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Full Length Article

Scalable creation of gold nanostructures on high performance engineering polymeric substrate

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ABSTRACT

The article reveals a facile protocol for scalable production of gold nanostructures on a high performance engineering thermoplastic substrate made of polyarylene ether nitrile (PEN) for the first time. Firstly, gold thin films with different thicknesses of 2 nm, 4 nm and 6 nm were evaporated on a spin-coated PEN substrate on glass slide in vacuum. Next, the as-evaporated samples were thermally annealed around the glass transition temperature of the PEN substrate, on which gold nanostructures with island-like morphology were created. Moreover, it was found that the initial gold evaporation thickness and annealing atmosphere played an important role in determining the morphology and plasmonic properties of the formulated Au NPs. Interestingly, we discovered that isotropic Au NPs can be easily fabricated on the free-standing PEN substrate, which was fabricated by a cost-effective polymer solution casting method. More specifically, monodispersed Au nanospheres with an average size of ~60 nm were obtained after annealing a 4 nm gold film covered PEN casting substrate at 220 °C for 2 h in oxygen. Therefore, the scalable production of Au NPs with controlled morphology on PEN substrate would open the way for development of robust flexible nanosensors and optical devices using high performance engineering polyarylene ethers.

1. Introduction

Gold nanoparticles (Au NPs) have attracted enduring research interests among numerous applications ranging from catalysis [1,2], nanomedicine [3–5], chemical sensors [6,7] to optical devices [8]. In recent decades, increasing efforts have been devoted to the localized surface plasmon resonance (LSPR) of gold nanoparticles, which is derived from the collective oscillation of free electrons in Au NPs upon incident light irradiation [9]. As a consequence, the strong light scattering, appearance of intensive surface plasmon absorption band and enhancement of localized electromagnetic field are observed for Au NPs in the visible light range [10,11]. More importantly, the LSPR properties of Au NPs, including extinction wavelength and intensity, are highly depended on the nanoparticles shape, size, spacing and the surrounding environment [12,13]. Thus, the modulation of Au NPs LSPR properties is basically realized by adjusting above parameters via various fabrication protocols including nanomanipulation methods [14], thermal annealing [15], self-assembly of gold nanoparticles [16], selective chemical etching [17], etc.

Among these protocols, the combination of vacuum evaporation and thermal annealing is regarded as a promising candidate due to its simple preparation route, low cost and large scale fabrication potential [15,18]. In this method, the (semi-)continuous evaporated gold thin film on a substrate was gradually transferred into separated nanoparticles during thermal annealing, which was denoted as the "solid dewetting" process that basically reduced the overall surface tension between gold film and substrate [19]. Unfortunately, Au NPs fabricated through this kind of approach suffered from a poor stability when they were exposed to aqueous solution, biological milieu and other practical application scenarios [20–22]. Thus, a myriad of strategies have been developed to enhance the stability of Au NPs on the substrate, including utilization of pre-modified substrates with organic/metal layer to improve the gold-substrate adhesion [23–25], introduction of inorganic/organic coating layer on gold [26–28], and high-temperature post-deposition annealing [29,30]. On the contrary to the former two protocols involving additional chemical agents, the later one is advantageous in terms of preparation of pristine gold nanoparticles. For instance, the bare Au NPs free of any surface capping

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agent can be firmly immobilized on a glass substrate after a thermal annealing at high temperature around 550 °C, which is quite close to the glass transition temperature of used glass substrate. In this way, the *in-situ* formulated Au NPs are partially embedded inside of the glass substrate, contributing to the outstanding stability [29]. In addition, although the effects of gold evaporation thickness and annealing conditions onto morphology of Au NPs generated on the rigid inorganic substrates have been intensively investigated [31–33], the fabrication and characterization of Au NPs on an organic/polymeric flexible substrate is hardly reported.

Inspired by the glass transition temperature (T_g) annealing idea, it is believed that the Au NPs on flexible substrate can be readily prepared via less energy demanding thermal annealing by using a transparent thermoplastic substrate due to its much lower glass transition temperature. However, the "solid dewetting" process of transforming gold thin film into Au NPs normally conducted at a temperature higher than 200 °C according to the most of published works [34–38], thus the commercial transparent thermoplastics, such as polymethyl methacrylate (PMMA), polystyrene (PS), polycarbonate (PC), etc. failed to serve as the reliable substrate because of their low T_g (<150 °C). Fortunately, polyarylene ether nitrile (PEN) is a high temperature resistant thermoplastic with the glass transition temperature in the wide range from 180 °C to 250 °C depending on the macromolecular structures, meanwhile PEN exhibits excellent film-forming ability, good mechanical properties, and chemical resistance [39,40]. Especially, the PEN containing phenolphthalin (PPL) moiety (PEN-PPL) has been previously reported to possess high T_g approaching to 260 °C, good visible light transmittance as well as blue emitting fluorescence [41,42]. Thus, we believed that PEN-PPL could be employed as the ideal substrate to enable Au NPs formation via the "solid dewetting" process.

In this work, Au NPs were successfully prepared on the PEN-PPL substrate through a facile protocol made of gold thin film evaporation followed by thermal annealing. Specifically, the effects of initial gold film evaporation thickness, annealing time as well as atmosphere on the morphology and plasmonic properties of Au NPs were systematically investigated using the extinction spectroscopy and scanning electron microscope. More importantly, we have obtained the anisotropic (irregular island-like morphology) and isotropic (spherical morphology) Au NPs on the spin-coated PEN substrate on a glass slide and the freestanding PEN casting substrate, respectively. Thanks to their controlled morphology and facile preparation, the Au NPs immobilized on PEN substrate will pave the way for the construction of flexible plasmonic nanosensor.

2. Experimental section

2.1. Preparation of PEN as flexible substrate

As shown in Scheme 1, the copolymer of PEN-PPL (number average molecular weight M_n of 11904, polydispersity index of 2.38) was synthesized from the nucleophilic substitute polycondensation of bisphenol A (BPA), phenolphthalin (PPL) and 2, 6-dichlorobenzonitrile (DCBN) according to the previously reported work [42], and the transparent PEN film was prepared by spin coating. Specifically, 0.2 g synthesized PEN powder was dissolved in 4 mL tetrahydrofuran (THF) solvent under magnetic stirring for 30 min to form a homogeneous solution. Prior to spin coating experiment, all the glass sides (1.5 × 1.5 cm) were intensively washed in the acetone and ethanol, followed by the vacuum drying at 50 °C for 15 min. Next, the prepared PEN solution was spin-coated onto clean glass slides, followed by drying in a vacuum oven at 80 °C for 30 min, and then the as-prepared spin-coated substrates were transferred into an evaporator for gold thin film deposition. On the other hand, the freestanding PEN substrates were prepared using classical polymer solution casting method. Specifically, 1 g synthesized PEN powder was dissolved in 10 mL dimethylacetamide (DMAc) solvent under magnetic stirring for 30 min to form a homogeneous solution. Next, the solution was casted onto a horizontal clean glass plate and subjected to the thermal treatment (stepwise increasing of temperature from 80 °C, 100 °C, 120 °C, 140 °C to 160 °C, 2 h for each step) to remove the solvent completely. Finally, the obtained flexible PEN substrates were cut into pieces (1.5 × 1.5 cm) and transferred into a vacuum evaporator for gold thin film deposition.

2.2. Preparation of gold nanoparticles by thermal annealing

Both spin-coated substrates and casting substrates were integrated with a shadow mask and then mounted in an evaporator equipped with a thickness monitor. Gold thin films with nominal thickness of 2 nm, 4 nm, 6 nm, 8 nm and 10 nm were evaporated under high vacuum (<1×10^{-6} Torr) using a deposition rate of 0.01 nm/s. The shadow mask was slightly rotated during evaporation to form a thin film with homogeneous thickness. Finally, the as-evaporated samples were transferred into a tube furnace for subsequent thermal annealing at different temperature in air or oxygen atmosphere.

2.3. Thermal analysis, spectroscopy and morphology characterization

The glass transition temperature of PEN was determined by a differential scanning calorimeter (DSC Q100, TA). The extinction spectra of the formulated Au NPs on PEN substrates were recorded using a conventional microscope (BA410E, Motic) equipped with a portable spectrometer (NOVA, Ideaoptics). All the samples were measured under the same magnification through an optical fiber (FIB-M-600-NIR, Ideaoptics). The surface morphology of Au NPs was characterized with a scanning electron microscope (SEM, JSM-5900LV, JEOL) operating at an acceleration voltage of 20 kV and an atomic force microscope (AFM, SmartSPM, AIST-NT) in the tapping mode.

3. Results and discussion

It is well-known that spin coating is one of the most popular methods to fabricate flexible substrate using polymeric materials [43]. In this work, the gold nanoparticles were created on a transparent substrate made of high temperature resistant PEN through metal film evaporation and thermal annealing, thus it is believed that the initial gold film evaporation thickness, annealing temperature, time and atmosphere could be the essential parameters to determine the morphology and plasmonic properties of obtained Au NPs.

3.1. Influence of evaporated gold film thickness onto LSPR of Au NPs

As shown in Fig. 1a, the as-evaporated sample with a gold film thickness of 2 nm exhibits a broad LSPR band around 670 nm, which is attributed to the presence of discrete Au NPs on the spin-coated PEN substrate. However, as the increasing of gold film evaporation thickness to 4 nm and 6 nm, the LSPR band of samples displays the typical feature of continuous gold films [44]. Therefore, it is clear that Au NPs cannot be formulated on the spin-coated PEN substrate free of thermal treatment unless very thin film is deposited.

In order to transfer the as-evaporated gold film on PEN substrate to Au NPs, the thermal annealing at appropriate temperature is indispensable. Considering that the glass transition temperature