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In situ coating of diatom frustules with silver nanoparticles†

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Diatom frustules decorated with silver nanoparticles between 10 and 20 nm in diameter, are accessible at room temperature under basic conditions using glucose as a reducing agent and without the need of linking agents. The process is sensitive to both pH and the time elapsed after plasma cleaning prior to decoration.

Nanosized particles possess unique physical and chemical properties relative to their bulk counterparts.[1,2] Inorganic nanoparticles are becoming an increasingly important material for device technology with applications in catalysis, biological labelling, nano-medicine, optoelectronics, data storage, composite materials and chemical sensing.[3–8] To construct new generation nanoscale devices, novel ways to organize nanoparticles into controlled structures are required. This challenge has involved a number of approaches including using organic monolayers, co-colloidal suspensions, chemical cross-linking crystallization and using oligonucleotides to self-assemble inorganic nanoparticles into ordered arrays.[9,10] All of these require the use of a linking agent or stabiliser, which can affect the catalytic and antimicrobial activity, for example, as well as the toxicology of the relative materials.[11,12]

Silver nanoparticles are of interest for a number of reasons. They have bactericidal effects and antimicrobial activity, and have been used as a preservative, mixed into plastics and in the medical field to treat burns and infections.[1,13–15] Moreover, arrays of silver nanoparticles can have localised surface plasmon resonance (LSPR) responses which could see them applied to quantitative real time biosensing platforms.[16] We demonstrate that the frustules of unicellular algae known as diatoms can be used as a scaffold for the formation of ordered structures of silver nanoparticles, without the need for the use of linking agents and stabilisers.

Diatoms possess silica exoskeletons, known as frustules, with intricately and precisely arranged porous architectures as highlighted in Fig. 1. The frustules have a diverse range of size and shape, and variation in density and size of the pores, depending on the species, of which there are hundreds of

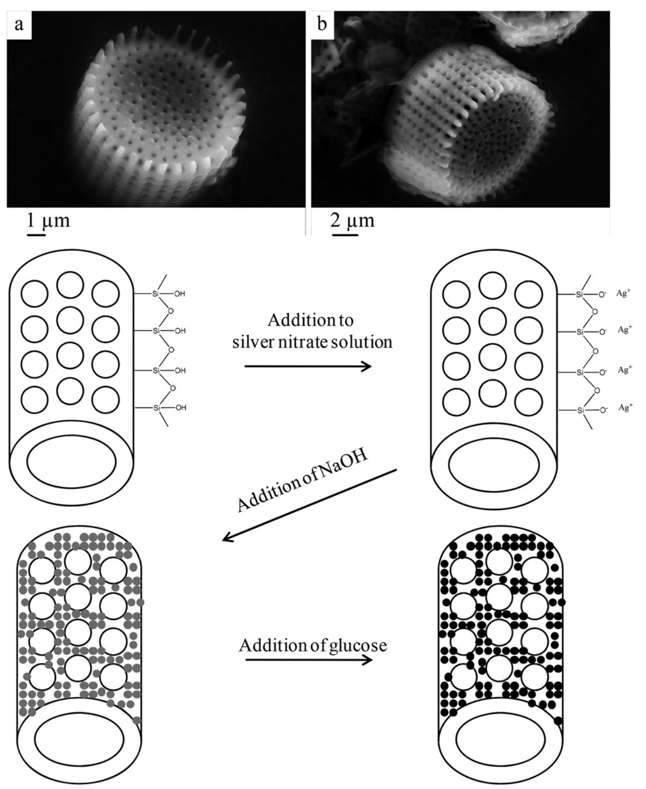

Fig. 1 Scanning electron microscope (SEM) images of diatom frustules after plasma etching (a and b) along with coating procedure schematic for plasma treated frustules being added to 4 mL 0.005 M $AgNO_3$, then the addition of 70 µL 0.5 M NaOH and finally the addition of 500 mg of glucose.

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thousands.[17] The frustule provides an inexpensive avenue for accessing highly ordered complex 3-dimensional structures that have potential applications in, for example, gas sensing, drug delivery, providing a catalytic surface and support, photonic crystal and large molecule separation.[18,19] Frustules are commonly used in filters, polishes and toothpastes, but for applications as advanced materials, functionalization with more technological relevant materials such as gold, iron oxide, titania or silver is a challenge. Previous work has established the ability to coat frustules with gold, titania and with titania metabolically inserted into the frustules during growth and development of the diatoms.[20–22] Most coating procedures, however, use a linking agent to bind the nanoparticles to the silica surface, such as poly-4-vinyl pyridine, phytic acid and citric acid.[22,23]

Herein we report a method of decorating the silica frustules of diatoms with silver nanoparticles of approximately 10 to 20 nm in size (Fig. 2), without the use of any linking agents (see ESI†). The as received mined frustules were cleaned by plasma treatment, followed by immediate immersion in a silver nitrate solution. Sodium hydroxide was added to facilitate the reduction process, in forming silver oxide particles bound to the surface, which are then readily reduced by glucose.[24]

The resulting decoration of the frustules is displayed in TEM and SEM images (Fig. 2). The darker spots on the TEM micrograph can be identified as silver nanoparticles from both the energy filtered TEM (EF-TEM) (Fig. 2e) and high resolution TEM (HR-TEM) (Fig. 2f). Fig. 2e is the EF-TEM of Fig. 2d, showing silver as the bright spots on the image. Only silver around the edge of the diatom can be identified as the thickness of the frustule further in to the centre makes the signal too weak to be detected. Comparing Fig. 2d and 2e clearly shows that the dark spots on the surface of the frustule in the TEM images are silver nanoparticles. Fig. 2f is a HR-TEM image of silver nanoparticles accompanied by its electron diffraction pattern showing a *d*-spacing consistent with the known (111) spacing of 2.36 Å for elemental silver.[25] The X-ray diffraction (XRD) pattern (see ESI†) confirms that the silver oxide has been reduced to elemental silver with its characteristic peaks at 37.9° (111), 44.0° (200), 64.3° (220), 77.1° (311) and 81.5° (222) and also the absence of the main silver oxide (111) peak at 32.9°.[26] ICP-MS analysis was carried out on the material and the silver composition was found to be 9.12% by weight, which is consistent with the volume of silver relative to the volume of associated silica of the frustule, taking density differentials into account.

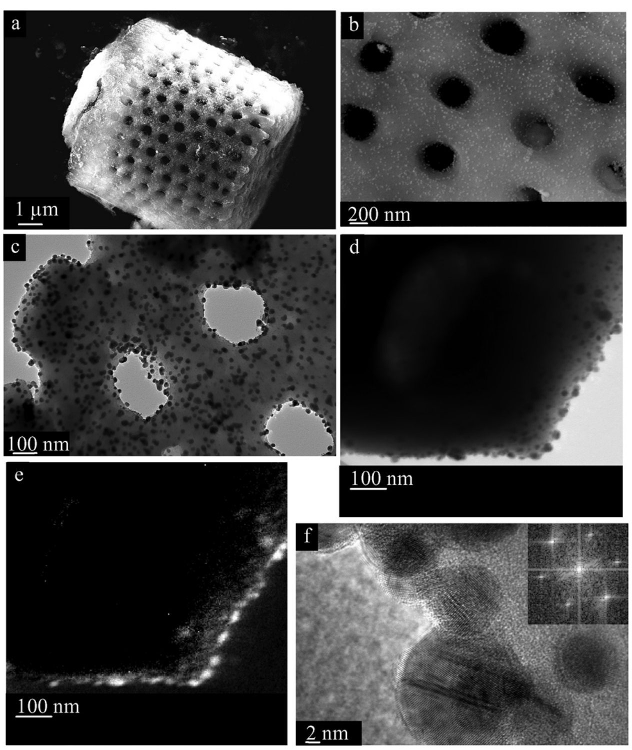

Fig. 2 Low resolution SEM (a), high resolution SEM (b) and TEM (c) images of silver coated diatoms. TEM (d) image and corresponding energy filtered TEM (e) of silver coated diatoms, and high resolution TEM (f), with corresponding electron diffraction pattern.

There is no evidence of agglomeration of the particles, which have an estimated average size of 11 nm using the Scherrer equation, which is consistent with the TEM images displayed in Fig. 2. This size is comparable to what is reported using other techniques for generating free standing nanoparticles but which require stabilising agents and less benign reductants.[1,16] For example particles smaller than 5 nm have been synthesised with narrow size distributions, however, they require the use of powerful reducing agents such as hydrazine hydrate and sodium borohydrate.[27] These materials present an issue in developing more benign processing using non-toxic reagents and avoiding the generation of a waste stream, unlike in the present case of using glucose. An exception in generating ultra-small silver nanoparticles, is the use of hydrogen as a reducing agent, in the confines of a narrow channel reactor.[28] The use of such a reactor in the present case is problematic because of the likelihood of blockage by the micron-sized frustules.

The decoration of the frustules was pH sensitive, with no evidence of silver nanoparticles attached to the surface under acidic conditions, but nonetheless the formation of a small amount of free standing silver nano-particles. This is likely caused by a lower reducing effectiveness of glucose in neutral and acidic conditions ($E° = -0.050$ V at pH = 7 and $E° = 0.600$ V at pH = 11). Under basic conditions the glucose reduction prowess improves and the silica surface develops a negative charge as the silanol groups are deprotonated.[29] Tuval and Gedanken reported two possibilities for the binding process between a silica surface and silver: either the silanol groups bind to the silver nanoparticles or the silanol groups bind the positively charged silver ions prior to reduction followed by nucleation and growth of the particles at the surface.[30] We carried out additional experiments with the aim of establishing the mechanism for silver nanoparticle attachment. After mixing the plasma cleaned diatoms in a silver nitrate solution for 30 minutes, the sample was washed *via* centrifugation (approximately 1900*g*). After the addition of base and glucose no silver nanoparticles were evident using TEM (see ESI†). When the suspension of frustules in a silver nitrate solution was mixed for over five minutes prior to the addition of NaOH, the attachment of nanoparticles decreased dramatically. This indicates that the silver ions do not attach to the silica surface of the frustules. Rather, they must be removed during centrifugation with no reaction evident during sodium hydroxide addition. In addition, when a colloidal suspension of silver nanoparticles was prepared separately and then immediately combined with the frustules after plasma treatment, there was no evidence for binding of the nanoparticles to the frustule surface. Moreover, when a suspension of frustules in a silver nitrate solution was exposed to base without undergoing reduction, the frustules were seen to be effectively decorated with silver oxide nanoparticles (see ESI†). This indicates that the silanol groups generated/exposed during the plasma treatment of the frustule are not effective in immobilising preformed silver nanoparticles but they can act as nucleation sites for the formation of silver oxide nanoparticles, which are then reduced to silver nanoparticles. The negatively charged silica surface, which is present in basic and neutral conditions due to an isoelectric point of between 2 and 5, attracts the positively charged silver ions resulting in a build up on the surface, and upon hydroxide addition silver oxide is precipitated.[31]

The significance of the plasma cleaning process is apparent in that it provides a pristine silica surface by removing any organic residues *via* the ion bombardment, and as reported by Bhattacharya *et al*., the plasma treatment also converts siloxane surfaces to predominantly silanol groups which are integral for particle binding.[30,32] Plasma cleaning also provides an environmentally cleaner and safer method for exposing the pristine surface of the frustule relative to other more common methods such as washing in piranha and sulphuric acid solutions, as well as requiring less time than the sonication method employed by Tuval and Gedanken. This is typically 3 hours in contrast to 15 minutes using plasma etching.[30] The catalytic activity of the material was tested in the sodium borohydride reduction of the rose bengal dye, as published by Jiang *et al*.[33] We found that the dye was reduced in less than 5 minutes in the presence of the silver coated diatoms, while in its absence no reduction was evident (see ESI† for details). Herein the catalytic process occurs by an electro-chemical mechanism, where silver nanoparticles-supported diatom frustules serve as an electron relay for an oxidant and a reductant. Importantly the substrate plays an important role in preventing the aggregation of the metal nanoparticles during the catalytic process, hence maintaining its activity.[33] Furthermore, enabling the ability to separate the product from the silver-silica composite by simple filtration.

In conclusion we have developed a simple yet highly effective method for decorating diatom frustules with silver nanoparticles 10–20 nm in size, which are devoid of surfactants. This involves reduction of *in situ* generated silver oxide particles attached to the surface, which is effective at room temperature using only glucose as a reducing agent with no requirement for any linking agents between the silica frustule and silver nanoparticles. The *method* of fabricating the silver nanoparticles attached to the surface is under basic conditions, and is independent of diatom species (frustule), which vary in shape and size, and size and distribution of the pores. Effectively harnessing the three dimensional porous structure of the diatom frustule as a scaffold for particle attachment can lead to a number of applications. These include catalysis where the diatom is easily recoverable by filtration, biomedical applications using the already known anti-microbial properties of silver combined with the porous biodegradable scaffold of the frustule for tissue engineering, and in localized surface plasmon resonance biosensors where silver nanoparticles have already been widely used.[34,35]

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