An insight into the electrocatalysis of uranyl sulphate on gold nanoparticles modified glassy carbon electrode

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A B S T R A C T

Monodispersed gold nanoparticles (AuNPs) were prepared on glassy carbon electrode by multiple galvanostatic pulse strategy in the absence of any template or additional chemicals. The cyclic voltammetry, differential pulse voltammetry, electrochemical impedance spectroscopy experiments and quantum mechanical calculations were performed to unravel the mechanism of electrocatalytic reduction of uranyl ($U^{VI}O_2^{2+}$) by AuNPs. The higher density of states of 5d band of gold nanoparticles and its strong interaction with the LUMO(U-5f) of $[U^{VI}O_2(\eta^1\text{-}OSO_3)(\boldsymbol{\eta}^2\text{-}O_2SO_2), 2H_2O]^{2-}$ was found to be the most probable reason for catalyzing the heterogeneous electron transfer reaction. This is the first report on the participation of the 5f-orbital of actinyl ion in the electrocatalysis at AuNPs.

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1. Introduction

Metal nanoparticles offer excellent electrochemistry compared to bulk counterpart because of their high effective surface area, high rate of mass transport through convergent diffusion and electrocatalytic action at the nanosurfaces. The bulk gold has filled 5d shell and the centre of the *d band* is too low in energy and thus both bonding and antibonding orbitals are situated below the Fermi level and are filled making the interaction repulsive. Thus bulk gold behaves as an inert material, with high stability in corrosive environments and low catalytic activity for most of the reactions. Therefore, bulk gold metal has not received any attention from the point of view of catalysis. On the contrary, supported gold nanoparticles (AuNPs) have been shown to exhibit high electro-catalytic activity for CO oxidation [1] and oxygen reduction.[2,3]

The resurgence of the research in actinide chemistry has been fuelled not only by their important technological and scientific attributes in nuclear power production, but also by the compli-cations in the actinyl redox chemistry playing crucial roles in the environmental dispersal of actinides. Of all the actinide ions, uranyl ion ($U^{VI}O_2^{2+}$) has been studied the most thoroughly, as it has the most stable oxidation state (VI) of uranium and, therefore, is

the prevalent form of natural uranium in the environment. $U^{VI}O_2^{2+}$ is chemically robust due to the presence of trans-dioxo bonds around the uranium and is highly oxidative in acidic solutions, exhibiting interesting and useful oxidation–reduction chemistry. The oxygen reduction on AuNPs occurs in the potential range -0.5 to -0.15 V vs. Ag/AgCl (saturated KCl) reference electrode,[2] which is in similar range of reduction potential of the uranyl ($U^{VI}O_2^{2+}$) complexes in sulphuric acid medium on mercury pool electrode.[4] Since, without forming amalgam, U(VI) is reduced in sulphate medium on mercury pool electrode to U(IV)-sulphate complex (which remains in the solution); thus we tried to explore the possibility of catalytic reduction of $U^{VI}O_2^{2+}$ on AuNPs. This is the first report on the electrocatalysis of $U^{VI}O_2^{2+}$ in 1 M H_2SO_4 at AuNPs supported on glassy carbon electrode (AuNPs/GC) evi-denced from cyclic voltammetry (CV), differential pulse voltam-metry (DPV) and electrochemical impedance spectroscopy (EIS) experiments. The molecular understanding of the electrocatalytic mechanism was investigated by the relative stability of molecular orbitals of the most abundant U(VI) complex in sulphuric acid solution by quantum chemical calculations.

2. Experimental

2.1. Chemicals

Extrapure ACS grade tetrachloroauric acid trihydrate [$HAuCl_4$, $3H_2O$], potassium chloride (KCl), uranyl nitrate hexahydrate

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[UO$_2$(NO$_3$)$_2$, 6H$_2$O] and hydrochloric acid (HCl) were used as received. All the solutions were prepared using ultra pure water (Milli-Q, Millipore, 18.2 MΩ cm). AR grade potassium ferrocyanide (K$_4$[Fe(CN)$_6$]), potassium ferricyanide (K$_3$[Fe(CN)$_6$]), sulphuric acid (H$_2$SO$_4$) were used without any further purification.

2.2. Electrochemical Experiments

The electrochemical experiments were performed at room temperature (T = 294 K) in a conventional three-electrode cell by using Autolab PGSTAT 30 and CHI-760D electrochemical work-stations. There was no affect of the uncompensated resistance in the voltammetric results, as it was automatically compensated by the workstation. A commercial glassy carbon (GC) (φ = 3 mm) or gold (Au) (φ = 2 mm) or AuNPs/GC electrode was used as the working electrode, Ag/AgCl/KCl (saturated) (E$_{Ag/AgCl}$ = +0.197 V vs. standard hydrogen electrode) was used as the reference electrode and a platinum wire acted as the counter electrode. All the potentials quoted are with respect to the Ag/AgCl reference electrode. Prior to performing the electrochemical experiments, the working solution was purged with high purity nitrogen for 15 min to remove the dissolved oxygen from the solution. The polishing of GC and Au electrodes in between the experiments was carried out by using alumina slurries with different powders of size down to 0.05 mm. After each polishing, the electrode was thoroughly rinsed with water and sonicated in ultrapure water in an ultrasonic bath for 30 min to remove any adsorbed substances from the electrode surface. DigiSim 3.03b was used to evaluate the kinetic parameters of the electrode reaction corresponding to the reduction of U(VI) in 1 M H$_2$SO$_4$.

2.3. Preparation of AuNPs/GC

Electrosynthesis is one of the promising techniques for preparing supported metal nanoparticles of controlled size, shape, crystallographic orientation. The AuNPs/GC was synthesised by multiple galvanostatic pulse strategy as reported by Guin et al. [5]. This template free electrosynthesis route produced AuNPs with controlled particle size dispersion without employing any surface stabilizing agent. The brief description of the synthesis of AuNPs/GC is given below:

Before the deposition of AuNPs, the GC electrode was polished to a mirror-like finish using alumina slurries with different powders of size down to 0.05 mm. After each polishing, the electrode was thoroughly rinsed with water and sonicated in ultrapure water in an ultrasonic bath for 30 min to remove any adsorbed substances from the electrode surface. The GC electrode was placed as the working electrode in the electrochemical cell having N$_2$ purged aqueous solution of 1 mM HAuCl$_4$ in 0.1 M HCl. The multiple galvanostatic pulse strategy was designed at PGSTAT 30 electrochemical workstation with a sequence of 1500 galvano-static pulses in such a way that the seed (or nucleation) pulse was applied only once at -0.64 mA cm^{-2} for 60 ms followed by short anodic pulse of 1.26 mA cm^{-2} for 5 ms to dissolve the subcritical nuclei. Then a pair of growth pulses at -0.46 mA cm^{-2} for 1 s and an anodic pulse at 1.26 mA cm^{-2} for 5 ms was applied 749 times. The galvanostatic pulse sequence is summarized below:

Seed (or Nucleation) pulse (P$_1$): j$_1$ = -0.64 mA cm^{-2}; t$_1$ = 0.06 s;
Anodic pulse (P$_2$): j$_2$ = 1.26 mA cm^{-2}; t$_2$ = 0.005 s;
Growth pulse (P$_m$): j$_m$ = -0.46 mA cm^{-2}; t$_m$ = 1 s (m = 3, 5, 7, . . . , 1499);
Anodic pulse (P$_n$): j$_n$ = 1.26 mA cm^{-2}; t$_n$ = 0.005 s (n = 4, 6, 8, ... , 1500);
Total number of pulses: 1500 (optimized)

The scanning electron microscopic (SEM) image revealed that tapped hemispherical AuNPs of diameter 350–400 nm and height
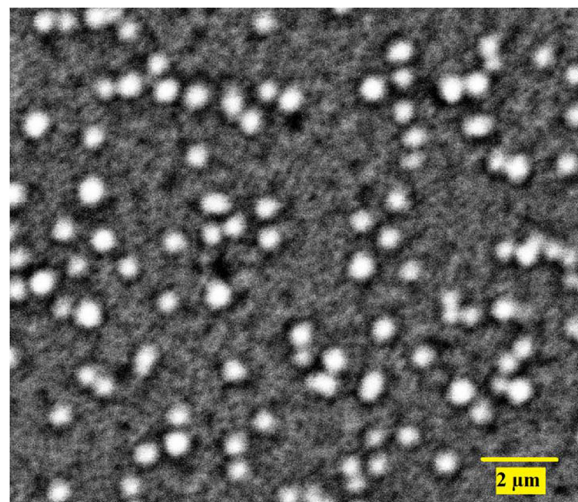

Fig. 1. SEM image of AuNPs/GC at 25000X.

25–30 nm were deposited on GC with a less particle population (Fig. 1). Henceforth, we would express the average height of NPs and the variation (i.e. range) of the heights of NPs by the terms "size" and "size dispersion", respectively *[Note: Metals having one or more dimensions (length or width or height) in the nanometer size range (1–100 nm) are known as 'metal nanoparticles']*. The synthe-sized particles showed a narrow dispersion in the particle size.

The geometry surface areas (A$_g$s) of Au, GC and AuNPs/GC are 0.032, 0.071 and 0.071 cm^2, respectively. The electrochemical surface area (A$_e$) of the working electrode was calculated by using the Randles-Sevcik equation from the slopes of the cathodic peak current versus the square root of the scan rate (ranging from 10–500 mV s^{-1}) plots obtained in the cyclic voltammetry experi-ments with 5 mM potassium ferricyanide in 0.1 M KCl. The number of electrons transferred and the diffusion coefficient of ferricyanide in 0.1 M KCl were taken as 1 and 6.73 $\times$ 10^{-6} cm^2 s^{-1}, respectively. [6] The A$_e$s of Au, GC and AuNPs/GC were calculated as 0.053, 0.121 and 0.107 cm^2, respectively, Unless specified, the current density (j) was calculated by using these values for the respective electrodes. The roughness factor (ρ = A$_e$/A$_g$) were calculated as 1.7, 1.7 and 1.5 for Au, GC and AuNPs/GC, respectively.

Cyclic voltammetric experiment was performed with AuNPs/GC in 1 M H$_2$SO$_4$ solution at a scan rate of 100 mV s^{-1}. The cathodic charge corresponding to AuO/Au reaction was found to be -7.39 μC. The effective surface area of Au (A$_{Au}$) was calculated as 0.019 cm^2 for the AuNPs/GC electrode assuming the charge density of the
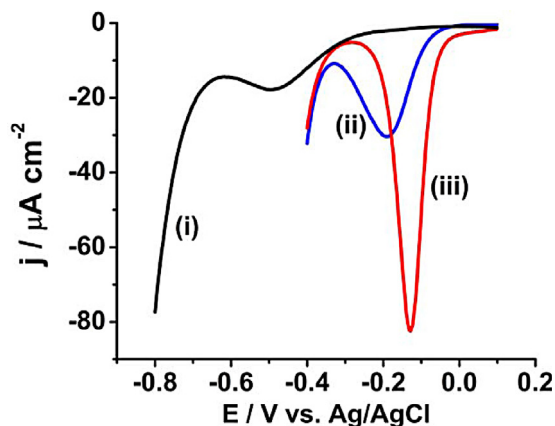

Fig. 2. DPV of 5 mM U(VI) in 1 M H$_2$SO$_4$ on (i) GC, (ii) Au and (iii) AuNPs/GC at 10 mV pulse amplitude.