Reductive surface synthesis of gold nanoparticles on silicate glass and their biochemical sensor applications^{a)}

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(Received 19 July 2012; accepted 31 October 2012; published online 10 December 2012)

Gold nanoparticles (Au NPs) were directly synthesized on the surface of polyvinylsilazane (PVSZ, $-\text{[(vinyl)SiH-NH}_2\text{]}-$) without use of extra reductive additives. The reductive Si-H functional groups on the surface of cured PVSZ acted as surface bound reducing agents to form gold metal when contacted with an aqueous Au precursor (HAuCl_4) solution, leading to formation of Au NPs adhered to silicate glass surface. The Au NPs-silicate platforms were preliminarily tested to detect Rhodamine B ($1\text{ }\mu\text{M}$) by surface enhanced Raman scattering. Furthermore, gold microelectrode obtained by post-chemical plating was used as an integrated amperometric detection element in the polydimethylsilane-glass hybrid microfluidic chip. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4769780>]

I. INTRODUCTION

In the past few years, gold nanoparticles (Au NPs) have attracted much interest as a novel platform for various applications in nanobiotechnology because of convenient surface conjugation with molecular probes, remarkable plasmon-resonant optical properties, and catalytic effects.^{1,2} In the solution phase synthesis in the presence of reductive agents such as citric acid, alkylamine, alkylthiol, cationic surfactants, and polymers, owing to high aggregation of Au NPs, highly dispersed nanoparticles are difficult to obtain without using organic stabilizer.³ Therefore, the approaches with prebound reductants on a certain support are quite desirable for highly dispersive Au NPs synthesis, which have been attempted in a variety of manner.⁴⁻⁶ These Au NPs have been directly synthesized or immobilized on solid matrices (like silica, titania, or polymer) through surface modification with functional groups that provide attraction to nanoparticles.⁷ Use of chemically modified silica with immobilized reagents having pronounced reducing properties is of considerable interest as a method for controlled synthesis of metal nanoparticles or nanoclusters.^{8,9}

Polydimethylsilane (PDMS) was widely employed as a microfluidic and biochip material because of low cost and mass reproduction. However, the absence of functional groups on the surface of PDMS has limited its surface engineering such as immobilization of nanoparticles or biomaterials. Therefore, various surface modification approaches have been taken to address the problems, including plasma treatment, polymer grafting, adsorption of polyelectrolytes, and detergents.¹⁰ Deposition of thin polymer films by chemical vapor deposition (CVD) or plasma

^{a)}Contributed paper, published as part of the special topic on Advances in Microfluidics and Nanofluidics 2012 conference in Dalian, August 2012.

^{b)}This research was performed while the author was at National Creative Research Center of Applied Microfluidic Chemistry, Pohang 790-784, South Korea.

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SCHEME 1. (a) Chemical structure of PVSZ. (b) Scheme for Au NPs-silicate synthesis on PVSZ coated PDMS support.

polymerization to define robust surface chemistry leads to high efficiency of analytical device by overcoming these limitations.^{11–13} These approaches have been extended to the deposition of reactive coatings, which result in surfaces containing amine, carboxy, hydroxy, and aldehyde groups.^{14–19} The high chemical reactivity of the functional groups enabled ready tailoring of the surface for analytical device functions. In particular, silicon hydride (Si-H) is an interesting functional group, which can easily be converted to silanol (Si-OH) species in the presence of water, and yields various surface functionalities through silylation reactions with some organics such as alcohols, carboxylic acids, amines, phenols, and thiols. DNA, enzyme, and protein immobilization on the Si-H terminated substrates (silicon wafer, silica) has been intensively studied for application in biosensors^{20–23} and column materials for analytical chemistry.²⁴ Moreover, *in-situ* Au NPs synthesis had been reported with PDMS substrate through adjustment of the ratio of curing agent (containing Si-H) and the PDMS monomer.²⁵ However, it required a long reaction time of overnight to produce nanoparticles due to the limited Si-H groups remained on the cured PDMS surface even under various mixing ratios of PDMS and curing agent by sacrificing the mechanical strength.

Recently, we reported allylhydridopolycarbosilane (AHPCS, $-\text{[(allyl)SiH}_2\text{-CH}_2\text{]}-$) and polyvinylsilazane (PVSZ, $-\text{[(vinyl)SiH-NH}_2\text{]}-$) derived silicate glass coatings for PDMS microfluidic devices via UV/thermal curing and consecutive hydrolysis treatment under basic condition.^{26–28} The Si-H groups of the polymer mainly contributed to forming the hydrophilic silicate glass phase in a controlled manner. Excellence in optical transparency, chemical stability, organic solvent resistibility, and electroosmotic flow properties was exploited in advancing a novel microfluidic device for organic synthesis and surface coating for microchip electrophoresis.

In this study, we present a novel application of PVSZ coatings for reductive surface synthesis of Au NPs (Scheme 1). The Si-H groups on the photo-cured PVSZ surface reduced Au (III) ions to form gold metal, resulting in interfacial Au_xSi bond, and competitively hydrolyzed to Si-OH surface. At the same time, the moisture sensitive silazane, Si-N, bonds are converted to form a silicate network when subjected to aqueous gold precursor solution. In contrast to the traditional dry process, the Au NPs adhered on PVSZ as a mediation layer was obtained by a simple wet process with no use of any expensive equipment. Moreover, the fabricated Au NPs-silicate microelectrode with strong interfacial adhesion was quite durable with reusability.

Eventually, sensor applications of the Au NPs–silicate platforms were investigated to detect Rhodamine B by surface enhanced Raman scattering (SERS) substrate, and also to determine dopamine (DA) and catechol (CA) compounds by electrochemical microelectrode fabricated in the microfluidic chip.

II. EXPERIMENTAL

A. Materials and reagents

PVSZ (HTT-1800, 50 cps at 20 °C) (Scheme 1(a)) was purchased from Kion company (Malta, NY, USA). Add 2 wt. % photo-initiator (Irgacure 369, Ciba Specialty Chemicals Inc.) and 2 wt. % thermal initiator (dicumyl peroxide, Aldrich) to the polymer base for coating. Rhodamine B, dopamine, catechol, and boric acid were obtained from Sigma-Aldrich.

B. Fabrication of PDMS chip

The PDMS chip was fabricated by following the photolithography replica molding method.²⁹ Viscous PDMS precursor was prepared by uniformly mixing PDMS prepolymer and curing agent (Sylgard 184, Dow Corning) at a ratio of 10:1 and poured it to a prepared micro-channel master, and was cured at 70 °C for 2 h after degassing. The channel is 2 cm-long, in 35 μm wide and 50 μm -deep. The injection length is 100 μm with double-T design.

C. PVSZ reactive coating

All operations of polymer coating and photo-curing proceeded in a nitrogen glove box. Before coating, plasma treatment (BD-20, ETP, USA) was performed to strengthen the adhesion between PVSZ and PDMS support. The PVSZ coating solution was prepared by mixing 2 wt. % of photo-(Irgacure 369) and thermal-(dicumyl peroxide) initiators, and was spin-coated on the plasma treated flat PDMS at 500 rpm for 10 s followed by 3000 rpm for 30 s to reach PVSZ coating thickness of ca. 30 μm . Then, the coated PVSZ polymer was consolidated by UV exposure (ELC-4100 UV light system, 20 mW/cm^2) for 20 min due to cross-linking reaction of unsaturated group via hydrosilylation route.²⁸ The PVSZ polymer coated PDMS was kept under dry nitrogen for the next step of Au NPs synthesis.

D. Au NPs immobilized PVSZ platform and Au NPs electrode patterning

To surface synthesize Au NPs, the polymer coated PDMS substrates were taken out of the nitrogen box, and immediately immersed into a range of aqueous Au precursor (HAuCl_4) solutions with various concentrations (0.25–10 wt. %) for different periods of reaction time (0.5–30 min). For SERS substrate, an adhesive tape-type shadow mask (Proteogen® 16 $\times$ 6, ϕ = 1 mm, Seoul, Korea) was used to mask undesired areas from Au precursor solution. Followed by nanoparticle synthesis in absence of extra reduction agent, the substrates were thoroughly rinsed with 0.1 M NaOH solution and water for 30 min to completely deactivate the residual Si-H to silicate, and dried. Finally, the specimens were undergone thermal curing process on hotplate under 150 °C for 3 h.

On the other hand, Au microelectrodes were fabricated on a PVSZ coated slide glass instead of PDMS support. The processes consists of a series of photolithography, PVSZ coating, photo-curing, Au NPs synthesis, Au wet plating, and photoresist (PR) stripping as detailed in Scheme 2. First, a glass slide was patterned with positive PR (AZ5214, Clariant) by the photolithographic method. The PR was developed away with developer (AZ MIF300, Clariant) revealing the desired electrode areas (bare glass surface). Then, the PVSZ mixture (containing photo- and thermal curing agent) was spin-coated at 6000 rpm for 60 s under N_2 atmosphere, leading to a thin PVSZ layer (ca. 10 μm) coated on top of the PR substructures. After being subjected to UV exposure (ELC-4100 UV light system, 20 mW/cm^2) for 20 min, the substrate was taken out of the N_2 box, and direct Au NPs synthesis as a seed layer was carried out by immersing in a 2.5 wt. % aqueous HAuCl_4 solution for 30 min. For forming the conductive electrode layer,

SCHEME 2. Schematic diagram of Au NPs-silicate microelectrode fabrication combined with photolithography. Inset image: enlarged photo view of fabricated micro gold electrode.

an additional Au wet plating (0.5 wt. % HAuCl_4 + 1 mM hydrazine for 1 h) was performed to further deposit more Au layers on the Au NPs pattern. After one hour of Au plating, a lift off process was conducted by submersion in ethanol to remove the PR and the Au layer remained on the PVSZ mediated glass surface. Two step processes of Au NPs seed synthesis and post-wet plating are required to obtain the uniform gold microelectrode with a strong interfacial bond. After electrode construction, the two pieces of microfluidic channel plate and electrode patterned glass was irreversibly bonded together by aligning the electrode set close to the end of PDMS channel under microscope to form a conformal PDMS-glass hybrid chip, which is the off-channel detection method as reported.³⁰ The dimension of the patterned gold electrode is $100\ \mu\text{m}$ (working) $\times$ $100\ \mu\text{m}$ (reference) $\times$ $200\ \mu\text{m}$ (counter).

E. Characterization

A number of measurements were carried out for Au NPs characterization. The morphology of the resulting Au NPs was characterized by field emission transmission electron microscope (FE-TEM) (Tecnai F20, philips). For obtaining the TEM image, one-drop of 0.5 wt. % PVSZ in anhydrous dimethylformamide (DMF) was dropped onto the TEM grid and UV cured. Then, it was treated with 0.25 wt. % aqueous Au precursor solution for 1 min. The obtained nanoparticle images were analyzed by the Image J program (v1.45, NIH). Surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific Multilab 2000, England) with Al $K\alpha$ X-ray source (1486.6 eV), and C1s peak at 285.5 eV was used as a reference. And the depth profile of chemical composition (1 wt. % HAuCl_4 , 30 min) was analyzed by Ar ion

sputtering at 3 KeV and XPS analysis. A multi-purpose attachment X-ray diffractometer (D/MAX-2500, Rigaku) was performed for Au NPs confirmation. The UV-Vis spectra were recorded on an AvaSpec 2048 (Avantes, Eerbeek, Netherlands) spectrophotometer. The surface enhanced Raman signal for Rhodamine B was measured by a high resolution dispersive Raman microscope (LabRAM HR UV/Vis/NIR, Horiba Jobin Yvon, France) using 5-mW, 633-nm He-Ne laser line. Rhodamine B (1 μ M, 20 μ l) sample was directly dropped onto patterned Au NPs substrates and adsorbed for 10 min. The remaining solution was then removed from the solution by nitrogen blowing.

F. Microchip electrophoresis and amperometric detection

A microchip electrophoresis setup, composed of a high voltage power supply (MP5; Spellman High Voltage Electronics, Plainview) and a VMP multichannel potentiostat (Perkin-Elmer Instruments, Boston, MA), was employed to test amperometric properties of the developed Au electrode. The off-channel end-column detection was performed with working electrode aligned at 40- μ m distance from the outlet of the microchannel in the detection reservoir (Scheme 2). Before the experiments, microfluidic channels were washed with 0.1 M NaOH for 5 min, and rinsed with water and running buffer for 2 min, respectively. A 2 mM (pH 8.8) borate buffer was used for the electrophoresis separations.

III. RESULTS AND DISCUSSION

A. Reductive synthesis of Au NPs on the PVSZ surface

The Au NPs synthesis on PVSZ derived silicate glass surface was investigated by various spectroscopic analyses. The photo-cured PVSZ substrates were subjected to aqueous Au precursor solutions as illustrated in Scheme 1(b). In the ATR (Fig. 1(a)) spectra of both photo-cured and synthesized Au NPs on PVSZ, the relative intensity ratio $I_{\text{Si-H}}/I_{\text{C-H}}$ significantly decreased from 3.73 to 1.23, as the Si-H peak intensity at 2150 cm^{-1} was decreased. It is believed that the Si-H groups take part in the oxidation to provide the electrons for the reduction of Au^{3+} ion to metallic Au in the aqueous system. It has been reported that the Si-H groups enable reduction of Pd^{2+} , Cu^+ , Cu^{2+} to the metallic states in organic or aqueous conditions.^{31–33} On the other hand, the unreacted Si-H bonds were hydrolyzed to form Si-OH bonds, and subsequently condensed to constitute Si-O-Si bonds in aqueous condition, which is consistent with the newly appeared Si-O-Si peak (1100 cm^{-1}).³² In addition, it should be cited from the previous report²² that the nucleophilic attack on Si atoms by -OH ions under NaOH deactivation condition hydrolyzes the silazane Si-N framework in the PVSZ to the siloxane Si-O-Si skeletal structure via condensation reaction of intermediately formed silanol, eventually leading to the phase conversion from PVSZ surface to silicate glass surface. At here, it is important to point out that the reductive Si-H functional groups on the surface of cured PVSZ acted as surface bound reducing agents to form directly Au NPs in the presence of Au precursor (HAuCl_4) solution, leading to formation of Au NPs adhered to silicate (Au NPs-silicate) glass surface by subsequent hydrolysis. And it is obvious that the silicate glass showed outstanding chemical resistance compared to the polymeric PVSZ phase, resulting in superior durability of the Au NPs-silicate surface.²⁶

The Au NPs generation was further monitored by UV-Vis spectroscopy. When the PVSZ substrate was contacted with HAuCl_4 solutions, a light pink color appeared at the surface layer of samples within minutes (Fig. 1(b)). The samples turn dark brown-red after interaction for 10 min. A maximum absorption peak was at 535 nm, that is assigned to the surface plasmon resonance, which is conclusive evidence for the presence of zero valence Au NPs.³⁴ Average diameter of the Au particles, determined by TEM, was 7 nm (Fig. 2). By varying the initial concentration of HAuCl_4 from 1.0 wt. % to 0.25 wt. %, the average size of reduced Au NPs was controlled from 12 ± 2 to 7 ± 2 nm. Excess HAuCl_4 resulted in a fast reduction of the Au (III) ions, with the formation of nanoclusters as a consequence. The surface density (by coverage) of Au NPs was related to the reaction time and the concentration of gold precursor. The surface

FIG. 1. Spectroscopic analyses of Au NPs generations. (a) ATR-IR spectra of Au NPs formation on the PVSZ surface. Sample for Au NP was subjected to 0.5 wt. % HAuCl₄ for 10 min, 0.1 M NaOH and water for 30 min, and thermal curing at 150 °C for 3 h. (b) UV/Vis absorbance of Au NPs on PVSZ obtained by changing HAuCl₄ concentration and the corresponding photo-images.

coverage of gold nanoparticles under HAuCl₄ concentration of 1 wt. % and 0.25 wt. % on the PVSZ film was 37% and 25%, respectively, as shown in Figures 2(c) and 2(d).

Figure 3 displays an XRD pattern of Au nanoparticles on the polymer surface. The crystallographic identifications of all the Au peaks are labeled, and it exhibited identical patterns as those reported earlier.³⁵ Figure 4(a) compares the corresponding Au_{4f} XPS spectra as a function of the total sputtering time for Au NPs obtained by 30 min synthesis with 1 wt. % HAuCl₄ solution. In the initial period of sputtering, the characteristic Au 4f_{7/2} and 4f_{5/2} features found at 83.9 and 87.6 eV, respectively, agree with the reported values of 83.9 eV and 87.6 eV for metallic gold.³⁶ Upon extended sputtering, new peaks at 84.8 eV and 88.4 eV at the shoulder emerged with decreased metallic Au NPs. This peak shift of 0.8–0.9 eV towards higher binding energy reveals the formation of new chemical species of Au. It is assumed that the gold silicide (Au_xSi) existed at the surface between the Au NPs and PVSZ, in agreement with the reported value of XPS feature at 85.0 eV (Au4f_{7/2}).³⁷ As an alternative interpretation, it is plausible that a significant amount of bombarding energy upon Ar sputtering may cause Au_xSi formation presumably by reactions among highly reactive etched-off species from surface materials.³⁸ The variation of XPS peak intensities of the atomic ratios of Au, Si, C, O, and N with sputtering

FIG. 2. TEM images of Au NPs in different scale on PVSZ thin film (one drop of 0.5 wt. % PVSZ solution onto TEM grid). (a) 0.25 wt. % HAuCl_4 for 1 min, 500 nm scale. Inset image, particle size distribution of Au nanoparticles (average: 7 ± 2 nm) on the 0.25 wt. % PVSZ film for 30 min; (b) the same condition as in (a), 10 nm scale; (c) 1 wt. % HAuCl_4 for 30 min, 500 nm scale; (d) 0.25 wt. % HAuCl_4 for 30 min, 500 nm scale.

time is shown in Fig. 4(b). The depth profile of Au intensity shows the highest intensity of 49 at. % at a near surface layer (0–400 s sputtering), indicating the presence of an Au cluster with Au, Si, O, C, and N average atomic ratio of 1:0.48:0.35:0.31:0. The Au atomic % gradually decreased until reaching to Au_xSi at a near PVSZ interface layer. Again, the Si-N bond was completely decomposed to form the organosilicate glass phase under hydrolysis under basic

FIG. 3. XRD pattern of Au NPs (1.0 wt. % HAuCl_4 , 30 min) on a PVSZ coated silicon wafer.

FIG. 4. (a) XPS Au 4f7/2 and 4f5/2 spectra of Au NPs on the surface of PVSZ derived silicate film at different sputtering times. (b) Atomic percentage variation of elements in Au NPs-silicate as a function of sputtering time. Au NPs synthesized under condition of 1 wt. % HAuCl₄ for 30 min.

conditions.²⁶ Summing up, Au NPs-silicate substrates were simply synthesized based on the PVSZ thin film process in the absence of anti-aggregation reagent. No complex and hazardous chemical process is involved in preparing the silica hydride (Si-H) layer.^{9,39}

B. Au NPs-silicate platform for SERS signal detection

As is well-known, assembling nanoparticles on solid substrates are versatile tools for SERS, and it has attracted considerable interest due to the signal enhancement and ease of fabrication. Here, the feasibility of synthesized Au NPs-silicate platforms was investigated for SERS substrates treated by different concentrations of HAuCl₄ for a certain period of time (30 min). Figure 5(b) shows the Au NPs-immobilized on a PVSZ derived silicate substrate fabricated by photolithography. Figure 5(c) shows SERS spectra of 1 μ M Rhodamine B adsorbed on the Au NPs-silicate substrates. In agreement with the reported values,⁴⁰ Raman-shifted peaks of Rhodamine B can be found for vibrational modes, such as peaks at 1359, 1503, 1570, and 1647 cm⁻¹, which correspond to the aromatic C-C stretching vibrational modes. The SERS intensity of Rhodamine B varied significantly with the topology of the substrate. The SERS

FIG. 5. (a) Adhesive tape-type shadow mask from Proteogen for Au NPs array (16×6 , $\phi = 1$ mm); (b) photo-image of Au NPs array-type SERS substrate; (c) SERS signal of $1 \mu\text{M}$ Rhodamine B solution recorded on a Au NPs-silicate (PVSZ) substrate treated by different concentrations of Au precursor (HAuCl_4) solution. (1) no Au NPs substrate; (2) 0.5 wt. % for 30 min; (3) 2.5 wt. % for 30 min. Laser line, 633-nm He-Ne (5 mW).

intensity increases with increasing HAuCl_4 concentration up to 2.5 wt. %, but further increasing HAuCl_4 concentration to 10 wt. % did not lead to significant increase in the intensity. An interpretation could be that Au nano cluster as a “hot spot” was generated through homogeneous aggregation, resulting in enhancing the plasmon coupling interactions. It is worth noting that the Au NPs-silicate platform presented here could be used as a possible SERS substrate. The behavior of this proposed SERS substrate is comparable with that reported focused ion beam method on amorphized silicon surface using (3-mercaptopropyl)trimethoxysilane (MPTMS) as reductant.²⁵ It could also be useful as a biochip platform for DNAs, proteins, enzymes as performed by biomolecular immobilization probe through the well-known gold-thiol chemistry.

C. Au microelectrode from Au NPs seed layer for electrophoresis-amperometric detection

Miniaturized electrodes are one of the most important components of microchip-based devices for separation and sensing. The integrated microelectrodes on glass wafer is readily fabricated by a low cost process using the developed Au NPs-silicate layer served as active seed layer for post gold chemical plating.⁴¹ DA and CA were selected to evaluate the electrochemical performance of this electrodes in electrophoresis (Fig. 6). The relative standard deviation (RSD) of detected signal intensities for $400 \mu\text{M}$ of DA and CA were 2.3% and 2.7%,

FIG. 6. Electropherogram of 4 mM DA and 5 mM CA with electrophoresis-ampereometric detection with integrated Au microelectrodes from the Au NPs seed layer. The injection channel of PDMS-glass hybrid chip was 8 mm long, and the separation channel was 20 mm long. A 20 mM borate buffer (pH 8.2) was used as the running buffer for five parallel measurements. The working electrode was aligned 40 μm away from the outlet of the separation channel, and a detection potential of 0.7 V (vs. Au reference electrode) was employed.

respectively ($n=5$). The separation efficiency of DA was 1.7×10^4 plates/m ($H=2.0 \times 10^{-5}$ m), at an applied electric field of 330 V/cm which was comparable to the reported value of 2.1×10^4 plates/m ($H=4.7 \times 10^{-5}$ m) at a similar electric field (348 V/cm) with a PDMS chip.⁴² The developed gold microelectrode was proved to be suitable for the integrated ampereometric detection element in the PDMS-glass hybrid chip. The chip was used more than 10 times for electrophoresis with no solution leakage during the electrophoresis performance. It indicated that the Au NPs-silicate microelectrode fabricated by a simple wet process revealed the comparable durability to metal mediated (Cr, Ni) gold microelectrode required with use of special dry process equipment. The proposed method for Au microelectrode fabrication is effective and low cost without needs of expensive metal sputtering machine and clean room facilities, which makes it quite suitable for ampereometric detection coupled with microchip-based electrophoresis.

IV. CONCLUSIONS

In conclusion, we have developed a facile route to reductive surface synthesis of Au NPs-silicate platforms that is based on the reactive Si-H functional group of the PVSZ polymer. The surface analyses including the XPS depth-profile confirmed the formation of gold silicide (Au_xSi) at the interface between Au NPs and the PVSZ surface and the phase conversion of the PVSZ surface to silicate glass surface. The likely formation of Au_xSi phase was interpreted by two cases: reaction between Si-H and Au ion, reaction among etched-off species upon Ar ions sputtering. The Au NPs-silicate platforms thus obtained by the simple method have been found to be potentially suitable as a SERS sensing substrate with the help of the photolithographic patterning method, and as an electrophoretic sensing microelectrode with post-chemical plating. It is plausible that the Au NPs-silicate substrates could be utilized for sensor applications in the field of biochemical chips for biochemistry.

ACKNOWLEDGMENTS

This study was funded by the Korean Government (MEST) (2012, University-Institute cooperation program) and the Creative Research Initiatives (CRI) project (R16-2008-138-01001-0(2008)) administered by the Korean Ministry of Education, Science and Technology.

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