



Green Electrodeposition of Nano Gold from Benign Solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in Alum: Urea Deep Eutectic Solvent

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Abstract

Deep Eutectic Solvents (DES) have demonstrated enormous potential in the electrodeposition of various materials, including metals and alloys. Usually, gold electroplating solution consists of toxic material of gold cyano compounds. This work demonstrates novel green electroplating of nanogold from Alum: Urea deep eutectic solvent (DES) containing chloro-gold compound ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$). Gold showed one stage redox system in this reduction solution at -0.2V and oxidation and oxidation maximum at -0.3V . The electroplated gold on brass at -0.7V for one and three hours gave a brown-colored layer containing nanogold particles with an average distribution of (31.16-33.44) nm. The crystalline structure of deposited gold is like a cubic crystal with 10 nm size. Scanning electron microscopy (Fe-SEM), energy dispersive X-ray analysis (EDX), atomic force microscopy (AFM), and X-ray diffraction were all used to follow up on this work (XRD).

Keywords: Deep Eutectic Solvent, green electroplating, gold nano particles.

1. Introduction

Gold is a relatively uncommon precious metal with a distinct beauty and is appreciated for its color. Because of its unusual physical and chemical qualities, exceptional ductility and malleability are still in high demand in jewelry, high-tech sectors, and medicinal applications [1], [2].

As a result of its excellent electrical conductivity, low contact electrical resistance for inserting connections, and outstanding corrosion resistance, gold has been used in substantial quantities by the electronic and electrical industries for the better part of the last four decades.[3]. Because gold is the most stable noble metal at the nanoscale, it serves a unique function in nanoscience and nanotechnology. As a result, designers of any nano-device that requires metallic components are likely to choose gold. Gold is a significantly stronger electron conductor than silicon, and its surface chemistry allows it to be employed as a platform for self-assembling layers of organic molecules [5].

Gold electroplating from cyanide baths, including the highly toxic $\text{KAu}(\text{CN})_2$ and KCN [6], has been widely used in the electric and semiconductor sectors.

Deep-eutectic solvents (DES), which were initially identified by Abbott et al. in 2003 [7], appear to be

particularly promising electrolyte classes in electrochemistry. DESs are liquid mixtures made of two parts, a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), that were developed as a new type of green solvent and a low-cost alternative to ionic liquids [7].

They self-associate to form a new eutectic phase with a melting point (below $100\text{ }^\circ\text{C}$) lower than the melting points of the individual components. [8]. DES has several advantages over ionic liquids, including low vapor pressure and a broad electrochemical stability window [9], as well as low cost and environmental friendliness [10], [11].As a result, they have sparked great interest in a wide range of applications, including electroplating, metal processing [12], nanotechnology [14], organic synthesis [16], and electrochemical energy storage [17].

The inclusion of metal ions in solutions for metal deposition, metal dissolution, or metal processing is now the most common application for DESs [18]. The greater solubility of metal salts in DESs over aqueous electrolytes is one of the primary advantages of employing DESs over aqueous electrolytes [8], [19], [20]. DESs have also been shown to play several roles in the nucleation, growth, self-assembly, and production of well-defined

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frameworks of metallic nano-particles. [10], [15], [21].

Gold electrochemical reactions have been explored in various ionic liquids and DESs. For example, Katayama et al. [22] reported electrodeposition of gold by reduction $[\text{AuBr}_4]$ -in, 1-butyl-1-methylpyrrolidiniumbis(trifluoromethylsulfonyl)amide ionic liquid, metallic Au was deposited on a glassy carbon substrate at -1.5 V vs. Ag/Ag(I). At the same time, Au nano-particles were formed and dispersed in the ionic liquid by potentiostatic cathodic reduction on a glassy carbon electrode at -2.5 V vs. Ag/Ag(I).

Kaminska et al. [23]. Obtained gold nano-particles at a solid|ionic liquid|aqueous electrolyte three-phase junction, an aqueous solution containing $[\text{AuCl}_4]$ – and 1-decyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ($\text{C}_{10}\text{mimN}(\text{Tf})_2$) ionic liquid, the electrodeposition shape of resulting Au nano-particles is highly angular and well-developed with a diameter of 110 ± 30 nm.

Leigh Aldous and co-workers [24] studied the electrochemistry of gold in non-haloaluminate, ionic liquid. The electrochemical behaviour of Na $[\text{AuCl}_4]$ has been investigated in $[\text{C}_4\text{mim}][\text{NTf}_2]$ (1-butyl-3-methylimidazolium bis [(trifluoromethyl) sulfonyl] imide ionic liquid. The electrodeposition of gold from dissolved Na $[\text{AuCl}_4]$ in $[\text{C}_4\text{mim}][\text{NTf}_2]$ is found to be a two-stage reduction process via the formation of $[\text{AuCl}_2]$. S. Kumar-Krisnan et al. [25] synthesize Au nanostructures in nonaqueous urea-choline chloride deep eutectic solvent DES. The effect of temperature on the controlled-shape synthesis of gold nanostructures under anhydrous conditions has been studied. Aoqi Li et al. [26] show that one of the most significant parameters for the precise morphological regulation of noble metal nanostructures in DESs is the water content. The appearance and structure of Au nanocrystals grew irregular as the water content in Reline DES increased. Alum: Urea DES is an interesting solvent. It exhibits the characterization of ionic liquids while also containing water molecules, which have been observed in the liquid coordinated to the ionic species of deep eutectic solvent and not in the free state. [27]. Metal electroplating was demonstrated in the DES for the electrodeposition of indium with the formation of nano deposited metals. [19].

This paper discusses the electrochemical behavior of Au (I) on a Pt disc working electrode. For the first time, gold was electrodeposited in alum-urea DES and the surface morphology of deposited gold at various deposition times on a brass substrate was investigated.

Materials and Methods

Reagents Preparation

Aluminum ammonium sulphate $[\text{AlNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$, (99.5%) and urea (NH_2CONH_2)(99.0%)

were obtained from Central Drug House (P) Ltd.(CDH). Aluminum ammonium sulphate and urea in a mole ratio of (1:5) were mashed separately, mixed, and heated gradually to 85°C with stirring until melted together, giving colorless liquid [28]. The resultant melt was gradually cooled to room temperature and remained liquid and stored in a sealed container. This Alum: urea deep eutectic solvent was purified before usage. The prepared Alum: Urea DES (30 ml) was purified from impurities by electro-reduction process at -1.1V for one hour followed by -0.6 V for four hours, at 30°C . Electrodes ($60 \times 5 \times 1$ mm) of copper as cathode and stainless steel plate ($50 \times 10 \times 1$ mm) as the anode was used which immersed in DES with 10mm apart.

The gold electrolyte solution was prepared by dissolving 0.01 M $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Merck, for synthesis) in purified Alum: urea deep eutectic solvent and stirred for 2hr at 45°C when a brown suspended solution was obtained.

Cyclic Voltammetry Technique

Cyclic voltammetry was performed using Digilvy-Dy2300 Bipotentiostat. Consist of three-electrode system comprising a platinum electrode ($2\text{mm}\Phi$) as the working electrode (WE), a platinum plate ($1\text{cm} \times 1\text{cm} \times 0.5\text{cm}$) as the counter electrode (CE), and a silver wire as the quasi reference electrode (QRE). The reference electrode was cleaned with (0.1M) HCl solution, and the platinum working electrode surface was polished with microalumin and finally rinsed with acetone and doubly deionized water to remove any residual particles. The substrate used in the electrodeposition process was mechanically polished with 4000 grit SiC abrasive paper cleaned in 40 vol.% HCl solution for 30 s to remove the oxides and contaminants on the surface of brass foil (CuZn alloy) substrate.

A potentiostat was used with a power supply (Thurlby 15V-4A, England power supply) to control the current and potential of the electrodeposition process, which was connected to the brass foil ($50 \times 5 \times 1$) mm as cathode and stainless steel plate ($50 \times 10 \times 1$) mm as anode and immersed in 20 ml of electrolyte solution at a depth of 10 mm. The distance between the cathode electrode and anode electrode was 10 mm, and the electrodeposition was carried out at a potential of -0.7 V for 1hr. and 3hrs. at 30°C . After electrodeposition, the specimens were rinsed with acetone and deionized water, and dried with an air blast at room temperature.

Characterization Techniques

Surface morphology of the deposited gold was characterized through field emission scanning electron microscopy using a model ZEISS SIGMA VP field emission scanning electron microscope (FE-

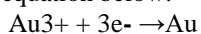
SEM) with a high-resolution system at an acceleration voltage of 15 keV, with energy dispersive X-ray spectrometry (EDX) mapping using a JEOL model 7001F field-emission gun scanning electron microscope and an Oxford X-ray spectrometer with a 10 keV acceleration voltage. The composition of the electrodeposit was determined by crystalline and phase identification of samples as determined using an X-ray diffractometer. The electrodeposit's composition was determined by crystalline and phase identification of samples using an X-ray diffractometer (XRD-6000) SHIMADZU-Japan employing a monochromatized radiation source of Cu-K of Cu(1.54060 Å) filtering wave at a tube voltage of 40 kV and a tube current of 30 mA. The scanning was carried out in the region of 2θ from 10° to 80° at step size 0.2° , and the time constant was 1.20s. The surface topography of the samples was analyzed by atomic force microscopy (AFM)(DME Denmark).

Results and discussion

Cyclic voltammogram of Au(III) in Alum:Urea Deep Eutectic Solvent

The cyclic voltammetry curve for the electroanalysis of suspended 0.01 M $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in purified Alum: Urea deep eutectic solvent was carried out between -0.8V to 1.2 V at a Pt disc electrode with the scan rate of 50 mV/s in 30C0. Significant redox peaks can be observed within the electrochemical window of Alum: Urea deep eutectic solvent, as shown in Figure(1.a,b).

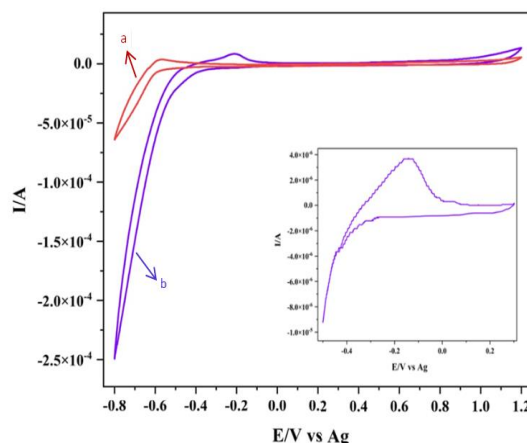
Sweeping the potential from -0.5 V to +0.5 V at a scan rate of 50 mV/s (see inset Figure) (1). The reduction peak was started very slowly at approximately -0.288 V and accelerated at -0.32V versus quasi-silver wire reference electrode. The Au(III) results in three-electron reduction; the only cathodic peak is considered to correspond to the reduction of Au^{3+} to Au metal as shown in the equation below:-



On the reverse oxidative sweep, large oxidation broadband is also present during the reverse potential scan with a maximum -0.141V related to the oxidation of gold and diffusion from the surface of the platinum working electrode to the DES. This indicates that the reduced gold metal cation was oxidized to Au^{3+} in one step with slow gold dissolution due to viscous Alum: Urea deep eutectic solvent. The electrochemical behavior of Au^{3+} in Alum: Urea deep eutectic solvent refers to no intermediates observed in cyclic voltammetry such as Au^{1+} , which are difficult to detect and very short-lived are unlikely to figure prominently in an oxidative electro dissolution process. Also, CV revealed no overpotential required for the nucleation

of gold nano-particles on the platinum working electrode.

This study revealed only one signal reduction step from Au^{3+} to Au0, in contrast to another study that identified two reduction steps in ionic liquid despite using a comparable platinum working electrode. Thus, Oyama et al. [28] investigated the redox reaction of $[\text{AuIICl}_4]^-$ at the Pt. electrode in 1-ethyl-3-methylimidazolium tetrafluoroborate room temperature ionic liquid (RTIL) (EMIBF₄). They proposed a two-step reduction technique for Au deposition at the Pt. electrode. After the metallic Au was deposited on the Pt. electrode surface, the following reduction of Au_3^+ on the Au deposit with a reduced electrodeposition overpotential may occur. This could indicate that the type of ionic liquid affects the gold cation coordination and complex compound generated by the ionic liquid used in this study.



Figure(1): **a**-Cyclicvoltammogram of ammonium Alum:Urea DES(1:5) recorded at (-0.8V to 1.2V); **b**-Cyclicvoltammogram of (0.01M) $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in(1:5) Alum:Urea DES record at (-0.8 to1.2) at 50 mV scan rate , Ag wire(QRE), Pt disc (WE) and Pt plate (CE) at 30°C.Inset Cyclicvoltammogram of (0.01M) $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in (1:5) Alum:Urea DES record at (-0.5,0.3) at 50 mV scan rate using Ag wire(QRE), Pt. disc (WE) and Pt. plate(CE) at 30°C.

Electrodeposition of Au on brass

Inset Figure (2, a): Electrodeposition was carried out at -0.7, resulting in a smooth, thin brown layer deposit adhering on the surface of the brass foil substrate. The surface morphology of the deposited gold layer studied using FE-SEM is composed of nano-sized gold particles in a nodular shape. Figure (2) and Figure 3: The size and morphology of deposited gold particles could be affected to some extent by the choice of the deposition time. Figure (2, b) shows a small nodular deposit of gold nano particles (AuNPs) that can be seen for about an hour

with an average particle size distribution of 31.61% nm.

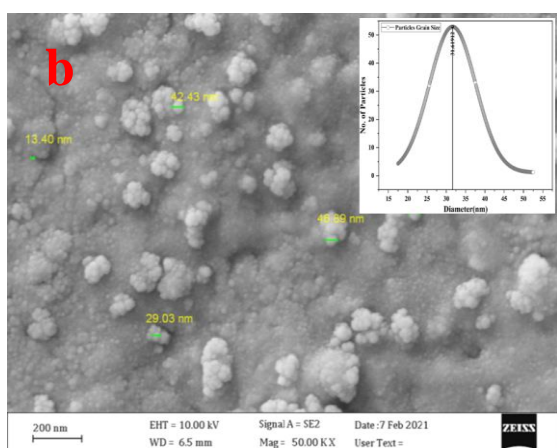
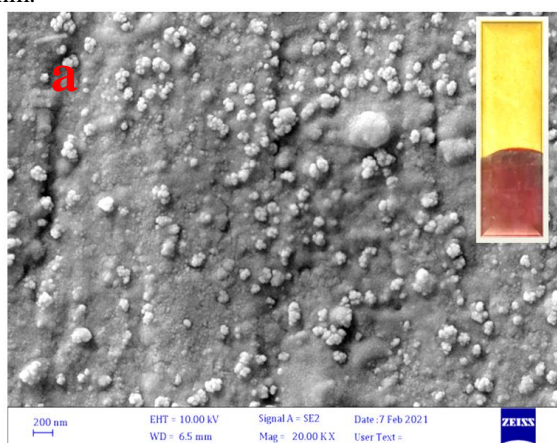


Figure (2): FE-SEM images of deposited gold nanoparticles on brass substrate at (a) 10.00kx. and (b) 50.00kx ; the insets is optical photograph of deposited gold on brass for 1hr.,inset particle size distribution histogram of the AuNPs obtained from the FE-SEM images.

On the other hand, increasing the deposition time to 3hrs. a smooth thick brown layer deposit adhere on the surface of the brass foil substrate inset Figure (3,a) resulted in increasing agglomeration and augmentation of the gold nano particles. Figure (3,b) with an average distribution of about (33.44) nm, inset Figure(3,b). The grain size increases with the increasing electrodeposition time as also stated by other workers[29],[30].

An optical adsorption peak of EDX was observed at approximately 2.30 keV, which is typical for gold nanoparticles [31]. The deposits contained in Au at three hours were relatively larger than deposits contained at one hour (compare 52.8% Au at 1 hr. with 66.8% Au at 3 hrs.). Figure (4). This suggests that Au is preferentially electrodeposited from a solution of Au(III) in alum: urea DES after one hour, and then slowly at subsequent times due to the dissolved gold in DES being depleted

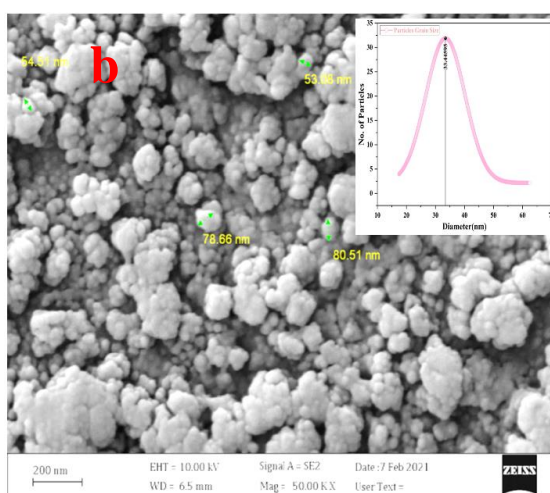
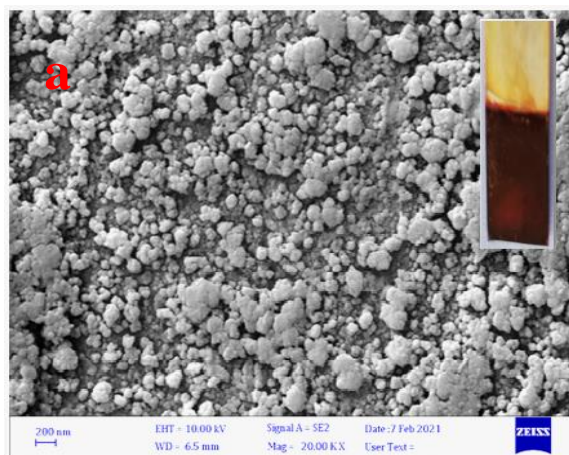
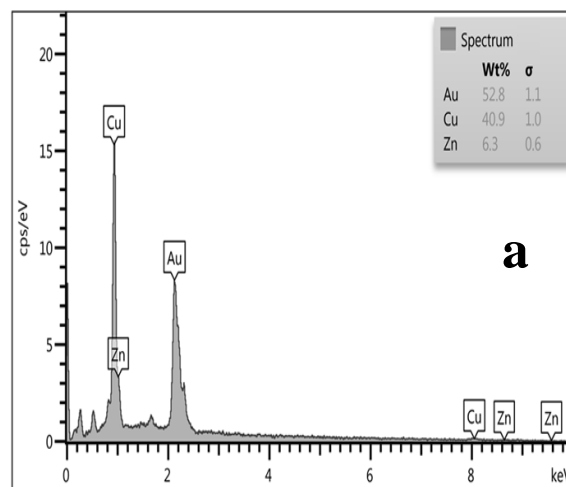


Figure (3): FE-SEM images of deposited gold nanoparticles on brass substrate at (a) 10.00kx. and (b) 50.00kx ; the insets is optical photograph of deposited gold on brass for 3hr.,inset particle size distribution histogram of the AuNPs obtained from the FE-SEM images.



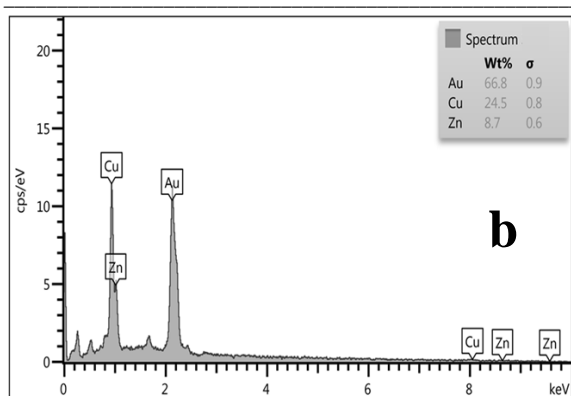


Figure (4): EDAX spectra of deposited gold nanoparticles from 0.01M $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in 1:5 mole ratio ammonium Alum:Urea DES solvent based ionic liquid at -0.7V and 30°C on brass substrate at (a) 1hr. and (b) 3hr.

AFM images for deposited Au at 1hr. and 3hrs. are shown in Figure(5). The deposited Au layer on brass substrate surfaces shows the average height of the adhered particles to be (332.6, and 555.9)nm. with average roughness value (Ra: 5.490 nm) and (Ra: 8.624nm) at one and three hours respectively. The layer thickness and surface roughness were found to increase with deposition time, as also reported by Malinský *et al.*[32]

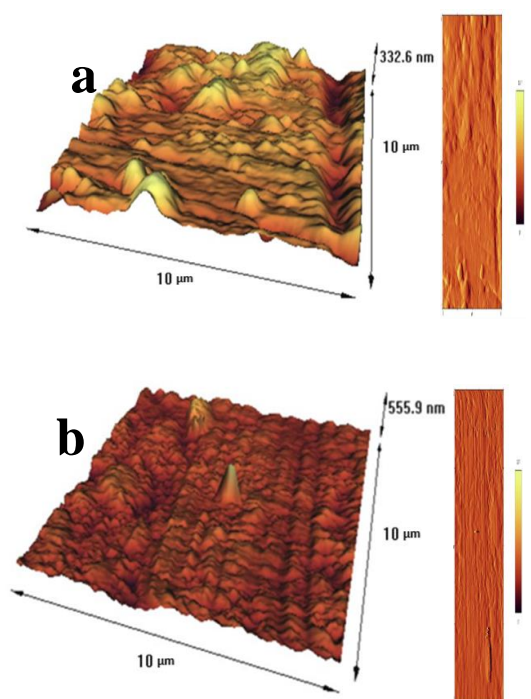


Figure (5): The 3D and 2D AFM images of deposited gold nanoparticles from 0.01M $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in 1:5 mole ratio ammonium Alum:Urea DES based ionic liquid at -0.7 V and 30°C for 1hr. on (a)brass (b) 3hr

Although XRD was not successful for a sample of deposited gold on brass for one hour, the sample obtained after 3 hours reveals the diffraction peak corresponding to (111), (200), (220) and (311) planes represented by indexed Au (ICDD Card #: 00-001-1174) and related to cubic crystal structure. The average crystalline domain size (t) of the Pd nanoparticles was calculated using the Debye-Scherrer equation [33].

$$t = K \lambda / \beta \cos \theta$$

Where λ is the X-ray wavelength in nanometres (nm), β represents the full width at half maximum (FWHM) of the diffraction peak in radians, and K represents a constant related to crystallite shape, usually taken as 0.9; and (θ) is the Bragg angle. The average crystallite size of Au NPs was calculated at (~10 nm) using the half width of the (111) reflection.

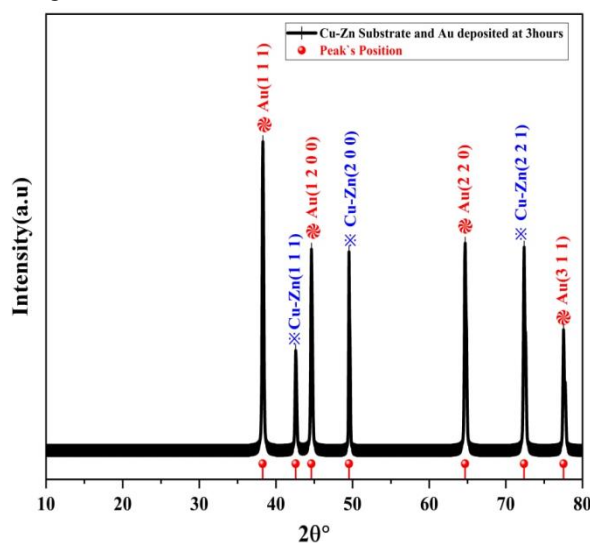


Figure (6): X-ray diffraction patterns of gold nanoparticles deposited from 0.01M $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in 1:5 mole ratio ammonium Alum:Urea DES solvent based ionic liquid at -0.7 V and 30°C on brass substrate at 3hr.

Conclusions

This work demonstrates the novel green electrodeposition of nano -gold on brass from a benign solution containing 0.01M $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in Alum:Urea deep eutectic solvent at -0.7V. The nanoparticles of around 33nm were of gold cubic crystal of 10nm size.

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