Supporting Information

In-situ coating of diatom frustules with silver nanoparticles

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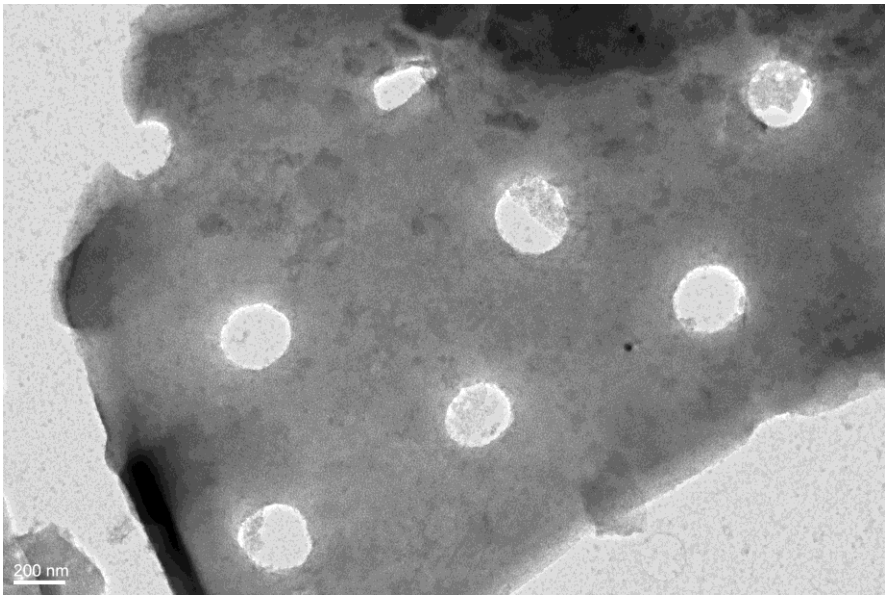
Materials and Methods

Diatom frustules (supplied by Mt Silvia Diatomite) were cleaned by a plasma treatment on the GaLa Plasma Prep 5 air plasma chamber, by applying a frequency of 40 kHz for 5 minutes at a power setting of 110 W, then agitated to expose untreated regions and then similarly treated again two more times. A solution of silver nitrate (0.005 M, 4 mL, AGR Matthey) was prepared and freshly plasma cleaned diatom frustules (10 mg) were added and shaken for 10 seconds, dispersing the silver ions throughout the solution. A Sodium hydroxide (Sigma Aldrich) solution was made up of concentration 0.5M and 70 µL was added to improve the reduction effectiveness of glucose and form silver oxide which bind to the surface and can be easily reduced.

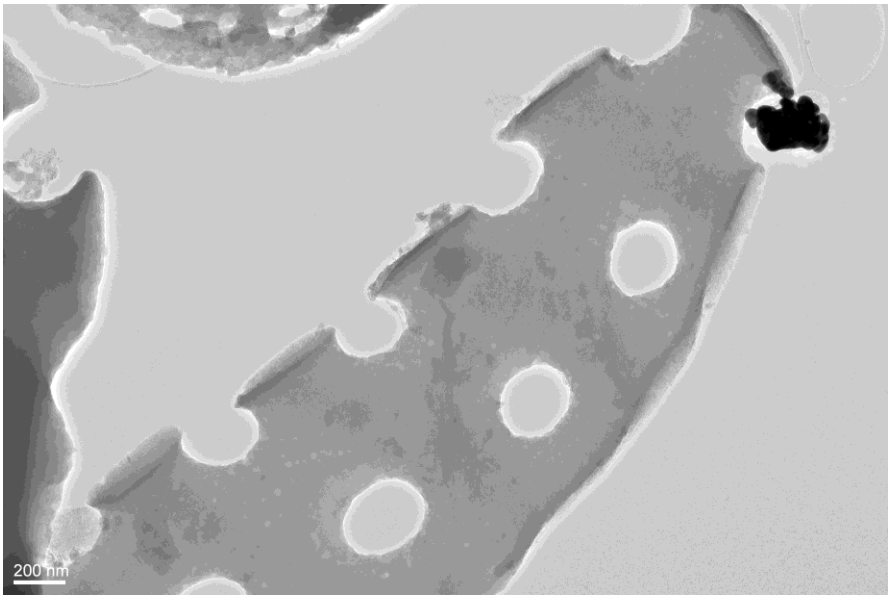
D(+)Glucose (500 mg, Ajax Chemicals) was added to reduce the silver oxide to elemental silver, forming 10-20 nm particles after a few minutes of vigorous mixing, as seen in Figure 2. The material had to be washed several times with milli-Q water by centrifugation to remove all the glucose and nitrate ions. This allowed the material to be characterised by SEM and transmission electron microscopy (TEM).

Frustule Coating Test 1 : Silver ion attachment



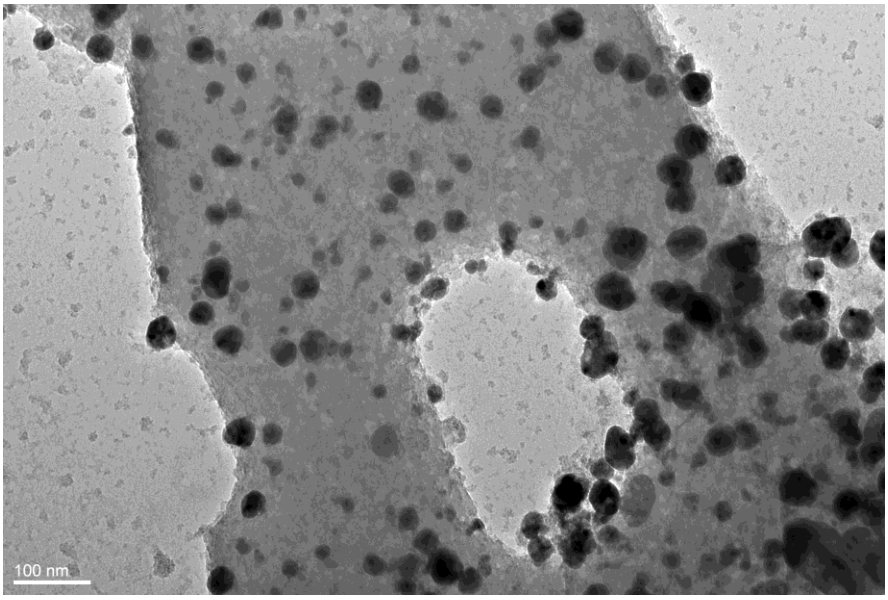
TEM of diatom frustule which was plasma treated, and then combined with a solution of 0.005 M silver nitrate for 30 minutes. The sample was then centrifuged at approximately 1900 g and then redispersed in 5 ml of milli-Q water. NaOH was added and then glucose to reduce and AgO to elemental Ag. The result shows no silver presence, indicating that the silver ions to not bind to the silica surface.

Frustule Coating Test 2 : Pre silver nanoparticles



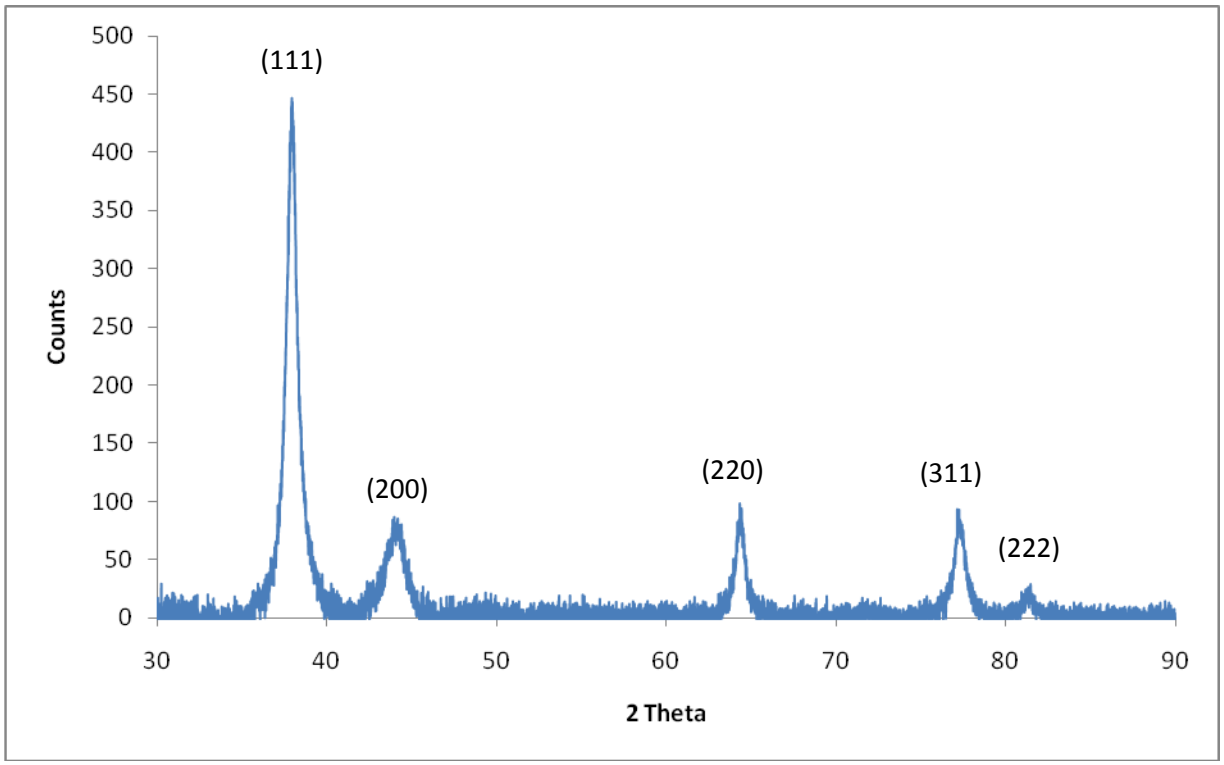
TEM of diatom frustule which was plasma treated, and then combined with a suspension of previously prepared silver nanoparticles. The silver nanoparticles were made in the same manner, 4 mL of 0.005 M $AgNO_3$ had 70 µL of 0.5 M NaOH added to it and then 500 mg of glucose. The silver nanopartcles were then washed via centrifugation at approximately 1900 g and combined with 10 mg of plasma cleaned diatom frustules. The results show the treated silica surface is not very effective at binding to already formed silver nanoparticles.

Frustule Coating Test 3 : Base added to form silver oxide



TEM of diatom frustule which was plasma treated, and then combined with 4 mL of 0.005 M silver nitrate. NaOH was then added to the material resulting in the precipitation of silver oxide particles on the surface, no glucose was added for reduction. The results show that the silver material binds to the surface of the silica frustule at the silver oxide precipitation step.

XRD of silver coated diatoms



XRD of diatom frustules coated with silver nanopartices showing the characteristic peaks of elemental silver accompanied by their respective miller indices.

Scherrer equation:

$d = 0.9\lambda/\Delta\cos\theta$

$\Delta = 0.74°$ $= 0.013$ rad

$\theta = 37.91/2$ $= 18.96°$

$\lambda = 0.154$ nm

d = 10.8 nm

Catalytic Testing

Solid rose bengal (2.6 mg) was dissolved in milli-Q water (20 mL). A portion of this dye solution (9 mL) was added to the silver coated diatom material (10 mg). Sodium borohydride (6.5 mg) was collected and placed into a separate sample vial. The dye and catalyst solution was then added to the solid sodium borohydride and the reaction monitored using UV/Vis spectroscopy.

Standards were done using just the dye solution and with the dye and uncoated diatoms, to ensure diatoms themselves were not catalytically active.