A Bio-Inspired Photopatterning Method to Deposit Silver Nanoparticles onto Non Conductive Surfaces Using Spinach Leaves Extract in Ethanol

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Abstract. Densely packed silver nanoparticles (AgNPs) were produced as continuous films on non-conductive substrates in a site-selective manner. The formation of the AgNPs were directed by blue light using extract from spinach leaves acting as photo-reducing agent. This bio-inspired production of reduced ions nanofilms benefit applications where seed conductive layers are required for the manufacture of metal parts embedded into plastics.

Keywords: Nature-inspired manufacturing · Biomimetism · Biomimicry · Additive manufacturing · Artificial photosynthesis

1 Introduction

Intense research efforts have focused on the synthesis and deposition of silver nanoparticles (AgNPs) due to their usefulness in plasmonics, electronics, biological sensing and as an antimicrobial agent [1–3]. Some applications require these silver nanoparticles to be assembled in a reproducible manner as micro- or nano-scale periodical structures such as arrays or lines of specific width and space. Usually, AgNPs are synthesized in a colloidal solution and then consolidated onto a substrate using laser sintering [4], microwave [5] or plasma treatment [6]. They can also be prepared using the bottom-up approach whereby metal ions are molecularly linked to the substrate onto which they are deposited and then reduced to form nanoparticles within the molecular network of the linker layer. The latter approach can easily anchor metal nanoparticles onto a strong electrostatic adhesive such as dopamine [7] or ion-exchange resins [8].

In that respect, surface hydrolysed polyimide or polyetherimide films are ideal substrate materials for hosting metal nanoparticle thin films [9, 10]. These metal thin films can be produced *in situ* with a controllable thickness within a surface layer of ion-exchange resins of the R-COO$^-$ type obtained as the result of alkaline hydrolysis of polyimide forming an amorphous layer of poylamic acid on its surface [8]. In addition, different reduction methods, including thermal, chemical or photo-induced, can be readily applied to such silver ion-exchange polyimide substrate (Ag$^+$-PI).

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Photo-induced reduction is the simplest route for replicating the desired patterns by regulating the shape of the light source such as in laser writing applications or by using a photomask as in photolithography. To the best of the authors' knowledge, reports regarding high-throughput photo-induced patterning of silver nanoparticle thin films that is compatible with large area substrate are still lacking due to the poor quantum yield of the photo-reducing agents or catalysts employed today.

Herein we demonstrate a nature-inspired strategy to reduce metal ions using photosystem 1 (PS I) found in spinach extract dissolved in ethanol. PS I is thought to be acting as the photo-reducing agent to produce patternable metal nanoparticles that meet the requirements of both production speed and process scalability. PS I comprises of light harvesting pigment proteins, amongst which chlorophyll is being most commonly referred to for photosynthesis.

2 Materials and Methods

For our purpose, the PS I and mineral agents contained in the leaves were simply extracted from spinach leaves by dissolving them in ethanol solvent, after using a blender to collapse the chloroplasts in the leaves which house the PS I. In a typical process, 100 g of fresh leaves was mixed with 500 ml of absolute ethanol in a blender and processed for 1 min. After passing the mixture through a 1:11 μm grade filter paper, 90 % of the liquid was then poured into a second flask and left to stand for some time for sedimentation. The process of filtration was then repeated again to avoid any debris in the extract solution. Next, 2 ml of the PS I and minerals extract solution were pipetted onto the surface of the Ag^+-PI substrate.

The substrate was originally prepared by a 2-step immersion: first into a 1 M KOH solution at 50 °C for 5 min, followed by a 0.01 M $[Ag(NH_3)_2]^+$ aqueous solution at room temperature for 5 min. As the preparation process involves only a couple of dipping process, substrates of large dimensions can readily be prepared depending on the size of the tanks that contain the two solutions described above. The photo-induced reduction step took up to five minutes using a 460 nm wavelength fibre delivered light emitting diode with an intensity of around 1270 mW/cm^2.

3 Results

Figure 1, top left, shows photographs of circular spots of silver patterns with an approximate diameter of 1 mm produced upon exposure to the blue light source at the tip of the optical fibre. The corresponding field emission scanning electron microscopy (FESEM) images where the growth of silver nanoparticles can be clearly observed in the same figure. Generally, particle size and density of the AgNPs increased with increasing exposure times. At 30 s exposure, AgNPs as small as 15 nm can be easily identified across the illuminated area. Some particles aggregated to sizes of about 70–80 nm. Within 60 s of exposure, the whole illuminated area was compactly covered with AgNPs. The smaller particles have an average size of about 30 nm and the larger aggregated particles about 70 nm. At 180 s exposure, a large amount of particles had aggregated to 40 nm or bigger, where, noticeably, some particles as large as 120 nm can be seen.

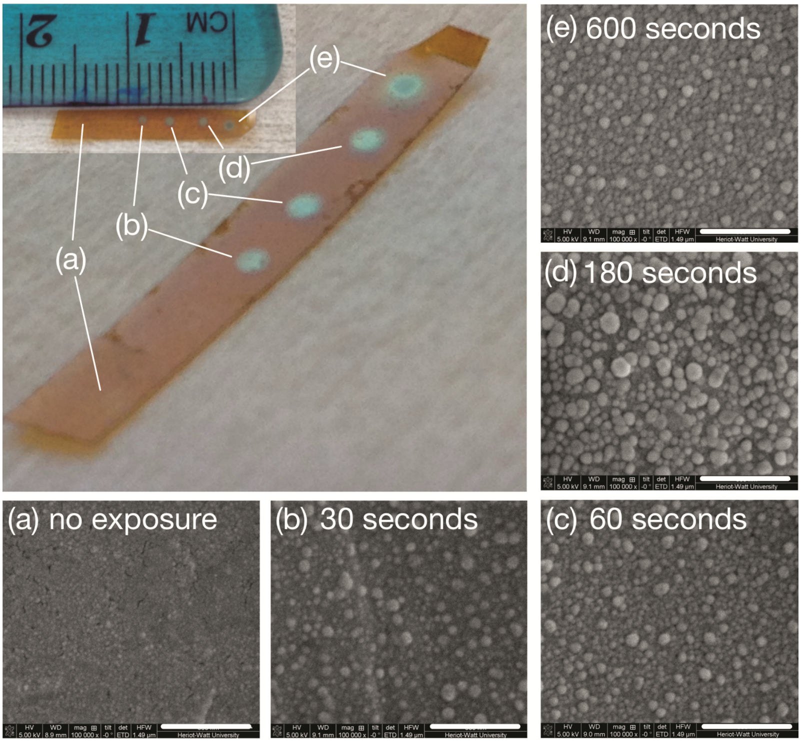

Fig. 1. Photographs and FESEM images of: (a) control background with no photo-induced reduction. (b–e) the location selective production of AgNPs on Ag^+-PI upon exposure to the light source for 30, 60, 180 and 600 s, respectively. Scale bar is 500 nm.

In the latter case the AgNPs are not compactly connected as in the case of the 60 s exposed sample indicating that the silver ion source in the substrate supplying the reaction has been depleted and left a void behind when the smaller particles aggregated to form bigger particles.

At the prolonged exposure of 600 s, a dark mark can be clearly seen in the photograph at the centre of the circular pattern in the Fig. 1 (top left). The excess photon energy under this exposure time perhaps induced some thermal effects on the substrate resulting in polymer restructuring. The corresponding FESEM micrograph in Fig. 1(e) suggests that a reaction, as yet not explained, seemed to have taken place, which removed the larger particles seen in Fig. 1(d). The small amount of AgNPs observed in Fig. 1(a) with no light exposure could be the result of spontaneous reduction of Ag^+ ions, which purely utilize the redox potential difference between impurity entities and the Ag + ions in the absence of a reducing agent.

4 Discussion

4.1 Short Exposure Time

The short exposure times required using a relatively low light intensity irradiation for the formation of high density AgNPs were surprising. Up to now, irradiation methods used for metal nanoparticle formation usually produce sparse particles from a dispersion in the liquid phase [11]. The enhancement reported here can be credibly contributed to the function of PS I extract. It is known that impurity of metal traces is present in the absolute ethanol solvent, however they did not contribute to the significantly faster photoreduction rate. Our previous work with the same Ag^+-PI substrate system using a synthetic photoreducing agent methoxy (ethylene glycol) and with the same absolute ethanol solvent required several hours of light exposure to obtain appreciable amount of AgNPs [9]. Although the PS I structure might have been altered from its natural membrane arrangements through the extraction procedure, it has definitely enabled a significant increase of the photoreduction rate. It would be interesting to study the performance in the photoreduction rate along side purified PS I, and the effects of different extraction methods and the different types of plant leaves as the source material.

The reason why the photo-induced reduction can be conducted in such a short time with a PS I coating on top of the Ag^+-PI is partly due to the efficient electron transfer within the PS I protein complex. Upon reception of the incident photon energy, rapid charge separation occurs within 10–30 ps, releasing an electron down an intra-protein energy cascade to an iron-sulfur complex called F_B^- [12]. When the PS I is in its natural environment, the soluble, iron-containing protein ferredoxin shuttles the electrons away from F_B^- to achieve a nearly perfect quantum yield [13]. In addition, the nucleation and

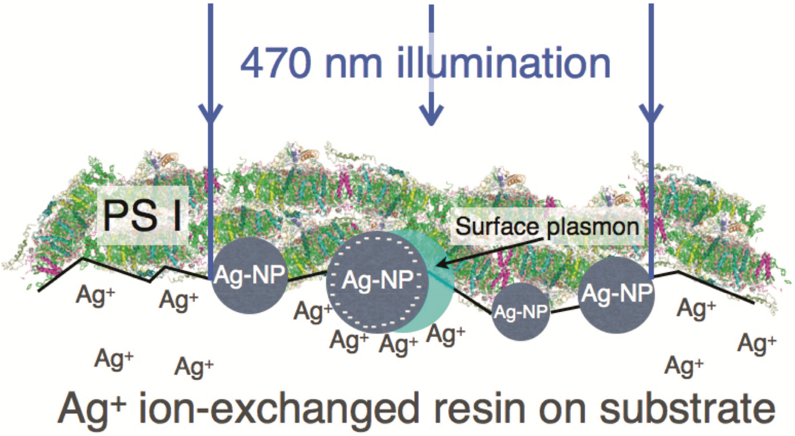

Fig. 2. Schematics of plasmon field enhancement and charge storage on the surface of AgNPs, which assist the photo-reduction of Ag^+ ions in the PS I/AgNPs hybrid system. The figure is a schematic representation of the assumed process with size of the nanoparticles not at the right scale. The substrate has a prior deposited Ag + ion-exchanged resin.

growth of the AgNPs in the present system benefit from a self-catalysed mechanism as illustrated in Fig. 2.

During the growth of the AgNPs, the PS I proteins are confined into the nano-cavities amongst the Ag aggregates. From this situation, two main driving forces can be attributed to the long range electron transfer from the PS I coating to the Ag^+ ions within the ion-exchange resins on the substrate. Firstly, the plasmon enhancement of photon fields within a hybrid system of PS I molecular complex and AgNPs aggregates has been modelled [14] and measured [15] to provide a several fold increase in the generation of excited state electrons. Secondly, the AgNPs act as ultra large surface area nanostructured electrodes for storing the excited electrons released from PS I as charges on the AgNPs surfaces [16] and thus minimising charge recombination. More recent studies carried out by the group seem to indicate that salts from the extract of spinach leaves might also contribute to the donation of electrons. This new information will be presented during the conference.

4.2 Three Potential Photoreduction Mechanisms

A cross-section FESEM image prepared by Broadband Ion Beam (BIB) machining is, shown in Fig. 3 and provides an insight into the photoreduction mechanisms. The process, developed and used by MCS Ltd, allows deformation and smear-free cross-sectioning without obscuring the AgNPs-polymer matrix. The BIB system allows representative sample sizes (up to 2 mm) to be cross-sectioned without mechanically touching the sample enabling absolute confidence that deformation or voids did not occur during the cross-sectioning procedures as in the FIB system.

There are three key features to note:

(i) The AgNPs produced by the photoreduction effectively formed a uniform nanocomposite layer within the modified polyimide substrate surface. No gradient of AgNPs distribution was observed across the layer. The electrons generated from the PS-I coating and the natural mireal salts from the leaves were effectively transferred into the surface-modified polymer substrate. This suggests that some electron relay mechanisms must be involved as suggested earlier, since there would inevitably be an illumination gradient as the light impinges into the surface of the substrate due to both the polymer molecules and the *in situ* growth of the AgNPs.

(ii) The uniform boundary of the AgNPs nanocomposite illustrates the diffusion-controlled and well-defined nature of the 2-step immersion surface modification process where the polyimide molecules were first hydrolysed by KOH followed by Ag^+ ion-exchange. The line of shade underneath the AgNPs nanocomposite layer represents a small amount of unreacted Ag^+ ions that were not reduced. An explanation could be that the rate of Ag^+ ion diffusion within the polymer matrix is much slower than the rate of the electron transfer.

(iii) A relatively high thickness of approximately 1.5 μm layer of AgNPs nanocomposite was produced. Clusters of AgNPs were created through their nucleation and growth, however they were unable to form chains of continuous network within the volume of the nanocomposite to render the layer electrically conductive.

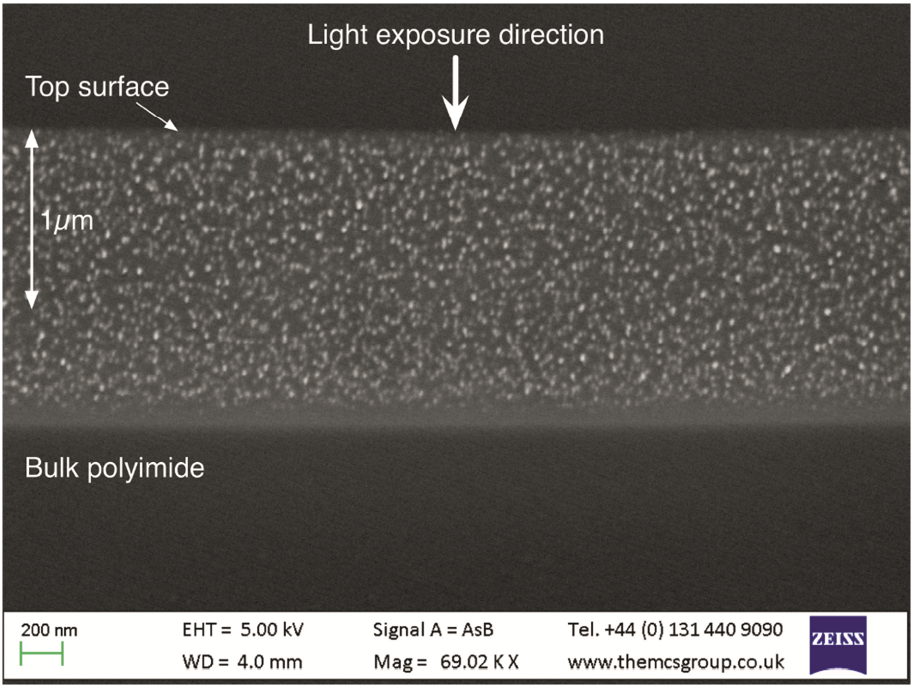

Fig. 3. FESEM image of a cross-section of the AgNPs nanocomposite within the surface-modified layer of the polyimide substrate.

5 A Scalable Nature-Inspired Manufacturing Process

Our approach in the synthesis and patterning of the AgNPs is easily scalable to large area industrial production. Regular methods commonly involve producing the AgNPs in a synthesis matrix first, followed by the separation of the particles and their consolidating onto desired locations on a substrate according to the following sequence:

1. Homogeneous mixing of the capping agent and the stabilizing agent with the metal ions.
2. Reduction of the capped metal ions.
3. Extraction of metal nanoparticles.
4. Purification to remove organic residues.
5. Consolidation and patterning onto a surface.

This procedure can take hours to perform. By first incorporating the metal ions into the ion-exchange resin, the molecular networks of the polymer served the role of a capping agent when the AgNPs were grown in situ within the surface layer of the substrate. As a result, significant production time is reduced in the present process:

1. Hydrolysis of polyimide by KOH immersion. 5 min.
2. Ion-exchange in a silver salt solution. 5 min.

3. Extraction of PS I and of the mineral salts form the leaves. The extract can be prepared separately and stored frozen prior to reaction. 30 min.
4. Exposure to light source for photo-reduction of silver ions. 1 min or less.

The requirement of the light intensity (around 1270 mW/cm^2) is also low enough such that a flood exposure lamp can be used for large area parallel production of AgNP patterns through a photomask. However ambient room lighting or daylight does not provide a large enough energy dose for any accelerated photoreduction of Ag$^+$ ions in the system here.

6 Conclusions

In summary, we have reported in this article a rapid strategy to photopattern macro-scale compact thin films consisting of AgNPs.

We propose some mechanisms involved in the outstanding electron transfer phenomenon, which resulted in the charge separation and transfer within the PS I coating. Furthermore, some electron relay systems must be present within the silver/polymer matrix to allow the electron transfer to proceed further and produce an almost 1.5 μm thickness layer metal matrix composite.

The whole production process itself can be as short as 11 min, if the PS I and mineral salts extract is prepared in advance. The absence of any toxic reducing agents or complex organic ligands in the whole production process also makes this patternable AgNPs nanocomposite fabrication method suitable for biological and sustainable applications.

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