Synthesis and Characterization of Silver and Gold Nano-Structures on Chitosan-Porous Anodic Alumina Nano-Composite

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ABSTRACT: This study was designed to probe the fabrication of unique silver and gold nano-structures engaging a self-designed chitosan-porous anodic alumina nano-composite as template. Porous anodic alumina have been manufactured by di-step aluminum anodization in oxalic acid electrolytic bath. The surface properties of porous anodic alumina were reinforced by chitosan neutralized in sodium hydroxide. Multifarious nano-morphologies of silver as well as gold nano-structures were observed. Furthermore, the long chitosan biopolymer chains were degraded by γ-irradiations and the same procedure was employed for modification of porous anodic alumina with γ-degraded chitosan. The morphologies of fabricated silver and gold

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nano-structures were investigated by scanning electron microscopy, while their composition was evaluated with the help of energy dispersive X-ray spectroscopy. X-ray diffraction study exposed face centered cubic phase for both silver and gold nano-structures. Reflection mode UV-Vis spectroscopy was used to ascertain reflection grooves in the absorption range of silver and gold nano-structures respectively. The technique does not involve any harmful reagent and show different selectivity than methods in general practice. The achieved results apprised that the fabricated nano-structures offer the advantages of biocompatibility and eco-friendliness for numerous biomedical uses.

KEYWORDS: Porous anodic alumina; Di-step aluminum anodization; Chitosan; Nano-composite; Gold and silver nano-structures.

INTRODUCTION

Recognition of Porous Anodic Alumina (PAA) as a scaffold material for fabrication of one-dimensional nano-materials started in early 1930’s. Afterwards, it fired the research at nano-scale owing to its simple synthesis in a self-ordered frame of nano-channels. Anodization of aluminum gives a unique pattern of closely organized hexagonal cells with central holes. Cylindrical nano-pores having high facet ratio are formed by supervising key factors like nature and concentration of electrolyte, temperature and voltage throughout anodization and electro-polishing procedures. High optical, thermal and chemical stability, remarkable mechanical strength, self-organized uniform pores, tunable aspect ratio, no toxicological danger and affordability are the contributing gains of PAA, which decorate PAA in the nano-research domain [1-12]. Various Nano-Structures (NS) have been fabricated employing hexagonal nano-pores of PAA through molten metal injection, thermal decomposition of metallic salts [13], pulse electro-depositions [14], direct current or alternating current electro-deposition [15, 16], simple deposition [17, 18] etc. One-dimensional metal NS like nano-wires [19], nano-dots and nano-rods of various materials [20, 21] have been handily fabricated utilizing PAA template. PAA is a promising substitute to other commonly explored nano-porous platforms for the manufacture of self-assembled collection of metal NS. Gold (Au), Silver (Ag), Nickel (Ni) and Ag-Au nano-wires had been fabricated via electro-deposition technique [22, 23]. Sanjay et al. observed the comparative loading of silver nano-structures (Ag NS) on PAA substrate by employing different methods [24]. Hexagonal array of PAA have been utilized as reaction vessels for synthesis of isolated and highly ordered nano-crystals [25]. Mono-disperse Ag nano-wires have also been synthesized using PAA template [26, 27].

The nano-channel frame of PAA membrane is restricted to a tubular and flat pattern with uniform pore diameter. The development and modifications in anodization procedures promise the fabrication of more intricate PAA membranes with diverse geometries, desired functionalities and surface properties. These modifications mark PAA chemical/physical selective towards target molecules [28]. The specific surface properties and surface area of PAA can be strengthened by amending the hydroxyl rich surface with appropriate functionalities. Functionalized nano-porous membranes open up new opportunities for advance applications, especially for biomedical applications, in catalysis or as separators and filters. Functionalization of PAA can be achieved by both organic and inorganic materials including metals [29], oxides [30-34], DNAs [35], proteins [36, 37], diamond [38, 39], diamond-like carbon [29, 38, 40] and polymers [41-46]. Polymers possessing necessary functionalities can either be infiltrated or covalently attached to the surface of PAA template. Polymer-modified PAA portray fortified selectivity, stability, binding capacity and biocompatibility in contrast to un-modified PAA surface [18]. Subsequent functionalized PAA membranes can be employed either to fabricate other functional NS (like nano-rods, nanoparticles, nano-tubes) or target the biomolecules.
The synthesis of polymer-supported metal NS is of considerable interest because polymers offer efficient stabilization as compared to the recognized ligands like sodium borohydride or sodium citrate. In recent times, polymers having amino (NH₂) group are widely used because only one constituent is responsible for the reduction and stabilization processes. Chitosan (CS), a co-polymer of β-(1-4-linked)-2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose, is a naturally harvested chitin derivative. Chitin, an amino functionalized, non-elastic polymer which is white in appearance. Cell walls of yeast, fungi and exoskeleton of crustaceans naturally contain chitin. CS is obtained by chitin deacetylation. The extent of deacetylation is controlled by the adapted synthesis procedure and nature of source [47-51]. High abundance, low cost, non-toxicity, bio-degradation, bio-compatibility and presence of metal anchoring functional (free hydroxyl and amino) groups are the sparkling features of CS usage [52-55]. Therefore, CS can be used as a reducing and also as a stabilizing agent for metal NS fabrication [56-58]. Heavy metal (Zn²⁺, Cu²⁺) contaminants have been effectively removed using CS-capped Au nano-particles [59]. Bo et al. employed poly (dimethyl siloxane) films modified with CS for gold nano-structures (Au NS) preparation [60]. Shi et al. synthesized CS-PAA membrane having uniform pores and porosity [18]. Li et al. synthesized Fe⁰ nanowires on PAA template modified with chitosan and employed them as an adsorption system for removal of heavy metal from water. The modified adsorbent depicted superior adsorption efficiency than when only CS or PAA was used [61]. Cu²⁺ capped CS-PAA membranes have been fabricated by activating the PAA membrane with 3-glycidoxypropyltrimethoxysilane followed by CS grafting. These membranes have been fruitfully employed to separate and purify hemoglobin from red cell lysate [62]. Nevertheless, some of these approaches reflect various shortcomings like tedious work-up method, prolong reaction times, harsh reaction environments and use of expensive and lethal chemicals. Hence, a safe and mild approach employing cheap and ecofriendly reagents is still required for such makeover.

A detailed literature survey disclosed that only a few studies have been done using PAA template in combination with CS for metal nano-particle fabrication. So far, no progress has been made to fabricate Ag and Au NS embedded in CS-PAA nano-composite template. Therefore, this study aims at exploring a new convenient approach for the fabrication of Ag and Au NS using PAA template modified by CS and γ-irradiated chitosan (γ-ICS) under normal atmospheric conditions. Also the modification technique is cheap, reliable and modifies the whole surface of the PAA membrane. In the reported procedure, chemical reduction of subsequent metal ions into zero valent nano-particles has been carried out under gentle environment utilizing chitosan as a stabilizing and reducing agent. The crystalline character and surface morphology of these NS have also been inquired. Energy Dispersive X-ray (EDX) spectroscopy and X-Ray Diffraction (XRD) results also ascertained the presence of Ag and Au NS on CS-PAA nano-composite template. This work validates the fabrication of crystalline Au and Ag NS with variable morphologies employing the cited scaffold.

EXPERIMENTAL SECTION

Chemicals and apparatus

During the entire study, oxalic acid, per-chloric acid, acetone (Riedel), phosphoric acid sodium hydroxide, ethanol, chromic acid (Merck), acetic acid, tetrachloroauric (III) acid (Sigma Aldrich), silver nitrate (Fisher chemicals) and aluminum sheet (99.99% purity, Sigma Aldrich) were used. All chemicals used throughout this work were of analytical grade. Di-distilled water (specific resistance 18.2 MΩ.cm) was used. Morphology of Ag and Au NS was examined with FEI-Nova Nano SEM-430. The X-ray diffraction patterns were recorded on Bruker D-8 Discover HR-XRD using CuKα radiation (λ=1.5406 Å). The statistical details were dispersed within array 2θ=10°-90° (0.02° step size). Perkin Elmer Lambda 950 Spectrophotometer (Spectralon as reference) was used to acquire UV-Vis-NIR diffuse reflectance spectra.

Synthesis and preparation of PAA

A sheet of 99.99% pure Al (0.5 mm thickness) was cut into 1 x 3 cm size and annealed for five days at 500 °C in common muffle furnace and then ultrasonically degreased in acetone for 20 min. Two electrode cell used for electro-polishing and anodization consists of aluminum as anode (working electrode) and graphite as cathode (counter electrode). Electro-polishing for 20 min...
at 20 V and 1°C temperature was done in alcohol-perchloric acid (4:1 v/v) (60 mL ethanol and 15 mL perchloric acid) solution to reduce surface roughness of Al strip. The electro-polished Al strip was anodized (first-step) in oxalic acid (0.3 M) solution for 3 h at 50 V and 1°C temperature. Alumina film, after first-step anodization, displayed a haphazard arrangement of hexagonal pores. The wet chemical etching technique was used to strip away this film at 80°C in (0.2 M) chromic and (0.4 M) phosphoric acid mixture for 3 h. The hollow pattern, obtained from oxide etching, provides nucleation sites for hexagonal and regular pore array formation during second-step anodizing. The second-step anodization, carried under same parameters as cited for first-step anodization, resulted in a regular hexagonal collection of pores. A aqueous solution of oxalic acid (0.3 M) was used for pore widening at room temperature for 30 min. PAA of 100-400 μm through thickness was used to fabricate nano-composite [63].

**Fabrication of Ag and Au nano-structures on CS-PAA nano-composite template**

Customary methods were employed to obtain CS from crab’s shells [50], having 75% deacetylation degree. CS is soluble in acidified water. Acetic acid (5%) was used to prepare CS solution. PAA template was immersed in saturated CS solution at room temperature for 24 h. Chitosan interacts with hydroxyl groups of PAA film ensuring a link between chitosan and PAA surface [72]. The polymer functionalized PAA template was dried and treated with sodium hydroxide (NaOH) solution. The polycationic CS was neutralized by the NaOH solution, which appeared as a hydrated gel-like precipitation [64]. Ag and Au NS were fabricated by submerging the CS-PAA nano-composite in 1 mM precursor (AgNO₃ or HAuCl₄.3H₂O) solution for 24 h. Schematic representation for metal NS fabrication on CS-PAA nano-composite is given in Fig. 1.

**Fabrication of Ag and Au nano-structures on γ-ICS-PAA nano-composite template**

Cobalt-60 γ-iradiator (Model JS-7900, IR-148, ATCOP) was used to irradiate CS at Pakistan Radiation Services Lahore. CS was exposed to various doses of gamma radiations stretching from 25 to 100 Kgy (dose rate=1.02 kGy/h). The irradiation was performed in air environment [69]. γ- Radiations degraded the long biopolymer chains and lowered their molecular weights. Tahtat et al. [65], Zainol et al. [66] and Baroudi et al. [67] suggested that irradiation decreases the molecular weight through de polymerization approach with insignificant influence on the chemical characteristics like deacetylation extent, functional groups of chitosan biopolymer. The γ-radiation dosages are secure, environmental favorable and free from initiator residues/chemicals [68-71]. The γ-ICS solution was prepared in 5% acetic acid. Ag or Au deposition on γ-ICS-PAA nano-composite followed the same quoted procedure as for the metal deposition on CS-PAA nano-composite. The experimental settings employed for the synthesis of metal nano-structures on CS and γ-ICS-PAA nano-composite are tabulated in Table 1.

**RESULTS AND DISCUSSION**

**Silver-chitosan/porous anodic alumina nano-structures (Ag-CS/PAA NS)**

Fig. 2(a-c) shows the scanning electron microscopy (SEM) micrograph of PAA and Ag-NS appeared after modification with CS. This practice gives information concerning the surface morphology of samples. PAA has a considerable number of hexagonal shaped pores, therefore there is a good probability for CS to adherent to the underlying alumina. Upon interaction of CS-PAA with Ag solution, the polar hydroxyl groups of CS bound the electropositive transition metal ions probably via electrostatic (i.e., ion–dipole) forces and reduce Ag⁺ to Ag⁰ [73]. Ag nano-structures were formed by reduction of Ag⁺ with chitosan. SEM images (Fig. 2(b, c)) reflect a zigzag pattern of Ag nano-flakes created in CS web associated with hexagonal cells of PAA.

The existence of 93.71 (by weight %) Ag in nanoparticles was also acknowledged by EDX analysis (Fig. 3).

XRD pattern draws four reflection peaks analogous to crystalline Ag peaks. Miller indices were assigned to each peak. These four peaks were allotted to diffraction from 20 = 38.01° (111), 44.28° (200), 64.46° (220) and 77.47° (311) of the Ag planes, correspondingly. The XRD peaks suggested face centered cubic phase for crystalline Ag with highly intense peak observed at index value of (111). Reflection peaks of CS biopolymer compatible to 20 = 53.02°, 40.49°, 27.78°, 20.33° and 18.6° were also detected (Fig. 4). These peaks are fingerprint for CS crystallinity, principally an intense peak at ~20° [74].
Table 1: Experimental settings for fabrication of Ag and Au nano-structures on CS-PAA nano-composite along with their designations.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Electro-polishing</th>
<th>1st Step Anodization (^a)</th>
<th>2nd Step Anodization (^b)</th>
<th>Bio-polymer-Porous anodic alumina nano-composite</th>
<th>Metal Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS/PAANS</td>
<td>20 V in C(_2)H(_3)OH-HClO(_4) at 1°C for 20 min</td>
<td>50 V in 0.3M C(_2)H(_6)O(_4) at 1°C for 3 h</td>
<td>50 V in 0.3M C(_2)H(_6)O(_4) at 1°C for 3 h</td>
<td>Saturated CS solution in 5% CH(_3)COOH at room temperature for 24 h</td>
<td>1 mM precursor (AgNO(_3) or HAuCl(_4).3H(_2)O) solution for 24 h</td>
</tr>
<tr>
<td>γ-ICS/PAANS</td>
<td>20 V in C(_2)H(_3)OH-HClO(_4) at 1°C for 20 min</td>
<td>50 V in 0.3M C(_2)H(_6)O(_4) at 1°C for 3 h</td>
<td>50 V in 0.3M C(_2)H(_6)O(_4) at 1°C for 3 h</td>
<td>Saturated γ-ICS solution in 5% CH(_3)COOH at room temperature for 24 h</td>
<td>1 mM precursor (AgNO(_3) or HAuCl(_4).3H(_2)O) solution for 24 h</td>
</tr>
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</table>

\(^a\) Wet chemical etching of 1st step anodized layer in a mixture of 0.4 M H\(_3\)PO\(_4\) and 0.2 M CrO\(_3\).H\(_2\)O at 80 °C for 3h.

\(^b\) Pore widening in 0.3 M C\(_2\)H\(_2\)O\(_4\) at room temperature for 30 min.

![Diagram](image1.png)

**Fig. 1:** Schematic diagram for metal nano-structure fabrication using CS/PAA nano-composite.

![Images](image2.png)

**Fig. 2:** (a) Di-step anodized aluminum strip showing a regular, closely organized hexagonal cells; (b, c) SEM micrograph of Ag-CS/PAANS showing formation of zigzag Ag nano-flakes.
Fig. 3: EDX image of Ag-CS/PAANS.

Fig. 4: XRD pattern of Ag-CS/PAANS.

Fig. 5: Diffuse reflectance plot of Ag-CS/PAANS.

Fig. 6: SEM micrograph of Au-CS/PAANS clearly showing Au NS deposition.

PAA is transparent towards UV-Vis spectroscopy. The UV-Vis diffused reflectance spectrum of Ag-CS-PAA nano-composites shows a sole, strong minimum just about 400 nm (Fig. 5). This groove corresponds to the characteristic Surface Plasmon Resonance (SPR) of the valence electrons of Ag nano-structures. Silver nanoparticles show a typical Plasmon band at around 400–420 nm [73]. The estimated particle size from the position of the reflectance minima is 20 nm [77, 78].

Gold-chitosan/porous anodic alumina nano-structures (Au-CS/PAANS)

SEM image (Fig. 6) shows Au NS deposited on the CS-PAA nano-composite as almost spherical nanoparticles. The various phenomenon for the uptake of gold metal ions by CS include adsorption, chelation and ion exchange. The amino groups of CS interacts with the metal ions either through chelation by utilizing the two amino groups from two glucosamine residues of the CS polymer chain, or through adsorption phenomena by active participation of its lone pair of electrons [76].

The EDX spectroscopy of the sample ratified the existence of Au NS. The weight percentage of Au was 29.06% as given in Fig. 7. Oxygen and aluminum peaks in EDX plot indicate the presence of Al₂O₃ of PAA.

In XRD pattern, the Brag reflections with 2θ values of 53°, 40.7°, 27.8°, 20.2° and 18.7° were recognized for the CS biopolymer [74, 75]. Reflection peaks corresponding to (111), (200), (220), (311) and (222) lattices were attributed towards face centered cubic Au. Preferential orientation of Au was along the (111) plane (Fig. 8). Aluminum reflection peaks (face centered cubic) corresponding to (200), (220) and (311) faces were also found.

The diffuse reflectance analysis (Fig. 9) of Au-CS/PAANS displayed a reflection minimum at 515 nm in the absorption series of Au nano-particles. The observed minimum corresponds to the typical SPR of valence shell electrons of Au nano-particles. Gold nanoparticles show a characteristic Plasmon band at ~520 nm and predicted size of 5 nm [73, 78, 79].
Silver-γ-irradiated chitosan/ porous anodic alumina nano-structures (Ag-γ-ICS/PAANS)

The length of chitosan biopolymer chains was minimized by irradiation with γ-rays. This enhances the association of chitosan chains to the PAA nano-hexagonal pore array. The widespread web of template hydrogen bonds prevents the aggregation of nanoparticles. γ-ICS stabilized the Ag⁺ ions as nano-banners of triangular shape. These silver nano-banners are interlinked with each other and grow along the faces of the triangle. SEM images (Fig. 10a, b) clearly show these triangular chains.

EDX plot (Fig. 11) also confirmed that these triangular chains belong to Ag. These nano-banners consist of 39.01 weight % of Ag. Al and O peaks of PAA were also observed in EDX plot.
In XRD pattern, two reflection peaks corresponding to crystalline Ag were noticed. These peaks appeared at 2θ = 38.01°, 44.28° and indexed to (111), (200) planes. The reported reflections are in good agreement with standard values of the face centered cubic metallic Ag (Fig. 12). Reflections equivalent to (111), (220) and (222) Al planes were also found, suggesting a face centered cubic phase for crystalline Al. The observed high intensity peak for Ag as well as Al has an indexed value of (111).

In UV-Vis diffused reflectance spectrum of Ag-γ-ICS/PAANS nano-composites, a single strong groove around 419 nm was observed (Fig. 13). This groove subscribes to valence electron SPR of the Ag nano-structures. 400-420nm is the typical Plasmon band range for silver nanoparticles [73]. From the position of the reflectance minima, the predictable particle size ranges from 40-50 nm [77, 78].

Associations of γ-ICS chains with PAA nano-hexagonal pores provides efficient stabilization to noble metal nano-particles via hydrogen bonding. SEM micrograph (Fig. 14a) reveals that γ-ICS stabilized Au in two attractive patterns i.e. dendritic structure and branched structure resembling the leaves of a pine tree. These fascinating patterns are evident in high magnification images (Fig. 14b, c). The observed branched structures may due to the nucleation effect of Au nano-particles [73].

Similarly, EDX map witnessed the belonging of these interesting patterns to Au (Fig. 15). The nano-pine leaves comprised of 75.90 (by weight percent) of Au.

Face centered cubic Al corresponding to the (111), (200), (220) and (311) planes were detected in X-ray diffraction spectrum. Al was preferably oriented along (111) Miller index. Sharp peaks corresponding to (111), (200), (220), (311) and (222) phases were also observed. These sharp peaks are indexed to highly crystalline, face centered cubic Au with special alignment along the (111) plane (Fig. 16).
The diffused reflection analysis of Au-γ-ICS/PAANS gave a reflection minimum centered at 540 nm. This groove evidenced the formation of gold nano-particles on porous anodic alumina modified with γ-irradiated chitosan as shown in Fig. 17. Typically gold nano-particles show SPR at about 520nm. The observed Plasmon value may be due to unique dendritic and nanopine leave arrangements [73]. Reflectance groove estimated gold nano-structure size is 60nm [78, 79].

The band gap energies for observed metal nano-structures can be calculated from their respective SPR wavelengths. These energies are given in Table 2.

**CONCLUSIONS**

- A simple, convenient, non-hazardous and reproducible procedure has been proposed for the preparation of Ag and Au NS using CS-PAA nano-composite. It was demonstrated that the combined stabilization and reduction effect of CS-PAA nano-composite is worth considering.
- PAA acted as guider and causes the alignment of polymer chains within the uniformly size pore array. The nano-porous nature of anodic alumina has also provided with regular anchoring points that are responsible for stability of the metal-polymer nano-composite film of the substrate.
- In case of γ-ICS, the gamma radiations lowered the molecular weight and crystallinity of CS by breaking the polymer backbone (dissociating the C–H and C–OH bonds of CS).
- CS and γ-ICS solutions uniformly associate with hex nano-pores of PAA and furnish many active sites for nucleation and crystal growth.
- During metal deposition, the amine functionality of CS will function as reducing agents for the formation of Au NS whereas electron rich oxygen atoms of hydroxyl groups of CS interact and reduce Ag⁺ to Ag⁰.
- Both, γ-ICS and non-irradiated CS furnished interesting morphologies for Ag and Au NS which include Ag nano-banners, Au nano-pine leaves, Au dendritic structures, zigzag silver nano-flakes and a spherical Au nano-particles respectively.
- XRD crystalline diffraction peaks demonstrated face centered cubic phases for Ag and Au NS.
- Reflection minima in the absorption ranges of Ag and Au NS strengthened the presence of Ag and Au NS upon the respective samples.
- Furthermore, the EDX data also insisted the existence of Ag and Au NS.
- This prospective method can be engaged for the mass fabrication of Ag or Au-CS/PAANS which may serve the medical industry and also help in metal removal as it is environmentally benign.
Table 2: Surface Plasmon Resonance (SPR) wavelengths, particle sizes and band gap energies of observed metal nano-structures along with their designations [77-81].

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>SPR Wavelength (m) x 10⁻¹</th>
<th>Size (nm)</th>
<th>Band Gap Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-CS/PAANS</td>
<td>4.00</td>
<td>20</td>
<td>3.10</td>
</tr>
<tr>
<td>Au-CS/PAANS</td>
<td>5.15</td>
<td>5</td>
<td>2.41</td>
</tr>
<tr>
<td>Ag-γ-ICS/PAANS</td>
<td>4.19</td>
<td>40-50</td>
<td>2.96</td>
</tr>
<tr>
<td>Au-γ-ICS/PAANS</td>
<td>5.40</td>
<td>60</td>
<td>2.30</td>
</tr>
</tbody>
</table>

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