

Growth of copper on diatom silica by electroless deposition technique

JULIET Q. DALAGAN^{1,2*}, ERWIN P. ENRIQUEZ², LAIN-JONG LI³, CHENG-TE LIN³

¹Chemistry Department, Xavier University-Ateneo de Cagayan, Corrales Avenue, Cagayan de Oro City, Philippines, 9000

²Department of Chemistry, Ateneo de Manila University, Loyola Heights, Quezon City, Philippines, 1108

³Research Center for Applied Sciences, Academia Sinica, Taiwan, ROC, 300

In this study, the growth of copper on porous diatom silica by electroless deposition method has been demonstrated for the first time. Raman peaks of copper (145, 213, and 640 cm^{-1}) appeared in the copper-coated, *Amphora sp.* and *Skeletonema sp.* diatom samples, confirming the successful deposition of copper. Scanning electron microscopy (SEM) indicated the presence of copper on the diatom silica surface. The 3D intricate structure of diatom was still evident by optical and scanning electron microscopy analyses when the diatom samples were immersed in the copper bath for only 5 hours. Incubating the diatom samples in the copper bath for 24 h produced a dense coating on the diatom surface and covered the intricate 3D structure of the diatom silica. These results present possibilities of the fabrication of hierarchically organized copper with 3D diatom replica structures.

Keywords: electroless deposition; porous diatom; Raman spectroscopy; diatom silica

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1. Introduction

Nature provides an alternative and low cost supply of materials which can be developed to fabricate well-defined and controllable materials that exhibit nanoscale features. Diatoms are examples of this kind of material. Diatoms are microscopic, photosynthetic unicellular algae that thrive in both marine and freshwater environment. One of their interesting properties is that they have the extraordinary capability to produce an amorphous silica shell or frustules which are nanoporous with distinct, impressive and intricate 3D architecture. Furthermore, the sustained production of a given diatom species may be used to generate massive numbers of frustules with the same 3D morphology. Their unique structural, mechanical, optical and photonic properties make them an attractive source for the development of new materials and devices. A range of applications using diatoms, such as light harvesting, optics, biophotonics, catalysis, sensing, filtration, microfluids, cell growth, nanofabrication and drug delivery, have been reported recently [1–9].

Diatom silica in its native form is inert amorphous silica. It requires modification of the 3D biomineralized structure to form into technologically tailored materials [10]. Replication of this complex diatom silica structure in other inorganic materials requires such methods as sol-gel synthesis, polymerisation and genetic/environmental manipulation. Diatoms with ceramic (MgO, TiO, Zn₂SiO₄, zeolites), semiconducting (Si-Ge) or organic (polyaniline) scaffolds have been reported. Metabolic insertion of dopants such as germanium, titanium or gallium into the diatom's hierarchical silica structure has also been studied [11]. To date, no study on diatom coated with copper has been reported yet.

This work demonstrates that copper can be deposited on diatom silica by electroless deposition technique. Yang *et al.* [10] used electroless metal deposition to coat the diatom silica surface with gold. The diatomaceous earth that they used, was

^{*}E-mail: j.dalagan@xu.edu.ph

from fossilized fresh-water diatoms. The gold deposition process involved sensitization, activation and gold plating on the diatom samples. They reported that the thickness of the gold film was dependent on the deposition time. A shorter deposition time (16 h) resulted in thinner film while a deposition time of 88 h covered the pore structure of diatom silica. This process has been successfully exploited to deposit platinum, gold, copper and nickel onto porous silicon [12].

Here, the diatom species used are *Amphora sp.* and *Skeletonema sp.* The former is a common benthic marine pennate diatom while the latter is a centric diatom that is typically found in freshwater rivers and lakes, tidal estuaries, and coastal waters. Copper is deposited on diatom silica via electroless deposition which is based on the autocatalytic redox reaction of copper onto catalytic and chemisorptive sites, such as palladium, on the surface. To induce chemisorption, the materials are immersed in SnCl₂ and PdCl₂ solutions in the sensitization and activation steps, respectively.

2. Experimental section

2.1. Isolation of Frustule Biosilica

The diatom species used in this study (Amphora sp., and Skeletonema sp.) were obtained from the Southeast Asian Fisheries Development Center Aquaculture Department (SEAFDEC-AQD), Tigbauan, Iloilo City and cultured using Guillards F2 medium at 25 °C. Diatoms were harvested after 7 days of culturing and cleaned as previously described [13]. 50 mL of concentrated diatom sample was centrifuged (Sorvall Legend RT centrifuge) at 4600 rpm for 30 min followed by 5 times washing of the pellets with distilled water. For complete removal of the organic matter covering in excess the siliceous frustules, concentrated sulfuric acid was used. The solution turned green after adding concentrated sulfuric acid. The acid was removed and the solution turned grayish white indicating removal of organic components in the diatom. The biosilica pellet was washed again 5 times with distilled water and ethanol. Biosilica pellets were oven-dried followed by vacuum drying. Dried biosilica was stored in a desiccator.

After the diatoms were harvested and cleaned, optical images were taken using an Olympus Tokyo microscope. The presence of different functional groups was monitored with an Affinity-1 Shimadzu FTIR instrument, using the KBr pellet method, and scanned at 4 cm⁻¹ resolution. Diatom morphology was observed using scanning electron microscopy (SEM), wherein the samples were placed on aluminum substrate, mounted using a conducting tape, and imaged using a Hitachi TM-1000 Tabletop Microscope. The accelerating voltage and emission current used were 15 kV and 70 mA, respectively.

2.2. Electroless deposition of copper on diatom silica

The diatom sample was deposited on Si wafer substrate by drop-casting and incubated with H_2O_2 for 24 h prior to sensitization [10].

Sensitization of sample. The diatom silica was immersed in 6 mL of sensitizing solution of 2 M HCl and 2.1 g/L of SnCl₂ (Alfa Aesar, anhydrous, 98%) for one hour then rinsed with deionized (DI) H₂O five times. The sensitization solution was aged for 3 days at room temperature before using.

Activation of sample. The sensitized diatom sample was subsequently immersed in 6 mL of the activating solution for one hour then rinsed with DI H_2O five times. The activation solution was composed of about 1 g/L of PdCl₂ in 0.2 M HCl.

Deposition of copper. The sensitized and activated diatom sample was immersed in 6 mL of copper solution bath for 24 h at 55 °C. The composition of the copper solution bath was 7 g/L of CuSO₄·5H₂O (Sigma-Aldrich), 25 g/L of potassium sodium tartrate (Fluka), 9.3 g/L of formaldehyde and 1.9 g/L of NaOH [14]. In another study, the deposition time was reduced to 5 h at the same temperature.

2.3. Characterization of copper-coated diatom silica

The morphology of copper on diatom silica was characterized by JEOL JSM 6380 Scanning Elec-



Fig. 1. The SEM images of cleaned diatoms: (A) *Amphora sp.*, and (B) *Skeletonema sp.*

tron Microscope (SEM) at the National Tsing Hua Univeristy (NTHU) with an operating potential of 15 kV and working distance of 10 nm. Raman spectra were collected in a NT-MDT confocal Raman microscopic system with laser wavelength excitation of 473 nm.

3. Results and discussion

3.1. Isolation and characterization of diatom silica

The diatom samples were cleaned by removing the organic components present in the diatoms. The original diatom cell suspension was brownish and it turned into green upon the addition of concentrated H₂SO₄. Excess of H₂SO₄ caused the color change of the diatom suspension into grayish white indicating that the organic components was removed [15]. Scanning electron microscopy (SEM) gave a magnified view of the architecture of the diatom species being studied. Acid oxidation with concentrated sulfuric acid removed the organic matter from the frustules or the cell walls of the biosilica, rendering the cell walls of the species to be porous. SEM images of the diatom samples in Fig. 1 reveal a unique and intricate design of the frustules. Figs. 1a and 1b show the structure and organization of the porous layers of the silica frustules of (a) Amphora sp., and (b) Skeletonema sp. These observations indicate the shape of each species. Amphora sp. shown in Fig. 1a, is elongated like a pen and it is classified as pennate. Skeletonema sp. in Figure 1b is considered as centric diatom. From the SEM images, the lateral size of the diatom can be estimated to be around 6 - 8 microns.



Fig. 2. FTIR spectra of cleaned diatom silica. Y-axis is offset for comparison and the x-axis is logarithmic to show the SiO_2 vibrational region around 1100 cm^{-1} .

To confirm that silica was isolated from diatom cells, FTIR analysis was done in the 4000 – 400 cm⁻¹ range. IR spectra in Fig. 2 show that siloxane and silanol groups are present. The band at 3430 cm⁻¹ is due to free silanol group (SiO-H) and the band at 1194 cm⁻¹ represents the siloxane (Si-O-Si) group stretching. The absorption peaks at 890 and 579 cm⁻¹ correspond to Si-O stretching of the silanol group and siloxane bending vibration, respectively [16].

The Brunauer-Emmet-Teller (BET) surface area of the diatom silica was measured using the N_2 adsorption/desorption isotherms. The calculated values are 11 and 2 m²/g for *Amphora sp.*, and *Skeletonema sp.*, respectively. The surface area of diatoms differs among species which may be attributed to an incomplete oxidation of the organic coating. This organic matter also differed for various species and was difficult to remove. Because it was not burned off completely, the silica pores could not be fully exposed. This led to a decrease in the surface area [17].

3.2. Electroless deposition of copper

The surface of the diatom silica is not inherently catalytic. Hence, the sensitization and activation processes are necessary. In previous studies on copper metallization of oxide surfaces such as porous alumina, the alumina was modified with silane containing amine group before it was sensitized with $SnCl_2$. In this manner, Sn^{2+} was bound to the sur-

face via complexation reaction with amine group during the sensitization process [18]. However, in the work of Yu et al. [10], they were able to deposit gold onto diatom silica without silane modification. The same results were observed in our experiment with copper. A special role was played by H₂O₂ incubation of the diatom silica prior to sensitization process. Addition of H₂O₂ increased the density of oxygen groups on the surface [10]. Tin chloride reacted with the oxygen groups in silanol forming the SiO-Sn-Cl complex during the sensitization process. The suggested reaction pathway is [19]:

$$-Si - OH + Sn(OH)_2Cl_2 \rightarrow$$

$$\rightarrow -Si - O - Sn(OH_2)Cl \qquad (1)$$

Tin chloride is not an active catalyst but it acts by surrounding Pd reducing Pd^{2+} to Pd^{0} during the activation step. The Pd-Sn catalytic core facilitates the conditions for electroless plating of copper by the following reaction pathways [13]:

$$Pb^{2+} + Sn^{2+} \rightarrow Pd + Sn^{4+}$$
 (2)

$$2\text{HCHO} + \text{Cu}^{2+} + 4\text{OH}^{-} \rightarrow$$
$$\rightarrow 2\text{HCOO}^{-} + \text{H}_2 + 2\text{H}_2\text{O} + \text{Cu} \qquad (3)$$

$$Cu^{2+} + H_2 \rightarrow 2H^+ + Cu \tag{4}$$

3.3. Characterization of copper-diatom silica

The presence of copper on diatom silica was determined using Raman spectroscopy. Bare diatom silica (without copper), copper foil (99.8%, 25 µm thick, Alfa Aesar), the control sample (Si wafer without diatoms) and copper-coated diatom silica were subjected to Raman analysis. Raman peaks at 145, 213, and 640 cm^{-1} were observed in the Cu foil and the diatom-Cu as shown in Fig. 3. These peaks were absent in the bare diatom and the control sample. For copper oxide, CuO, as demonstrated by Xu and co-workers [20], the Raman spectra showed the dependence on the grain size in the samples, the intensity of the laser radiation, and



temperature. The Raman peaks for CuO nanoparticles were observed at 288, 330 and 621 cm⁻¹. The Raman peaks for Cu-diatom (24h, 5h) have been also shown in Fig. 3 for comparison. The Raman spectra show the same Cu peaks regardless of deposition time.

The morphology of copper-diatom silica was monitored by scanning electron microscopy (SEM). As can be seen in Fig. 4, the diatom silica which was incubated for 24 h (condition 1) in Cu bath (B, E), had a very dense Cu covering on the surface, which resulted in less distinct 3D features of the diatoms. In the work of Yu et al. [10] the deposition time affected the thickness of the gold deposited on the pores of the diatom. Similar findings were observed here, particularly when the deposition time of copper was reduced to 5 h. For shorter deposition time, the coating is not too thick and the 3D structure of the porous diatom silica remains visible as seen in Fig. 4 (C, F).

The deposition of copper on the diatom silica was also compared in terms of the Raman intensity of copper peaks. Fig. 3 shows that Amphora-Cu has higher peak intensity than Skeletonema-Cu. This trend could be attributed to the surface area of the diatom species which is related to the accessible silanol and siloxane groups. Consider-





Fig. 4. SEM images of Amphora (A, B, C) and Skeletonema (D, E, F): A, D - before copper deposition; B, C, E, F – after copper deposition: B, E (24 h deposition time), C, F (5 h deposition time).

ing their specific surface area, *Skeletonema sp.* has lower surface area than *Amphora sp.*, which implies that *Skeletonema sp.* has fewer silanol and siloxane groups able to serve as available binding sites for SnCl₂ (scheme 1) [12]. The complex formation (sensitization step) in Scheme 1 is the first step in electroless deposition on a noncatalytic surface such as diatoms. If this step is effective, then more Sn-Pd catalytic sites are formed, which leads to more sites with nuclei chemisorptions on the surface. This eventually facilitates the autocatalytic redox reduction of Cu^{2+} to Cu^{0} and induces higher intensity of Raman shift.

4. Conclusions

We have demonstrated, for the first time, that copper can grow on non-catalytic diatom silica by electroless deposition technique. The growth of copper involved three major steps: the first is the sensitization of diatom surface with tin (II) chloride, the second step is the activation of the surface with palladium choride and the last step is the electroless deposition of copper by the autocatalytic reduction of Cu^{2+} to Cu^{0} . The deposition time of Cu played a significant role because it determined the thickness of the Cu film deposit. In the recent study, 24 h incubation of diatom in Cu bath at 55 °C revealed a dense loading onto diatom surface while 5 h incubation, at the same temperature, showed the 3D architecture of diatom silica. The successful deposition of copper onto diatoms could be exploited for the fabrication of hierarchically organized copper with 3D diatom replica structures. This material may exhibit excellent catalytic properties. Copper coated diatom can be a catalyst for the templatedirected chemical vapor deposition of graphene. The intricate architecture of 3D biological template such as diatom can be harnessed for the fabrication of graphene-based electrode materials for lithium ion batteries and supercapacitors.

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