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Nitrate and Nitrite Electrocatalytic Reduction at Layer-by-Layer Films Composed of Dawson-type Heteropolyanions Mono-substituted with Transitional Metal Ions and Silver Nanoparticles

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ABSTRACT

A series of Dawson-type heteropolyanions (HPAs) mono-substituted with transitional metal ions (α_2-$[P_2W_{17}O_{61}Fe^{III}]^{8-}$, α_2-$[P_2W_{17}O_{61}Cu^{II}]^{8-}$ and α_2-$[P_2W_{17}O_{61}Ni^{II}]^{8-}$) have exhibited electrocatalytic properties towards nitrate and nitrite reduction in slightly acidic media (pH 4.5). The immobilization of these HPAs into water-processable films developed via layer-by layer assembly with polymer-stabilized silver nanoparticles led to the fabrication of the electrocatalytic interfaces for both nitrate and nitrite reduction. The LBL assembly as well as the changes in the HPA properties by immobilization has been characterized by electrochemical methods. The effects of the substituent ions, outer layers and the cationic moieties utilized for the films assembly of the developed film on the performances of nitrate electrocatalysis has been elucidated.

1. Introduction

Inorganic and organic compounds of nitrogen are one of the most abundant in the human body and are involved in many biological, environmental and industrial processes. In nature, the nitrogen cycle controls the reaction pathways of inorganic compounds of nitrogen. The human alteration substantially alters the nitrogen cycle caused the general increase of both availability and the mobility of nitrogen over large terrestrial regions [1]. Inappropriate drainage of waste water and over-manuring with natural and synthetic fertilizers is becoming a severe environmental concern [2–5]. In particular, being the main source of the drinking water, ground waters are characterized worldwide as having increased nitrate concentration [6]. Being extensively used in industrial [7] and biomedical applications [8–10], nitrite is one of the most reactive substances in the nitrogen cycle and has a significant toxicity for humans, being the main cause of blue baby syndrome [11]. Consumed nitrate is also reduced to nitrite by enteric bacteria, which might subsequently lead to serious health risks [12,13]. The maximum admissible concentrations for nitrates in drinking water is 50 mg/l (0.8 mM) in the European Drinking Water Directive [14–16].

The technologies for nitrate elimination from water are classified into physico-chemical, biological and catalytical processes [15,17]. Being preferred for economical reasons, physico-chemical techniques such as ion exchange, reverse osmosis and electrodialysis do not convert nitrate to harmless compounds but only remove it from the water. Heterogeneously catalyzed nitrate reduction reaction (NRR) to nitrogen for groundwater remediation has been developed [18–20] as one of the alternatives. Biological denitrification is costly, complex and a slow process accompanied with a co-production of large quantities of sludge [4382]. Electrochemical techniques of denitrification via NRR have attracted special interest because of the possibility of operation in high nitrate concentrations [4,20]. The electrode materials that reveal high activity in NRR are limited to noble metals and their bimetallic alloys [4,20] as well as graphene [21]. However, most of these electrocatalytical systems require high acidity [4] or alkalinity [22,23] for effective NRR. The electrocatalysis of NRR has been observed on electrodes functionalized with transition

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metal ions cyclams at rather negative potentials (ca. -1.4 V vs SCE) [24–29].

Heteropolyanions (HPA) are a well-known class of inorganic metal oxygen cluster compounds, which possess excellent electrochemical properties, enabling them to accept and donate multiple electrons reversibly without decomposition. This redox feature renders the HPA excellent electrocatalysts for a variety of substrates [30–32]. Different strategies for the immobilization of HPAs into thin films on electrode surfaces have been adopted [30,33–35], with particular attention being afforded to the employment of the Layer-by-Layer (LBL) technique. This technique is based upon the electrostatic interaction between oppositely charged species from dilute solution [36–38]. Nanocomposite materials which are based on inorganic nanoparticles and polymers offer unique properties, such as, optical, magnetic, catalytic, thermal and electrochemical, which depend on particle size, shape, dimensions and surrounding environment [39–43]. The unusual properties of metallic nanoparticles are due to the collection of high energy surface atoms compared to the bulk solid material.

HPAs have been previously shown to be effective electrocatalysts for the reduction of nitrite [34,44–47] as a standard reaction for the assessment of HPA electrocatalytic performance [48]. Rare examples of transitional metal ion-substituted HPAs demonstrated the electrocatalytic activity towards NRR in mild acidic media (approx. pH 5) [49–56]. The accumulation of transitional ion centers within the HPA cage is associated with an enhancement of the catalytic properties of these atoms, with the complementary advantage to generate highly reduced products by the electrons from the reduced W-O framework as electronic storage [31]. The favorable effect on NRR catalysis of accumulation of substituent ion within the same molecule has been shown for sandwich-type Cu^{2+}- [52] and Ni^{2+}-multisubstituted HPA [52,57] in comparison with monosubstituted derivatives. Starting with the reduction to nitrite by the HPA, the whole reaction goes through nitric oxide (NO) [55] down to ammonia [48]. The significant cathodic overpotential up to 750 mV is observed for NRR electrocatalysis with HPA in comparison with nitrite reduction illustrating the low reactivity of the nitrate ion [49]. Recently we reported the achievement of NRR at the same potential as nitrite reduction observed on crown-type HPA multi-substituted with Cu^{2+} or Ni^{2+} ions immobilized via LBL assembly with silver nanoparticles (AgNP) [58].

In this paper, we report the studies of NRR happened at the same potential as nitrite reduction wave achieved on Dawson-type HPA mono-substituted with transitional metal ions and immobilized via LBL assembly with polymer-stabilized AgNPs. The influence of the incorporated AgNPs on the film's properties and performance has been studied by electrochemical and physical methods. It has been found that the outer layer of the LBL assembly strongly affects the morphological and electrocatalytic properties of films with suficient enhancement of film's electrocatalytic ability being observed with AgNP incorporation.

2. Experimental

2.1. Materials

The lacunary α/β-$K_{10}[P_2W_{17}O_{61}]^{10-}$ Dawson-type HPA was synthesised and characterised according to the literature [59]. The potassium salts of the transition metal ion-substituted $_{\alpha2}$-$[P_2W_{17}O_{61}Fe^{III}]^{8-}$, $_{\alpha2}$-$[P_2W_{17}O_{61}Cu^{II}]^{8-}$ and $_{\alpha2}$-$[P_2W_{17}O_{61}Ni^{II}]^{8-}$ Dawson HPA were synthesised according to the literature [60]. Potassium ferricyanide, potassium ferrocyanide, hexaammineruthenim(III) chloride, silver nitrate (99.99%), poly(ethyleneimine) (PEI, MW ~ 25,000), poly(sodium 4-styrenesulphonate) (PSS, MW ~ 70, 000), poly(diallyldimethylammonium chloride) (PDDA, MW ~ 20, 000) and all the other chemicals were purchased from Sigma–Aldrich. Highly purified water with a resistivity 18.2 MΩ cm (ELGA PURELAB Option-Q) was used for the preparation of all the electrolytes and buffer solutions. The following solutions have been used for the measurements: 0.1 M Na_2SO_4 (the pH was adjusted to 2–3), 0.1 M Na_2SO_4 + 20 mM CH_3COOH (the pH was adjusted to pH 3.5–5), 0.1 M Na_2SO_4 + 20 mM NaH_2PO_4 (the pH was adjusted to pH 5.5–7). The pH of the solutions was adjusted with either 0.1 M NaOH or 0.1 M H_2SO_4.

2.2. Instrumentation

UV-Vis spectra were recorded on a UV-1800 Shimadzu Spectrophotometer in conjunction with quartz cells with path lengths of 1 cm. Scanning electron microscopy (SEM) images were obtained with a Hitachi SU-70. X-ray photoelectron spectroscopy (XPS) was done with a Karatos AXIS-165, Monochromatic Al Kα radiation of energy 1486.58 eV. High resolution spectra were taken at a fixed pass energy of 20 eV. Morphological analysis was carried out on a Zeiss SUPRA 40VP, Field Emission-Scanning Electron Microscopy (FE-SEM), by setting the acceleration voltages at 10 kV.

2.3. Preparation of PEI-stabilized AgNP

A mixture of 100 ml of a 10 mM solution of $AgNO_3$ and 3 ml of 2% (W/W) PEI was heated for 15 minutes with constant stirring. A brown colloidal solution was obtained without precipitation [61].

2.4. Electrochemical procedure

All electrochemical experiments were performed with a CHI660 electrochemical work station employing a conventional three-electrode electrochemical cell. A glassy carbon electrode (GCE, 3 mm diameter, surface area 0.0707 cm^2) was used as the working electrode, a platinum wire as the auxiliary electrode, and a silver/silver chloride as the reference electrode (3 M KCl) in aqueous media in all experiments unless otherwise stated. Prior to use the working electrode was successively polished with 1.0, 0.3 and 0.05 μm alumina powders and sonicated in water for 10 min after each polishing step. Finally, the electrode was washed with ethanol and then dried with a high purity argon stream. All solutions were degassed for 20 min with high purity argon and kept under a blanket of argon during all electrochemical experiments.

2.5. Layer-by-layer (LBL) assembly

A freshly polished GCE was immersed in the 8% (v/v) PDDA solution for 30 minutes for initial surface modification. The electrode was then rinsed thoroughly with deionised water and dipped in a 3.4 mM solution of the corresponding HPA in pH 2 buffer solution for 20 minutes to allow the initial anionic layer to adsorb (Step 1). The modified electrode was rinsed again thoroughly with deionised water and dried with a high purity nitrogen stream. This yielded the PDDA/HPA modified electrodes, which were then dipped in a water solution of AgNP for 20 minutes (Step 2). The electrode was then washed and dried with nitrogen. To build the desired number of layers, steps 1 and 2 were repeated in a cyclic fashion. The outer layer of the multilayer assembly was chosen so as to be either anionic or cationic in nature.

2.6. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy was undertaken employing a 10 mM potassium ferricyanide and 10 mM potassium