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Research paper

In situ synthesis of gold nanocrystal-embedded poly(dimethylsiloxane) films with nanostructured surface patterns

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ABSTRACT

Gold (Au) nanocrystal-embedded PDMS films were synthesized by simply depositing a precursor solution on the PDMS film. The resulting PDMS films, inside which many Au nanocrystals with dimensions smaller than 50 nm were uniformly embedded, showed unique nanostructured surface patterns. The morphological evolution of the films proceeded along different pathways depending on whether the film was chemically treated with O_2 plasma. The hybrid films were systematically characterized by carrying out scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and Fourier-transform infrared spectroscopy analyses. Mechanisms explaining the formation of the Au nanocrystal-embedded PDMS films and the morphological evolutions during the synthesis were proposed based on the results. The developed approach provides a simple route for fabricating metal nanocrystal-embedded polymer films with unique structures and without the need for special equipment.

1. Introduction

Metal nanocrystal-embedded polymer nanostructures have been extensively studied because of their potential applications, ranging from electronic and optical devices to biosensing and antimicrobial agents [1–5]. In general, in order to fabricate the hybrid nanostructures, two types of synthetic approaches can be applied: *in situ* and *ex situ* methods [6]. The *ex situ* method first involves forming metal nanocrystals, followed by dispersing them into a polymer matrix [7–8]. In the *in situ* approach, a metallic precursor is dissolved in a polymer or polymerizing solution and then reduced to form the metal nanocrystals; in this way the metal nanocrystals are generated inside the polymer matrix [9–10]. Since *ex situ* processes require long process times and continuous effort, *in situ* methods are preferred [11]. However, a facile synthesis of metal nanocrystal-embedded polymer nanostructures *via* an *in situ* method has not yet been developed and is hence of particular interest.

The choice of polymer plays an important role in determining the functionality of the hybrid nanostructures. Poly(dimethylsiloxane) (PDMS) is one of the most widely used polymers due to its many useful properties such as optical clarity in the visible and ultraviolet region, good thermal and oxidative stability, gas permeability, and non-toxic nature [12–13]. Other important features of PDMS are its solid nature, high flexibility and ease of processing [14]. The micro-/nanohierarchical structures of the master mold can be easily transferred to the surface of the PDMS by carrying out soft lithography, which is a cost-effective, simple, and nondestructive pattern transfer technique [15]. The inclusion of metal nanocrystals embedded in PDMS films with ordered surface nanostructures may be expected to impart additional beneficial properties and extend its uses to applications such as antimicrobial agents, separation materials, and catalysts [16–19].

In this paper, we report a novel method for producing Au nanocrystal-embedded PDMS films, one that involved simply depositing a precursor solution on the PDMS films with controlled surface patterns. This new procedure was shown to have several advantages over previously reported procedures. First, the new synthetic method was found to be a facile protocol for the *in situ* production of Au nanocrystal-embedded polymer-based nanostructures. In our investigations, it did not require additional reducing agents and stabilizers, and the nanocrystals were uniformly embedded within the PDMS matrix while still being chemically accessible to the substances soluble in PDMS. In addition, the synthetic results were easy to reproduce, and the synthesis did not require special equipment. Finally, the morphologies of the hybrid films could be varied by applying a chemical treatment with O_2 plasma. Here, we present a detailed study of the structural and morphological changes displayed during the formation of the hybrid nanostructures made using this method.

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2. Experimental

2.1. Preparation of the three-dimensional (3D) colloidal crystal master mold

Emulsifier-free emulsion polymerization was used to synthesize submicron PS particles, and the 0.1 wt PS colloidal suspensions (40 mL) was prepared by using deionized water as a dispersing solvent to assemble 3D colloidal crystals. A small amount of polyvinylpyrrolidone (PVP; $M_w = 55$ kDa, Aldrich 856568) was added to the suspension. Then, the glass substrate was dipped vertically into the PS colloidal suspension. The slide glasses (76 mm × 26 mm) were purchased from Waldemar Knittel, Inc. (Germany). The glass substrates were cleaned with ethanol and treated with oxygen plasma to make their surfaces hydrophilic. The colloidal suspensions were placed in a furnace at 60 °C and water was evaporated at a rate of 0.7 mL/h.

2.2. Synthesis of Au nanocrystal-embedded PDMS films

The 3D colloidal crystal master mold was passivated with chlorotrimethylsilane (Aldrich 386529) by using vapor deposition in a vacuum chamber. Then a PDMS prepolymer solution containing 10% curing agent (Sylgard 184, Dow Corning) was poured onto the prepared master mold. The cast prepolymer was cured in an oven at 60 °C for 4 h. After the curing reaction was completed, the PDMS elastomer was carefully peeled off from the master mold and the polymer substrate was heated at 65 °C. An ethanol solution of 100 mM $HAuCl_4$ was deposited on the prepared substrate and left there for 3 h.

2.3. Characterizations

Scanning electron microscopy (SEM) images were recorded using a field-emission scanning electron microscope (Sirion, FEI) operated at an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) images were obtained using a Philips Tecnai F30 microscope operated at 200 kV. The SEM (or TEM) sample was prepared by placing a drop of the final product (suspended in DI water) on a silicon wafer (or carbon-coated copper grid), and then drying the sample in a fume hood. The investigations of the morphologies of the products were also carried out in air using a Multimode AFM equipped with a Nanoscope IV controller (Veeco Metrology Group, USA). Fourier transform infrared (FT-IR) spectroscopy was performed to understand the mechanism by which Au ions were reduced in the PDMS matrix. The FT-IR device (Thermo Nicolet 5700, USA) was equipped with an attenuated total-reflection (ATR) diamond crystal accessory. Contact angles (CA) were measured by using a Dataphysics OCA system (Germany) at room temperature.

3. Results and discussion

In order to fabricate Au nanocrystal-embedded PDMS nanostructures with nanostructured surface patterns, a 3D colloidal crystal was used as a master mold. The fabrication process was simple, and Fig. 1 schematically illustrates the process. A high-quality 3D colloidal crystal was prepared using the vertical deposition method [20]. The colloidal crystal master was passivated with chlorotrimethylsilane using the vapor deposition method, which allowed us to peel off the PDMS mold without it being damaged by the colloidal crystal master mold. Then, the PDMS replica mold was fabricated by pouring the PDMS prepolymer onto the 3D colloidal crystal. After curing the PDMS in an oven at 60 °C, PDMS films with a concave regular structure could be carefully peeled off. The low interfacial energy and elasticity of PDMS allowed the mold to be detached from the 3D colloidal crystals film without being damaged [21]. Finally, an ethanol solution of 100 mM $HAuCl_4$ was deposited on the PDMS substrate for 3 h at 65 °C.

The process by which the Au nanocrystal-embedded PDMS films formed was examined by monitoring the morphological evolution of these films. Fig. 2A shows a typical top-view SEM image of a PDMS replica mold with a regular concave structure. A hexagonal array of round holes separated by PDMS walls was observed in this image, which showed that the reciprocal structure of the colloidal crystal surface was transferred to the surface of the PDMS film. After depositing an ethanol solution of $HAuCl_4$ on the PDMS substrate and leaving it there for 1 h, no considerable change was observed in the arrangement of the holes, as shown by comparing Fig. 2A and B. However, the diameters of the holes decreased and the walls became thicker. Upon increasing the deposition time to 3 h, the holes continued to shrink and the walls continued to swell, as shown by comparing Fig. 2A, B, and C. The PDMS film surface was initially uniform and smooth, but became uneven and rough after the ethanol solution of $HAuCl_4$ was deposited. Fig. 2D shows an SEM image of the sample treated for 3 h and tilted at angle of 45°. This image clearly showed the changed concave structure of the PDMS film. Fig. 2E and F show low-magnification SEM images of the sample treated with the ethanol solution of $HAuCl_4$ for 3 h. These images revealed that highly ordered surface patterns were produced over a large area. To characterize the surface modification after the deposition of the ethanol solution of $HAuCl_4$ for 3 h, an AFM analysis was carried out (Fig. S1). The average height, *i.e.*, the average distance from the bottom points of the holes to the tops of the walls, was

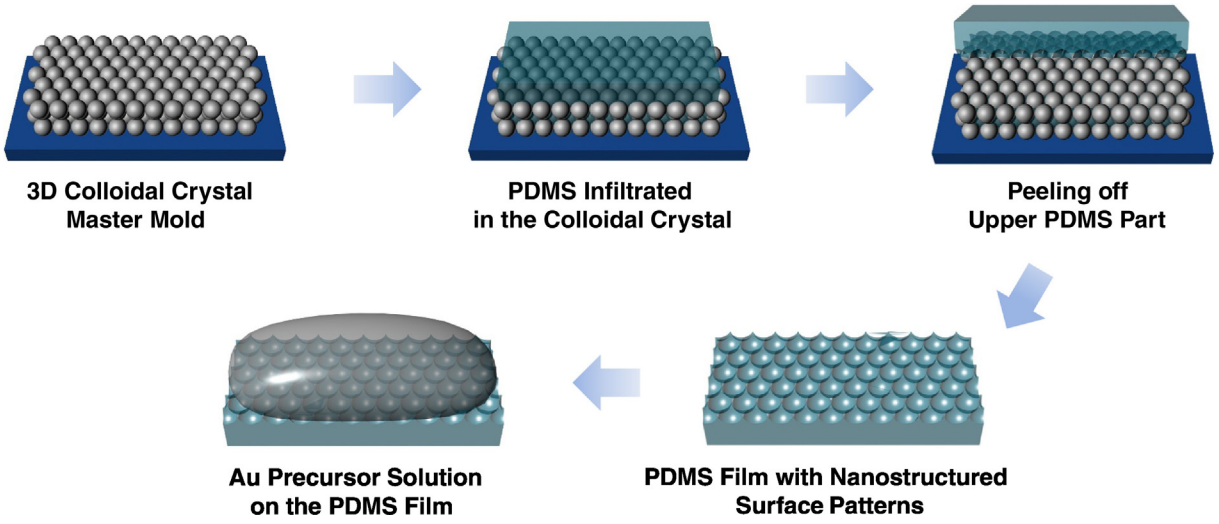

Fig. 1. Schematic illustration of the synthesis of Au nanocrystal-embedded PDMS film with nanostructured surface patterns.