

Galvanic replacement mediated transformation of Ag nanospheres into dendritic Au-Ag nanostructures in the ionic liquid [BMIM][BF₄]

Andrew Pearson, Anthony P. O'Mullane, Vipul Bansal, and Suresh K. Bhargava**

School of Applied Sciences, RMIT University, GPO Box 2476V, Melbourne VIC 3001, Australia

Fax: +61 3 9925 2882; Tel: +61 3 9925 2121

**E-mail: vipul.bansal@rmit.edu.au / suresh.bhargava@rmit.edu.au*

Electronic Supplementary Information

Experimental Details

Materials. Silver nitrate (AgNO_3), sodium borohydride (NaBH_4) and potassium tetrabromoaurate dihydrate ($\text{KAuBr}_4 \cdot 2\text{H}_2\text{O}$) were purchased from Sigma-Aldrich; sodium oleate, formaldehyde and hydrazine was purchased from BDH; and 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}][\text{BF}_4]$) was purchased from Ionic Liquid Technologies (IoLiTec). All chemicals were used as received.

Synthesis of Silver Nanoparticles. Silver nanoparticles were synthesized by reducing silver nitrate in an aqueous solution containing a mixture of sodium borohydride and sodium oleate by following a procedure previously reported by Efrima *et al* (W. Wang, S. Efrima, O. Regev, *Langmuir*, 1998, **14**, 602.). Briefly, in 50 mL of 5 mM AgNO_3 , 50 mL of another solution containing 20 mM NaBH_4 and 2.5 mM sodium oleate was added with rapid stirring in an ice bath. The solution immediately turned bright yellow indicating the formation of silver nanoparticles. The solution was heated to 70 °C with continuous stirring to decompose any excess NaBH_4 and then allowed to cool at room temperature. The final concentration of silver nanoparticles in water was 5 mM and was used as such without any further modification.

Galvanic Replacement Reaction. 5.87 mg of $\text{KAuBr}_4 \cdot 2\text{H}_2\text{O}$ was dissolved separately in 10 mL each of MilliQ deionized water and the ionic liquid $[\text{BMIM}][\text{BF}_4]$ using an ultrasonic bath, leading to 1 mM $[\text{AuBr}_4]^-$ stock solutions in water and IL respectively. In a 5 mL final reaction volume, 0.5 mL aliquots of 5 mM Ag nanoparticles were mixed with differing volumes of $[\text{AuBr}_4]^-$ stock solutions, resulting in gold salt ($[\text{AuBr}_4]^-$) to silver nanoparticles (Ag^0) molar ratios of 0 % (control), 0.1 % (1:1000), 1 % (1:100) and 10 % (1:10) respectively. The galvanic replacement reactions between Ag nanoparticles and $[\text{AuBr}_4]^-$, both in H_2O and $[\text{BMIM}][\text{BF}_4]$, were allowed to continue at room temperature for 48 h to nullify any time-progression effects. The reaction products were centrifuged; pellets were washed three times with MilliQ water, and redispersed in 0.5 mL of MilliQ water for further characterization and electrocatalysis experiments.

Electrochemical Measurements. Voltammetric experiments were conducted at (20 ± 2) °C with a CH Instruments (CHI 760C) electrochemical analyzer in a 3 electrode configuration. A 3 mm glassy carbon (GC) electrode (Bioanalytical Systems) was used as the working electrode and polished with an aqueous 0.3 μm alumina slurry on a polishing cloth (Microcloth, Buehler), sonicated in deionized water for 5 min, and dried with a flow of nitrogen gas prior to use. The reference electrode used was a Ag wire in [BMIM][BF₄] and an Ag/AgCl (aqueous 3 M KCl) electrode in aqueous solution. The counter electrode in all cases was a Pt wire. The potential with respect to the Ag QRE was checked regularly using the ferrocene/ferricinium redox couple as an internal standard where the formal potential was found to be 0.25 V. All electrochemical experiments were commenced after degassing the electrolyte solutions with nitrogen for at least 10 min prior to any measurement.

Instrumentation. Samples for transmission electron microscopy (TEM) analysis were prepared by drop-casting the samples onto a carbon coated copper grid. TEM measurements were performed using a JEOL 1010 TEM instrument operated at an accelerating voltage of 100 kV. X-ray diffraction (XRD) measurements were performed on a Bruker AXS D8 Discover with general area detector diffraction system (GADDS), and UV-visible spectroscopy (UV-Vis) measurements were performed using a Cary 50 Bio-spectrophotometer. For electron dispersive X-ray spectroscopy (EDX) analysis, samples were prepared by centrifugation and washing three times with deionized water, followed by drop-casting on a sample holder (containing Al, Cu and Fe), which were subjected to EDX measurements on a FEI Nova NanoSEM instrument coupled with EDX Si(Li)X-ray detector. Quantitative elemental analysis of samples was performed by collecting EDX on 5 different regions and averaging the obtained values.

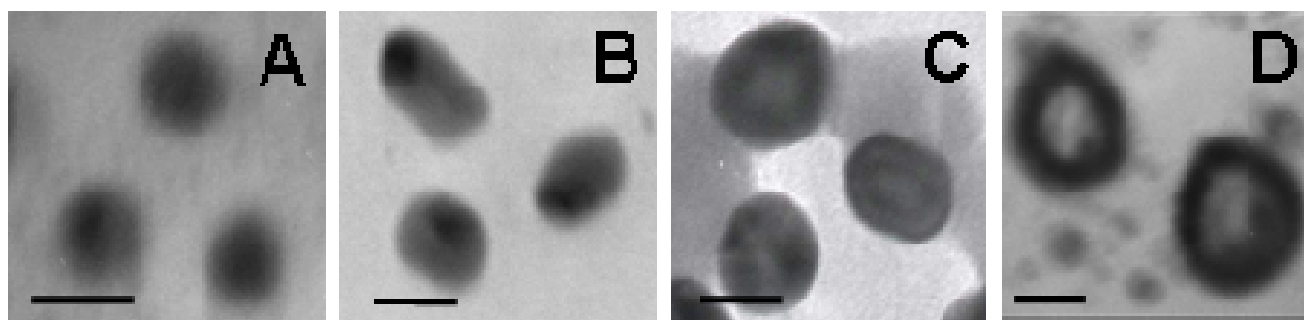


Fig. S1. TEM images of oleate-capped Ag nanoparticles in water before (A), and after galvanic replacement with (B) 0.1 %, (C) 1 %, and (D) 10 M % of $[\text{AuBr}_4]^-$ ions for 48 h. Scale bars correspond to 20 nm. The as-synthesized Ag nanoparticles were found to be fairly monodispersed with a quasi-spherical morphology and an average diameter of 15-20 nm (A). The replacement reaction of Ag nanoparticles with increasing amount of $[\text{AuBr}_4]^-$ ions leads to dissolution of Ag nanoparticles in surrounding water, and simultaneous reduction of Au onto preexisting Ag nanoparticles. This eventually results in thick-walled Au-Ag nanoshells (C and D) via a pin-hole forming step (B).

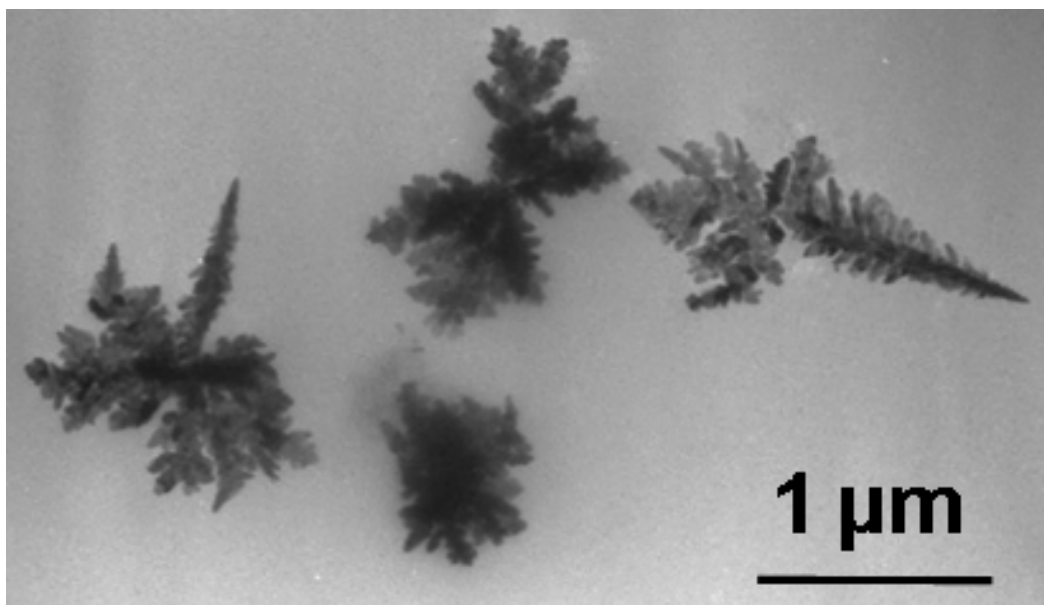


Fig. S2. Lower magnification TEM image showing Au-Ag nanostructures formed after galvanic replacement of spherical Ag nanoparticles with 10 M % of $[\text{AuBr}_4]^-$ ions in the ionic liquid $[\text{BMIM}][\text{BF}_4]$. The absence of smaller particles in the sample is notable.

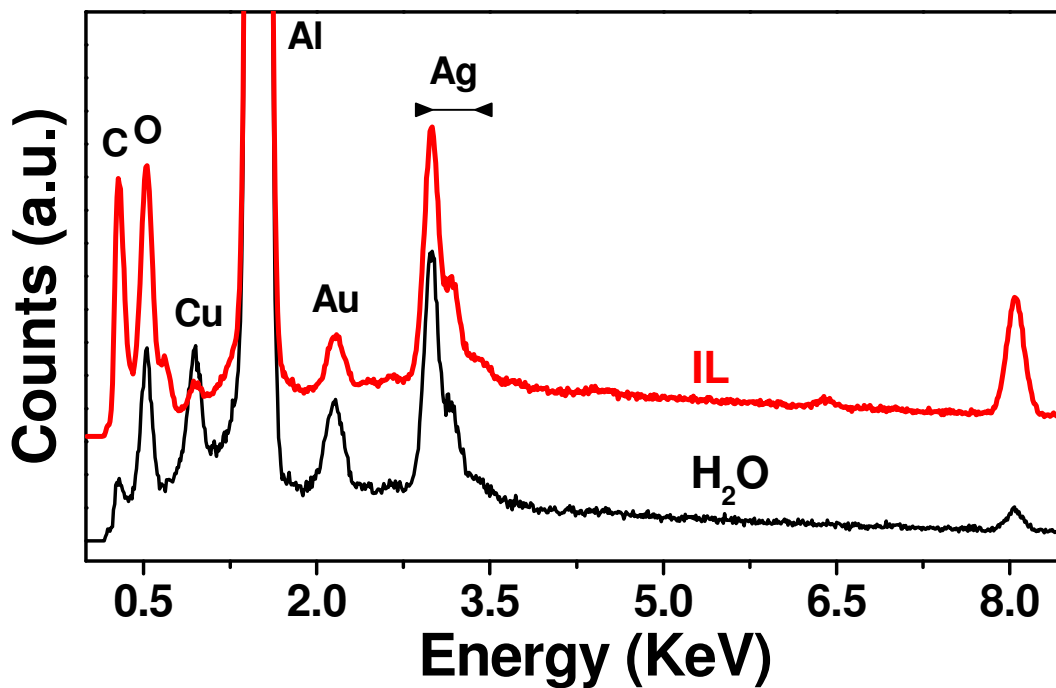


Fig. S3. EDX spectra of reaction products obtained through galvanic replacement reaction between Ag nanoparticles and 10 M% $[\text{AuBr}_4]^-$ ions in water and IL $[\text{BMIM}][\text{BF}_4]$. The Al, Cu and Fe signature peaks arise from the EDX sample holder. The presence of both Au and Ag signals in EDX spectra indicate the formation of bimetallic Au-Ag nanoshells in water, and bimetallic Au-Ag nanodendrites in $[\text{BMIM}][\text{BF}_4]$.

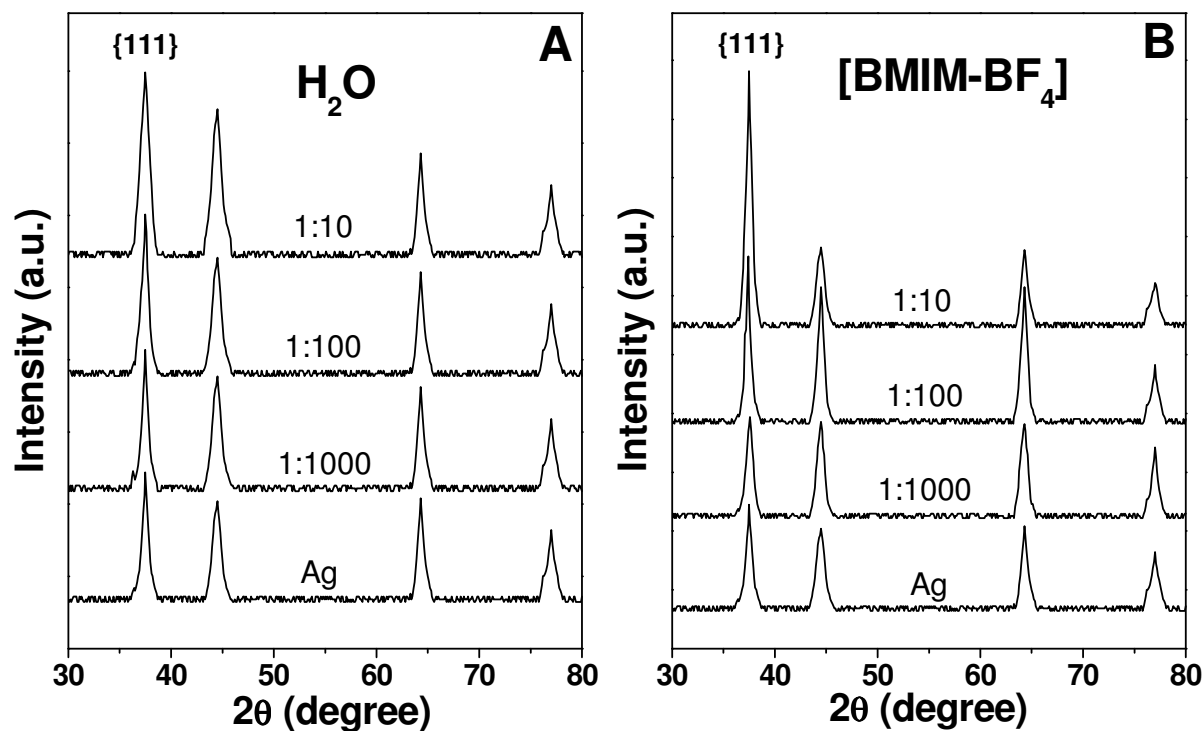


Fig. S4. XRD patterns of reaction products obtained through galvanic replacement reaction between Ag nanoparticles and increasing concentration of [AuBr₄]⁻ ions in (A) H₂O, and (B) [BMIM][BF₄]. The XRD patterns match with the fcc structure of Au and Ag, both of which have very similar lattice parameters. The increased intensity of {111} crystal plane from the nanodendrites synthesized in [BMIM][BF₄] is notable.

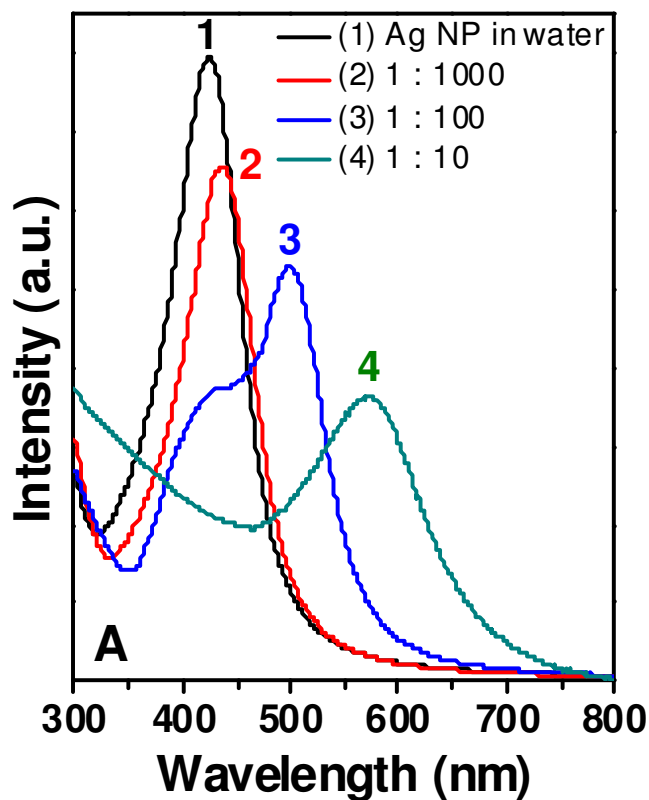


Fig. S5. UV-Vis spectra of Ag nanoparticles before (curve 1) and after galvanic replacement with 0.1 M% (curve 2), 1 M% (curve 3), and 10 M% of KAuBr_4 (curve 4) in water for 48 h. In the aqueous system, Ag nanoparticles show a narrow SPR with peak at ca. 425 nm, which is attributable to 15-20 nm spherical Ag nanoparticles (curve 1). Upon reaction with 0.1 % $[\text{AuBr}_4]^-$ ions, the SPR reduces in intensity, along with a red-shift to ca. 436 nm (curve 2). These two changes in Ag SPR can be respectively attributed to the dissolution (oxidation) of preexisting Ag nanoparticles into Ag^+ ions, and simultaneous formation of Au-Ag alloy on their surface (similar sized Au nanoparticles absorb at 520 nm).^{2,6} When an increased amount of $[\text{AuBr}_4]^-$ ions (1 %) is reacted with Ag nanoparticles, Au-Ag alloying is clearly evident from a further red-shift to ca. 500 nm, along with reappearance of a dampened Ag SPR signature at ca. 425 nm, which is due to consumption of more Ag nanoparticles by additional $[\text{AuBr}_4]^-$ ions (curve 3). A further concentration increase of $[\text{AuBr}_4]^-$ to 10 % results in an SPR peak at significantly longer wavelengths (570 nm) than that normally observed at 520 nm for similar-sized spherical gold nanoparticles (curve 4). Previous studies have assigned such strong red-shifts to the formation of Au nanoshells, as is observed in TEM (Fig. S1). Moreover, the Ag SPR at 425 nm appears non-existent, which indicates further dissolution of the template Ag nanoparticles.

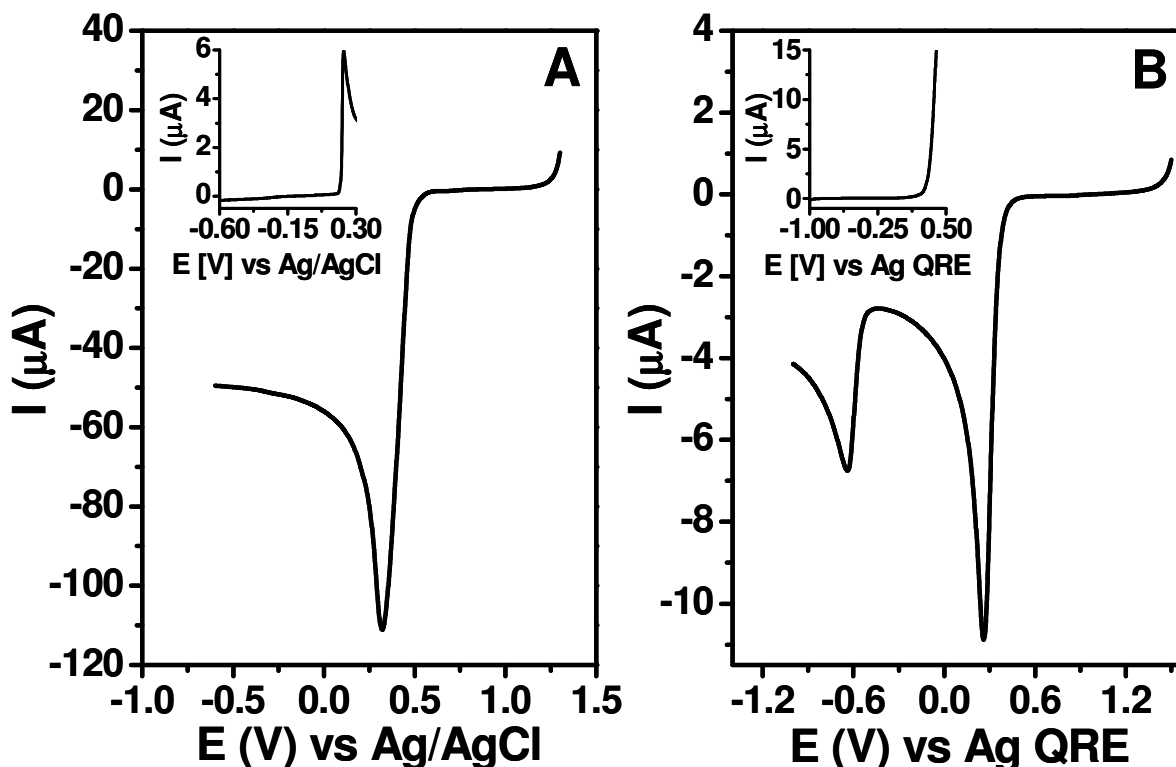


Fig. S6. Linear sweep voltammograms (LSVs) recorded at a GC electrode at 10 mV s^{-1} for the electroreduction of 10 mM KAuBr₄ in (A) H₂O and (B) [BMIM][BF₄]. Inset shows LSVs for a Ag electrode in (A) 10 mM KNO₃ and (B) [BMIM][BF₄], but in the absence of [AuBr₄]⁻. For the aqueous solution, 10 mM KNO₃ was added as supporting electrolyte to closely correlate with the ionic strength of the solution under which the gold deposition process was carried out (10 mM KAuBr₄). It can be seen from the inset in (A – H₂O) that the onset for Ag oxidation occurs at ca. 0.18 V and reaches a maximum at ca. 0.22 V, which is prior to the commencement of gold electroreduction from KAuBr₄ at ca. 0.56 V which reaches a maximum at ca. 0.32 V. This difference in potential (>0.18 V required for Ag oxidation and <0.56 V required for Au reduction) is the driving force for the galvanic replacement of silver with [AuBr₄]⁻ in the aqueous solution and results in 3 Ag atoms being consumed for every [AuBr₄]⁻ ion being reduced. In the case of Ag oxidation in [BMIM][BF₄], the LSV was carried out in neat [BMIM][BF₄], as supporting electrolyte is not required due to the high ionic conductivity of this IL. In [BMIM][BF₄], Ag oxidation occurs prior to the onset of the electroreduction of KAuBr₄ which is similar to the aqueous medium (B - IL) and the onset potential required for Ag oxidation is at ca. 0.20 V. Therefore, the data suggests that Ag has only sufficient reducing power to drive reduction of [AuBr₄]⁻ to [AuBr₂]⁻, but it cannot drive its further reduction towards Au⁰, which commences at a much lower potential of ca. -0.50 V in [BMIM][BF₄], and would have otherwise lead to formation of metallic gold (Au⁰). This was briefly discussed in the main communication.