

Electrochemical Studies Carried out in Deep Eutectic Solvents and Colloidal Suspensions

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Salts in solvent are a prerequisite for performing electrochemical experiments as they provide the necessary ionic conductivity to the solvent. However, the solubility of salts often becomes a challenge for applications (such as in batteries) that require very high ionic conductivity. Added to this there are applications such as solar cells, where the presence of solvent can have detrimental effects on the efficiency of the product. A class of liquids called “Ionic Liquids” have shown that one or two solute by itself without any solvent can be a “Solution” for many applications. By designing compounds that are bulky in size and lesser in charge, room temperature ionic liquids can be made out of solid salts even without the use of solvents. However, ionic liquids are often designed and are not readily available and if available they are of high cost. Now to solve the problem a more improved concept called Deep Eutectic Solvents (DES) has been put forth by Abbott *et al.* By this concept, large hydrogen-bonded complexes of low symmetry are prepared from readily available bulk organic compounds (Fig.1b). For example, a simple thermal mixing of a quaternary ammonium chloride such as choline chloride (MP 300 °C) and urea (MP 133 °C), can form a room temperature ionic liquid. Within a short span of introduction, DES has been used as a medium for various applications such as enzymatic, organic synthesis, metal extraction, electrofinishing, solar cells, and energy devices.

* Dr. Anu Renjith, Post Doctoral Fellow from Indian Institute of Sciences, Bangalore, is pursuing her research on “Ortable Electrochemical Analyzer using Nanocomposites based Chemically Modified Electrodes for Rapid Detection of Adulterants and other Contaminations in Food and Beverages.” Her popular science story entitled “Electrochemical Studies Carried out in Deep Eutectic Solvents and Colloidal Suspensions” has been selected for AWSAR Award.

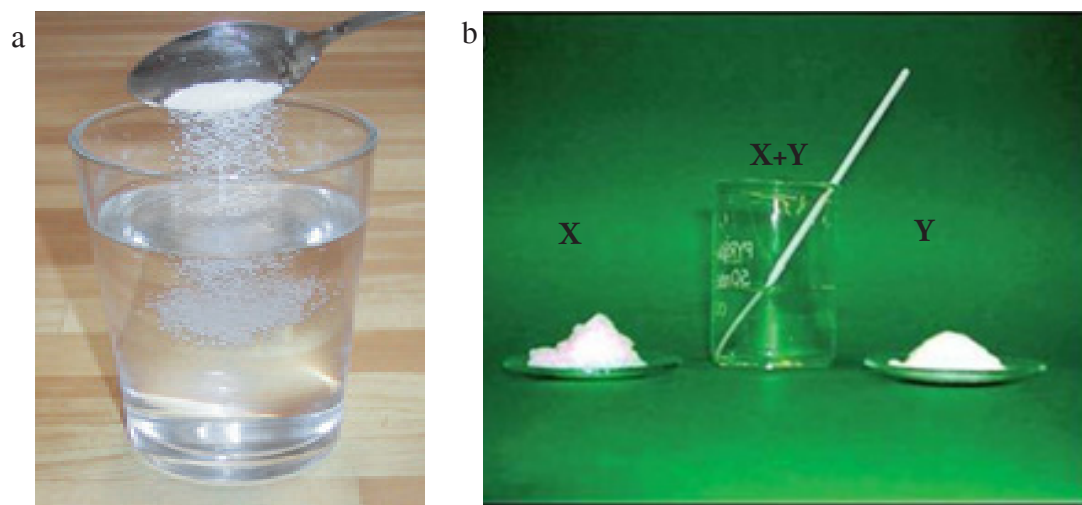


Figure 1. (a) Conventional solution of a solute in solvent (b) Deep eutectic solvents formed from two solutes ($x+y$)

Our studies have been focussed on using DES as a medium for preparing electrodeposited nanoparticles for “ready to use” applications. Electrodeposition was carried out using anodic dissolution technique (metal wire is dissolved as ions at anode and are electrodeposited as nanoparticle clusters at the cathode) to ensure well-adherent nanoparticle surfaces that can be used even in applications requiring vigorous conditions of solvent, heat or perturbation. The procedure involved the electrochemical dissolution of a silver wire at a constant low current density in DES. The dissolved metal ions from the Ag wire get simultaneously reduced at the cathodic metal substrate (Pt/Rh wire). These form clusters of nanoparticles stabilised by the Mercaptophenyl boronic acid (MPBA) molecules present in the medium. *So what is the significance of DES in electrodeposition?* The inherent ionic conductivity of DES avoids the use of supporting electrolyte which are otherwise inevitable in electrodeposition. During electrodeposition in aqueous medium, while hydrogen evolution at the cathode can lead to poor deposition of nanoparticles, the protons formed from water at anode can passivate the anode preventing further dissolution. These problems associated with the hydrogen and oxygen evolution in aqueous medium at the cathode and the anode are not observed in DES. Added to this, DES can dissolve any passivating oxide species due to their complex formation ability.

Since silver nanoparticles are excellent enhancers of very weak Raman signals, we have explored the application of utilising the AgNP modified substrate for SERS (surface enhanced Raman spectroscopy). A huge SERS enhancement of Raman signal of analytes such as Methylene blue and Rhodamine B was observed on the mesoporous silver substrate after removing all the stabilizer molecules from the surface by the method of high temperature calcination. It was estimated that the mesoporous silver film shows an enhancement by a factor of 10^5 for Methylene Blue which suggests its excellent potential for using in ultra-trace detection of analytes.

DES as an electrolytic medium for the preparation of non-Pt based metal nanoparticle and core-shell alloy nanoparticles was also explored by us. For example, the gold nanoparticles modified graphite substrate prepared in this medium had superior electrocatalytic properties for methanol electrooxidation reaction with lower activation energy making them useful even at ambient temperatures. We have also studied DES medium for the electrochemical synthesis of core-shell nanostructures comprising of Au core and Pd shells and deposition on graphite substrate (Fig.2) []. *The method used was the first report of a single step preparation and deposition of core-shell nanoparticles on a solid substrate using a standalone medium without the use of supporting electrolyte, stabilizers and reducing agent.*

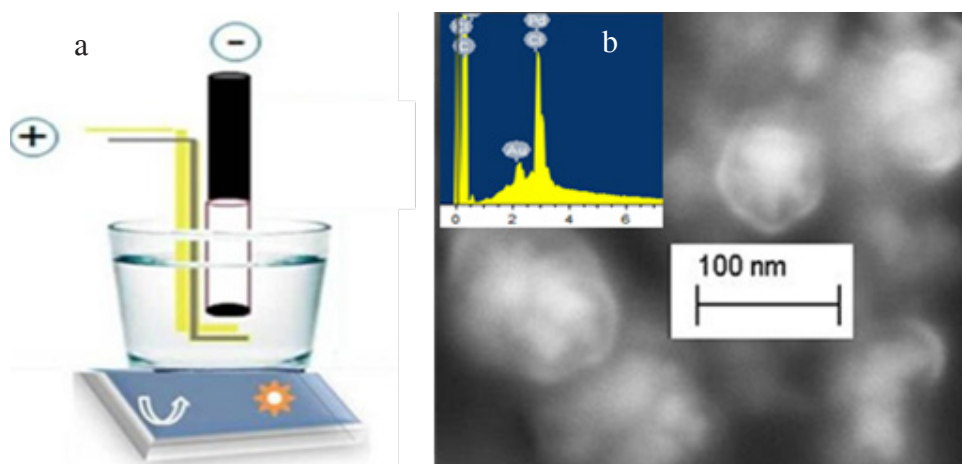


Figure 2. Schematic representation of anodic dissolution technique for the electrodeposition of Au@Pd nanoparticle in DES medium (b) SEM images of graphite rod modified with Au@Pd NPs

The mesoporous film was examined in detail for its electrocatalytic applications and was found to be a very good catalyst for methanol oxidation and hydrogen evolution reactions. In all the above cases, the nanoparticle modified surfaces were characterized using FESEM, EDAX and electro-analytical techniques.

We have also developed a novel non-polymeric colloid suspension based on hydrogen bonding interactions of tetra butyl ammonium salt and ethylene glycol (Fig. 3). The colloid suspension exhibited certain unique physical properties and was demonstrated as a medium for monitoring enzyme kinetics by electrochemical method. The gel containing a constant amount of enzyme was allowed to react with different concentrations of substrate. The enzyme-substrate reaction resulted in the formation of ions which is monitored as a function of the ionic conductivity of the colloid suspension measured by electrochemical impedance spectroscopy. The rate of the reaction in the colloidal matrix was found to obey Michaelis–Menten equation. The electrochemical method employed here with the colloidal medium acts as a simple robust method to follow enzymatic reactions in a soft medium mimicking biological environment.



Figure 3. Photographs of the vial containing the colloidal suspension and a teflon coated magnetic pellet at (a) $T > 60^{\circ}\text{C}$ and (b) RT

The sharp reversible sol-gel phase transition of the colloid at 55°C was utilised as a matrix for dispersing nanomaterials such as CNT, graphene and metal nanoparticles. A few of such dispersions of nanoparticles (CNT, Graphene, Fe_3O_4 NP, AgNP) in the colloid are shown in the Fig.3. A vial containing 0.5 mg/ml nanoparticles in sol were initially sonicated at a temperature of about $50\text{-}60^{\circ}\text{C}$. As soon as a stable dispersion of nanoparticles was achieved, the nanoparticle matrix was plunged into cold water. The sudden drop in temperature brings about the phase transition of sol gel, thus freezing the well dispersed state of nanoparticles brought about by sonication. The nanoparticle dispersion obtained in the colloid has the potential for use in electrochemical biosensors, electronic and optoelectronic applications.