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Electrocatalytic oxidation of nitric oxide at TiO_2–Au nanocomposite film electrodes

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Abstract

Structured films of TiO_2 (anatase) nanoparticles (ca. 6 nm diameter) and gold nanoparticles (nominal 20 nm diameter) are formed via a layer-by-layer deposition procedure. TiO_2 nanoparticles are deposited with a Nafion polyelectrolyte binder followed by calcination to give a mesoporous thin film electrode. Gold nanoparticles are incorporated into this film employing a poly(diallyldimethylammonium chloride) polyelectrolyte binder followed by calcination to give a stable mesoporous TiO_2–gold nanocomposite. This methodology allows well-defined and structured films to be formed which are re-usable after a 500 °C heat treatment in air.

Electrochemical experiments are performed in aqueous KCl and buffer solutions and for the oxidation of nitric oxide, NO, and nitrite in phosphate buffer solution. It is shown that the NO oxidation occurs as a highly effective electrocatalytically amplified process at the surface of the gold nanocomposite probably with co-evolution of oxygen, O_2. In contrast, the oxidation of nitrite to nitrate occurs at the same potential but without oxygen evolution. A mechanistic scheme for the amplified NO detection process is proposed.

Keywords: TiO_2; Gold; Nanoparticle; Colloid; Cermet; Voltammetry; Nitric oxide; NO; Nitrite; Nitrate; Electrocatalysis; Sensors

1. Introduction

Titanium oxide, TiO_2, is a widely used wide band gap semiconductor material with applications in solar cells [1], photocatalysis systems [2], as a catalyst support [3], and as a pigment. Thin mesoporous films of TiO_2 formed via layer-by-layer deposition at electrode surfaces allow molecular redox systems [4] or redox proteins [5] to be immobilised and connected to the electrode. The formation of TiO_2–gold nanocomposites [6] or cermets [7] has been reported previously based on sol–gel methods [8], sol adsorption processes [9], sputter coating [10], and with TiO_2 nanotube materials [11]. The resulting nanocomposite materials are of considerable interest due to non-linear optical effects and in heterogeneous catalysis where the TiO_2–gold nanocomposite allows low temperature oxidation of carbon monoxide [12,13], mild hydrogenation processes [14], and a range of photocatalytic reactions [15].

Metal nanoparticle arrays at electrode and sensor surfaces are of considerable interest [16]. Gold nanoparticles have been employed in nanostructured assemblies [17] and attached to electrode surfaces, for example, by seed growth methods [18]. Gold nanoparticle systems have been applied in electrocatalysis, for example, for the determination of arsenic(III) [19], have been incorporated into biosensor devices [20], and have found a wide range of applications in assemblies for catalysis [17]. A deposition and size tuning approach for gold nanoparticles on mercapto-modified surfaces has been developed [21]. Charge transfer and tunnelling effects have been investigated at gold nanoparticle decorated electrode surfaces [22]. In this study a simple method for the formation of structured TiO_2–Au composite films is developed.

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Nitric oxide, NO, is an important short lived intermediate in many biological systems [23] and the in situ detection of low level NO in complex matrices remains a challenge. Monitoring of NO with electrochemical sensors has been achieved at carbon nanostructure electrodes [24], with nickel phthalocyanine complexes [25], iron porphyrinato complexes [26,27], nickel porphyrinato compexes [28], with proteins such as cytochrome *c* [29] or hemoglobin [30–32] immobilised at electrode surfaces. The mechanism of the reduction and oxidation of NO has been studied at platinum and a range of other metal surfaces [33]. For the oxidation of NO on gold in 0.1 M H_2SO_4, poor reproducibility and a complex mechanism have been reported [33]. Weak interaction of NO with the gold surface is believed to lead to the first one-electron transfer process which is followed by hydrolysis of NO^+ to nitrite. In a second redox step the nitrite intermediate is oxidised in a two-electron process to nitrate.

The oxidation of nitric oxide has been reported at gold and gold nanoparticle electrodes [34] as well as at gold-Nafion composite films [35]. Gold has been demonstrated to act as an electrocatalyst (when compared to tin-doped indium oxide (ITO) electrode surfaces) and gold nanoparticle assemblies have been employed as a very sensitive nitric oxide sensor in muscle cells. Recently a TiO_2-Nafion film immobilised at glassy carbon has been reported as a nitric oxide sensor electrode [36].

In this study a simple and versatile procedure for the formation of layered TiO_2–gold nanocomposites is reported. The resulting films are characterised and tested for the oxidation of nitric oxide in phosphate buffer solution at pH 7. A surprisingly high (“amplified”) anodic current for the oxidation of nitric oxide is observed and attributed to a simultaneous oxygen evolution process catalysed by the gold nanoparticle surface in the presence of NO. A mechanism for this electrocatalytic co-oxidation process is suggested.

2. Experimental details

2.1. Chemical reagents

Chemical reagents such as Nafion perfluorinated ion-exchange resin (5 wt%, in a mixture of lower aliphatic alcohols and H_2O), poly(diallyldimethylammonium chloride) (35 wt% in H_2O), phosphoric acid (85 wt% solution in water ACS reagent), NaOH, KCl, nitric oxide (all Aldrich), ethanol (Fisher Scientific), tris(2,2-bipyridyl)ruthenium(II) chloride ($Ru(bipy)_3Cl_2$, Ventron, Germany) and gold colloid (20 nm diameter, ca. 0.01% in HAuCl, Sigma–Aldrich) were obtained commercially and used without further purification. TiO_2 sol (ca. 6 nm diameter, anatase, 30–35% in aqueous HNO_3, pH 0.5, TKS-202) was obtained from Tayca Corp, Japan. Solutions were prepared using deionised water with a resistivity of not less than 18 MΩ cm.

2.2. Instrumentation

Voltammetric experiments were performed with an Autolab PGSTAT20 system (Eco Chemie, Netherlands) in a standard three terminal electrochemical cell with a saturated calomel reference electrode, SCE, (Radiometer, Copenhagen) placed ca. 0.5 cm from the working electrode and a 2 cm × 2 cm platinum gauze counter electrode. The working electrodes were made from tin-doped indium oxide (ITO) coated glass (10 mm × 60 mm, 15 Ω per square, Image Optics, Basildon, UK). The ITO electrode was rinsed with ethanol, heat treated in a furnace (Elite Thermal Systems Ltd.) for 1 h at 500 °C, and re-equilibrated to ambient conditions prior to use. Field emission gun scanning electron microscopy (FEGSEM) images were obtained on a Leo 1530VP Field Emission Gun SEM system. Prior to voltammetric experiments solutions were de-aerated with argon (BOC). All experiments were conducted at a temperature of 22 ± 2 °C.

2.3. Layer-by-layer formation of TiO_2–gold composite films

A layer-by-layer deposition strategy was chosen in order to prepare structured thin layer systems. Two types of electrodes were prepared with: (i) only mesoporous TiO_2 and (ii) a TiO_2–Au composite film (Fig. 1 summarises the process).

The deposition procedure for the mesoporous TiO_2 electrode consisted of a sequence of liquid immersion steps with: (i) a TiO_2 sol (6 nm diameter, 3 wt% in nitric acid, pH ca. 2) for 60 s followed by rinsing with distilled water and drying in air, (ii) dipping into Nafion anionomer solution (ca. 3 wt% in methanol) for ~10 s followed by rinsing with methanol and distilled water. This completed a single layer deposition for the simple TiO_2-Nafion film and the cycle was repeated to add more layers. After deposition of the required number of layers the electrodes were calcined at 500 °C in air for 1 h to leave a purely inorganic mesoporous anatase film.

The deposition of the TiO_2–Au nanocomposite film involved the same sequence of dipping steps as mentioned above with additional steps (iii) dipping into poly(diallyldimethylammonium chloride) solution (ca. 0.03 wt% in H_2O) for ~10 s followed by rinsing with distilled water, (iv) soaking in the 20 nm gold colloid for 30 min followed by rinsing with distilled water and drying in air. Before the next layer of the TiO_2–Au nanocomposite can be added, the electrode is dipped once again into the poly(diallyldimethylammonium chloride) solution for ~10 s, rinsed with water and then dipped into Nafion solution for ~10 s and rinsed with water. This completes a single layer TiO_2–Au deposition. The deposition steps could be repeated to increase the thickness of the film. After the deposition of the required number of layers the electrodes were calcined in air at 500 °C for 1 h. A typical SEM image of a TiO_2–Au nanocomposite film is shown in Fig. 2. The thickness of the films is approximately