticle composite thin films fabricated by solvent-induced self-assembly and spin-coating

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ABSTRACT

Self-assembled poly(4-vinylpyridine)-grafted gold (Au) nanoparticles (NPs) and polystyrene-*b*-poly(4-vinylpyridine) block copolymers were fabricated by the introduction of a selective solvent to a common solution. The assembled mixtures were spin-coated onto solid substrates to fabricate composite gold/polymer thin films composed of copolymer-hybridized Au NPs and independent copolymer micelles. The obtained composite Au thin films had variable localized surface plasmon resonance (LSPR) bands and microscopic morphologies upon vapor annealing with selective solvents because the adsorption and dissolving of solvent molecules into the films could rearrange the copolymer block. The hybrid nanostructured Au thin films may have potential in vapor sensing and organic assays.

1. Introduction

Since the early 1990s, efforts have been made to assemble gold nanoparticles (Au NPs) into well-defined two-dimensional (2D) monolayer arrays, or thin films toward many possible functional applications [1–3]. Mulvaney's seminal work fabricated colloidal Au monolayers by electrophoretic deposition on carbon coated copper grids [1]. In another breakthrough, Schmitt et al. prepared Au monolayers through electrostatic interactions on solid substrates, their work reported unusual optical characteristics containing information on single colloids, mutual interactions, and even the surrounding environment [2]. After that, Au thin films fabricated from alkylthiol-modified Au NPs became an active multidisciplinary research topic [4–6]. The distinct features of nanostructured 2D Au arrays can be summarized by outlining recent achievements. First, Au thin films fabricated by alkylthiol-functionalized Au NPs were found to have vapor sensitive conductivities [7,8], they were hence widely investigated as electrical chemiresistors for sensing different vapor analytes [9–11] and even organic molecules in aqueous solutions [12,13]. Second, Au thin films were demonstrated to have special localized surface plasmon resonances (LSPR) [14–16], so that highly ordered 2D Au superlattices showed strong collective LSPR bands due to the near-field coupling of adjacent nanoparticles [17] and were employed to detect biomolecular binding [18]. Third, they were considered as crucial substrates for surface-enhanced Raman scattering [19–23] with stable and reproducible enhancement factors of 10^5–10^7 [19–21]. In addition, activated Au thin films were used to catalyze selectively the oxidation of methane as a heterogeneous nanostructured catalyst in fuel cells [24,25].

Particularly when alkylthiol ligands were replaced by thiol-terminated polymers, the resulting polymer-modified Au NPs could be readily assembled into 2D nanostructures on solid substrates [26–28]. Monolayers of polystyrene-coated Au NPs with controlled interparticle distances showed typical dipolar near-field interparticle plasmon coupling of LSPR [29,30]. Such polymer-modified Au nanoparticle films have an advantage that the polymer thickness can be feasibly controlled by changing the polymer molecular weight. Furthermore, self-assembled block copolymer micelles have attracted much interest as functional monolayers due to their ability to form well-defined nanostructures [31–34]. For instance, Möller and coworkers used metallized block copolymer micelles to fabricate various 2D/3D nanopatterns through lithographical approaches [35,36]. In this paper, poly(4-vinylpyridine)-grafted Au NPs (Au@PVP) and polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-PVP) copolymers were combined to fabricate composite Au thin films. Scheme 1 illustrates that the introduction of a selective solvent, toluene, into a DMF solution of Au@PVP and PS-*b*-PVP copolymers leads to a cooperative self-assembly of Au@PVP and PS-*b*-PVP block copolymer into copolymer-hybridized Au NPs, and another simultaneous independent self-assembly of PS-*b*-PVP copolymers into inverse micelles. The hybridized Au NPs and copolymer micelles are then spin-coated onto solid substrates to fabricate composite Au films. Three copolymers comprising similar PVP blocks and largely different PS blocks were employed for comparison. Moreover, vapor annealing of selective solvents to the composite Au thin films was demonstrated to observe the interactions between vapor molecules and the film components.

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2. Materials and methods

2.1. Materials

Au@PVP nanoparticles were prepared through a previously reported surface-initiated atom-transfer radical polymerization [37]. The molecular weight of grafted PVP chains was determined to be about 14 kg/mol with a polydispersity of 1.3. The PS-*b*-PVP block copolymers (BCPs, subscript molecular weights) PS_{22k}-*b*-PVP_{22k}, $PS_{41.5k}$-*b*-$PVP_{17.5k}$, and PS_{122k}-*b*-PVP_{22k}, were purchased from Polymer Source Inc. All other chemicals and solvents were purchased commercially and used without purification.

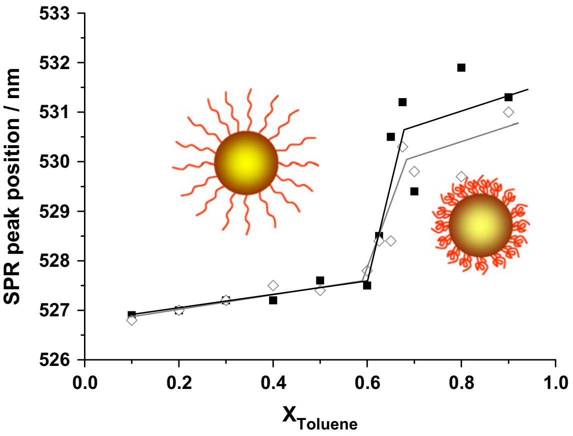

Fig. 1. Variation of surface plasmon peaks of Au@PVP (black squares and fitted black line) and Au@PVP/PVP_{22k}-*b*-PS_{22k} mixtures (open diamonds and fitted gray line) by toluene content.

2.2. Self-assembly of Au@PVP and PS-b-PVP induced by solvent change

The critical toluene content in the toluene/DMF mixture which caused the transition of extended PVP chains to collapse was determined from the change in localized surface plasmon resonance (LSPR) property of Au@PVP solution. In detail, 0.1 mL DMF solution of pre-synthesized Au@PVP (0.44 mg/mL by gold atoms) was added to each of 0.1, 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, and 1.7 mL DMF, followed by the slow addition of toluene to reach a total volume of 2.0 mL under gentle stirring. UV–vis spectra of these nine mixed solutions were then recorded on a Varian CARY 5000. The critical toluene content was further verified by the Au@PVP and BCP mixtures. PS_{22k}-*b*-PVP_{22k} solution was added to the Au@PVP solution in DMF to get a mixture of Au@PVP and BCPs, in which the concentration of Au and the copolymer was about 0.35 mg/mL and 0.5 mg/mL, respectively. Subsequently, the change in the characteristic LSPR band of the Au-containing mixture after toluene addition was also monitored.

2.3. Spin-coating of Au@PVP and BCP inverse micelles on solid substrate

PS-*b*-PVP copolymers were dissolved in DMF at a concentration of 5 mg/mL. First, 0.02 mL Au@PVP solution (1.1 mg/mL) was added to 0.005–0.08 mL copolymer solution, followed by DMF dilution to 0.2 mL. Then, 0.5 mL toluene was added drop-wise un-

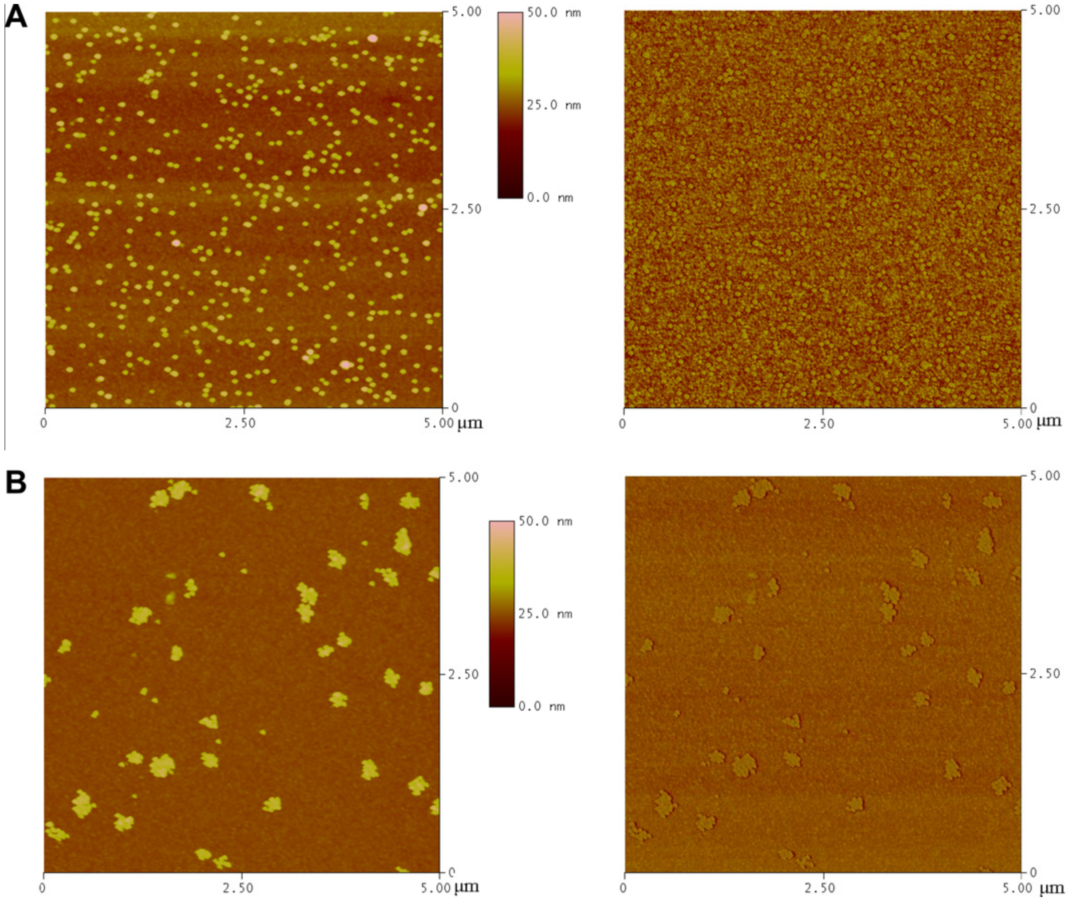

Fig. 2. Tapping mode AFM images of spin-coated Au@PVP particles on silicon wafer in toluene/DMF mixtures with (A) 30% and (B) 70% toluene. Left: height-contrast; right: phase-contrast. Plan scales: 5 μm × 5 μm.