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# Facile room temperature deposition of gold nanoparticle-ionic liquid hybrid film on silica substrate



<sup>a</sup> Department of Bioprocess Engineering, Chonbuk National University, Jeonbuk 561-756, Republic of Korea

<sup>b</sup> Division of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonbuk 561-756, Republic of Korea

<sup>c</sup> Department of Chemistry and London Centre for Nanotechnology, University College London, London, WC1E 6BT, UK

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#### ABSTRACT

This work presents facile synthesis of gold nanoparticle (Au NP)-ionic liquid hybrid film of <10 nm by a simple two-step process at room temperature by deposition of Au NPs suspended in 1-hexyl-1methyl-pyrolidinium bromide, on Si (111) substrates. FTIR results demonstrated that ionic liquid properties remain unaltered during and after Au NP synthesis, and even coating on Si (111) substrate. XRD, XPS, and XAS spectral data confirm the presence of Au(0) while EXAFS data indicated the presence of small particles or incomplete surface species. Cross-sectional analysis using FE-SEM and edge length measurement using AFM showed that the film thickness is ca 10 nm.

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#### 1. Introduction

Room-temperature ionic liquids (RTILs) are regarded as environmentally benign solvents because of their favorable characteristics like nonvolatility, nonflammability, and high stability. RTILs can dissolve a wide range of inorganic species and biological substances, thus, these are being widely used as solvents. Due to high electrochemical stability, negligible vapor pressure, and easily tunable physicochemical properties, ionic liquids are now finding applications in chemical synthesis, catalysis, separation technology, immobilized lubricants and the fabrication of conventional electrochemical devices [1–3]. These unique physicochemical properties of ionic liquids (ILs) are useful for the creation of new technological applications as well as the improvement of existing technologies. In particular, RTILs have potential applications in the development of highly active and selective, environmentally benign catalytic systems; antireflective coatings in solar cells, and electrochemical devices [4–7]. Nevertheless, ILs are still considered expensive the toxicities of ionic liquids is still debated. Researchers have used pyrrolidinium ionic liquids as alternatives to pyridinium and imidazolium ILs due to their sparing solubility is water [8]. Hence

\* Corresponding author.

E-mail addresses: chemkishore@gmail.com (D.H.K. Reddy), ysyun@jbnu.ac.kr (Y.-S. Yun).

there is a challenging need for developing systems that require minimal amount of IL without altering their unique properties remain unaltered.

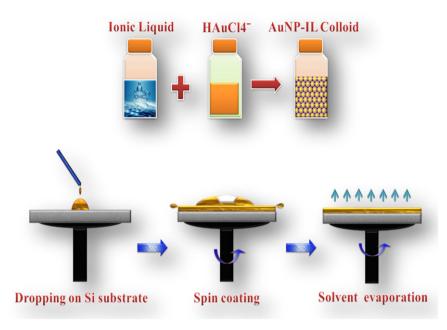
There is an emerging interest drawn towards the development of hybrid systems using ILs as one of the key components [9,10]. These heterogeneous hybrid systems are preferred in industrial processes compared to homogeneous ones, due to the ease of product extraction and catalyst recovery in a heterogeneous system [11]. Hence, it is meaningful to construct a heterogeneous system consisting of RTIL and metal nanoparticle, which unifies the conductive physicochemical properties of ILs and catalytic properties of the metal nanoparticles. To date, the majority of technologically valuable metals have been electrodeposited from ionic liquids [6,12]. Nevertheless, it is essential to consider the economic viability, recyclability, and ease of handling. From the viewpoint of materials, it would be a promising strategy to construct an inexpensive yet high-performance RTIL-metal nanoparticle thin film. A recent example of metal nanoparticle coated on the silicon substrate was demonstrated by Wan et al. [13] where light trapping in silica solar cells coated with gold and dielectric (TiO<sub>2</sub>, SiO<sub>2</sub>) nanoparticles was studied thoroughly. Another report by Mo et al. [9] presents the synthesis of ultrathin, wear resistant films for application in micro/ nanoelectromechanical devices. Gold nanoparticles (Au NPs) modified with ligands have shown a noticeable increase in conductivity due to this several gold probes have been developed by surface modification of Au NPs [14]. Anisotropic gold nanostructures have been successfully synthesized using several ionic liquids [15-17]. Bouvy et al. [18] synthesized gold nanosheets and nano-polyhedra in pyrrolidinium-based ionic liquids by thermal reduction method. Hence, by combining the







<sup>\*\*</sup> Correspondence to: Y.-S. Yun, Department of Bioprocess Engineering, Chonbuk National University, Jeonbuk 561-756, Republic of Korea.



Scheme 1. Schematic diagram showing the synthesis of Au NPs in RTIL-ethoxyethanol mixture and its coating on Si (111) substrate.

unique physicochemical and optoelectronic characteristics properties of Au NPs and ionic properties of ionic liquids, we portray an integrated Au NP-IL hybrid (Au NP-IL) system coated on a silicon substrate.

The novel aspect presented here is the deposition of Au NP-ionic liquid thin film at the room temperature on Si (111) substrate; in contrast to many other previous reports where an ionic liquid used as a medium during electrodeposition of metals on the desired substrate. The schematic of Au NP-IL thin film fabrication process that involves two simple procedures was shown in Scheme 1. We used 0.1% 1-hexyl-1methylpyrrolidinium bromide [[HMPyrro] Br<sup>-</sup>] as reducing agent and ethoxyethanol as a capping agent for the synthesis of crystalline Au NPs, followed by spin-coating on Si(111) substrate, at room temperature. Various characterization techniques such as X-ray scattering

#### techniques including X-ray diffraction, X-ray photoelectron spectroscopy, and synchrotron-based X-ray absorption spectroscopy were used to understand the nature of Au NPs deposited on Si(111) substrate.

#### 2. Experimental

#### 2.1. Au NP synthesis and thin film coating

Fabrication of Au NP-IL thin film on silica substrate was accomplished via facile two-step approach (Scheme 1). In a first step, Au NPs were obtained by mixing a solution of HAuCl<sub>4</sub> with ethoxyethanol containing different concentrations of ionic liquid [HMPyrro]  $Br^-(w/v)$ , under ambient conditions, without the addition of any other reducing

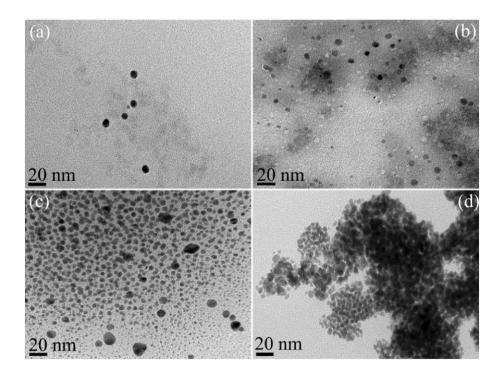


Fig. 1. HRTEM images of Au NPs synthesized in 0.1% [HMPyrro] Br- using different concentrations of HAuCl<sub>4</sub> solution (scale 20 nm): (a) 1 mM, (b) 0.025 M, (c) 0.05 M, and (d) 0.1 M.

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