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Organically dispersible gold and platinum nanoparticles using aromatic amines as phase transfer and reducing agent and their applications in electro-oxidation of glucose

A. Nirmala Grace [a,*], K. Pandian [b,*]

[a] Nanotechnology Group, School of Electrical Sciences, Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India
[b] Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai 600025, Tamil Nadu, India

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Abstract

A single step method for the synthesis of Au and Pt nanoparticles by the spontaneous reduction of chloroaurate and chloroplatinate ions using hexadecaaniline molecules has been described. The importance of this work is that hexadecaaniline acts as a multifunctional molecule that accomplishes the complexation of aqueous chloroaurate and chloroplatinate ions by phase transferring them to $CHCl_3$ medium and their subsequent reduction to yield Au and Pt nanoparticles in organic phase. Furthermore the metal reduction is followed by polymerization of the amine to yield polyaniline, which subsequently caps the Au and Pt nanoparticles. The process of reduction of the auric and platinic metal precursors and the subsequent capping of the Au and Pt nanoparticles has been elucidated by various analytical techniques like UV–vis, X-ray diffractogram (XRD) and transmission electron micrographic (TEM) analysis. Such prepared nanoparticles are utilized for the fabrication of novel modified electrodes towards the electrocatalytic oxidation of glucose.

Keywords: Gold nanoparticles; Platinum nanoparticles; Hexadecaaniline (“16-mer); Phase transfer agent; Oxidative polymerization

1. Introduction

Owing to their extreme small size, the characteristic of nanoparticles, which makes them different from macroscopic solids, is that the surface atoms have a very high percentage. In view of this characteristic, metal nanoparticles hold important applications in the area of catalysis [1,2], electronics [3] as well as electron microscopy markers [4], in DNA detection [5], etc. Gold nanoparticles, in particular, have received substantial attention with surplus of applications ranging from catalysis, single electron tunneling [6], non-linear optical devices [7] to DNA sequencing [8], etc. There are a number of synthetic procedures for obtaining gold nanoparticles over a wide range of sizes [9,10] and shapes [11–14] that may be classified depending on whether the particles are synthesized in aqueous or organic medium. Much of the experimental procedures that exist in the literature are for the synthesis of gold nanoparticles in polar aqueous phase [9]. The synthesis of gold nanoparticles in organic medium is thus a considerably newer area of research whose origin may be traced to the seminal work of Brust et al. Here, the authors have demonstrated the phase transition of chloroaurate ions into toluene using a phase transfer agent such as tetraalkylammonium bromide and thereafter the gold ions are reduced by sodium borohydride to yield gold nanoparticles capped with alkanethiol molecules [15]. In addition, Pt nanoparticles are also of great interest because of their excellent catalytic activity [16–20]. A number of strategies have been developed to synthesize metal nanoparticles in polar and nonpolar medium as the colloidal stability, particle size and its properties depend strongly on the precise method of preparation. One of the main downside of water-based metal nanoparticle synthetic protocol is the poor control on the size and such nanoparticles prepared are not easily redispersible in water after extraction from the aqueous phase [21,22]. Ionic effects limit the concentration of nanoparticles prepared in aqueous phase, which is a significant drawback in biological applications where high nanoparticle concentration is desirable [5]. In contrast, very high concentrations of

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* Corresponding authors.
E-mail addresses: nirmala_gladys@yahoo.co.in (A. Nirmala Grace), jeevapandian@yahoo.co.uk (K. Pandian).

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metal nanoparticles may be readily achieved when the nanoparticles are synthesized in organic medium, thus overcoming the difficulties experienced in water-based synthesis.

One of the main challenges in the preparation and application of nanoparticles is how to transfer the particles into different physicochemical environments. Sarathy et al. have demonstrated that colloidal gold, platinum and similar particles first synthesized in water may be transferred into a non polar environment such as toluene by acid facilitated co-ordination of the particles with thiols in toluene [23]. Various salts have also been used for the effective phase transfer of metal nanoparticles. Hirai et al. have reported that colloidal silver particles in water could be effectively phase transferred to non-aqueous system with the aid of sodium chloride in the presence of oleate ions [24]. Wang et al. reported that the phase transfer of oleate-stabilized Ag nanoparticles from water phase to non-aqueous phase induced by a low concentration of ortho phosphoric acid or perchlorate salt [25]. Pt nanoparticles prepared by $NaBH_4$ reduction in an aqueous medium were phase transferred to toluene solution containing dodecanethiol using phase transfer inducer HCl [26]. In addition to alkanethiols for surface modification of nanoparticles, few reports are based on the surface modification of gold nanoparticles using alkyl amines [27,28]. Complexation of alkylamine molecules with aqueous gold nanoparticles at a liquid–liquid interface may be used as an alternative route to gold nanoparticle phase transfer from organic solvents [29]. The self-assembly of alkyl amines on metal nanoparticles has been investigated. 4-Hexadecyl aniline has been used for the synthesis of organically dispersible Au and Pt nanoparticles. The phase transfer of colloidal gold nanoparticles synthesized in aqueous phase into organic phase has been done using octadecylamine as phase transfer agent [30–34].

Anilines are highly susceptible to undergo oxidative polymerization in the presence of an oxidizing agent at acidic pH to polyaniline. Among the various amines, aliphatic amines have been investigated for the synthesis of various metal nanoparticles [30–33]. Aniline has been used as stabilizer for previously synthesized water-soluble metal nanoparticles [35] wherein they have used an external polymerizing agent, viz. ammonium persulphate for the polymerization of aniline.

Electrocatalytic oxidation of sugars has been studied extensively over the past three decades, not only because of the great importance of sugar sensing, specifically in human blood, but also for their potential use as fuels for fuel cell applications [36]. Both gold and platinum electrodes are attractive metals towards the oxidation of glucose both in neutral and alkaline mediums [36,37]. Efforts are being carried out to increase the catalytic activity of such metal electrodes. In view of this regard, nanoparticles modified electrodes have been fabricated in our present study to probe the electrocatalytic oxidation of glucose.

In this present investigation, we have used oligomer of aniline, viz. “16-mer” also called as hexadecaaniline both as reducing as well as phase transfer agent for the synthesis of Au and Pt nanoparticles. The oxidizing nature of chloroauric acid and chloroplatinic acid polymerizes aniline compound and in turn the chloroaurate and platinate ions are reduced into gold and platinum nanoparticles respectively, which are subsequently capped by polyaniline. By reducing Au and Pt ions to nanoparticles, hexadecaaniline in-turn gets oxidized to polyaniline which caps the nanoparticles formed in the solution thus substantiating that “16-mer” is a multifunctional molecule performing effective phase transfer, reduction and subsequent capping of the nanoparticles formed in the solution. Further we have developed a simple and novel approach for the electrocatalytic oxidation of glucose using nanoparticles modified electrodes. This simple approach and findings will be useful not only for the basic understanding of catalysis, but also for supporting the recent interest in fuel cell development based on metallic nanoparticle catalysts.

2. Experimental

2.1. Chemicals

Chloroauric acid ($HAuCl_4$), hydrochloride of *N*-phenyl-1,4 phenylene diamine (98%), anhydrous hydrazine (98%), hexadecylamine was obtained from Aldrich. Ammonium peroxydisulphate (98%), ferric chloride hexahydrate (99%), ammonium hydroxide, hydrochloric acid, ethanol, $CHCl_3$ was obtained from commercial sources. D(+)-Glucose was from Fluka.

2.2. Instrumentation

The samples were characterized by using UV–vis spectroscopy (Perkin-Elmer Spectrometer Lambda 25) in 400–800 nm range. X-ray diffraction (XRD) measurements were carried out using Rich Seifert P3000 employing the Cu $K\alpha_1$ radiation. A drop of the synthesized nanoparticles was suspended onto a copper coated grid. The grids were dried in a desiccator overnight and examined with transmission electron microscopy (TECHNIE 10) with an accelerating potential of 80-kV. Electrochemical measurements were performed using CHI 600A model using a three-electrode type electrochemical cell. The working electrode was platinum electrode along with platinum and a saturated calomel electrode (SCE) as counter and reference electrodes respectively. All potentials in the paper were presented in SCE scale. The solutions were deaereated by bubbling highly purified nitrogen gas before all the electrochemical measurements.

2.3. Synthesis of teraaniline from N-phenyl-1,4 phenylene diamine

Tetramer of aniline has been synthesized have been synthesized from a previous reported procedure [38]. Briefly, ferric chloride hexahydrate (0.1 mol) was dissolved in 100 ml of 0.1 M HCl at room temperature. The hydrochloridesalt of *N*-phenyl-1,4 phenylene diamine (dimer, 0.1 mol) was suspended in 500 ml 0.1 M HCl with strong mechanical stirring for 0.5 h at room temperature. The ferric chloride solution was added to the dimer suspension, with effective stirring for 2 h. After 2 h, the suspension was filtered by vacuum filtration. The precipitate collected was transferred into 500 ml of 0.1 M HCl. The resulting suspension was stirred for 1 h and filtered. The washing process