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Enhancement of Nitrite and Nitrate Electrocatalytic Reduction through the Employment of Self-Assembled Layers of Nickel and Copper-Substituted Crown-Type Heteropolyanions

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Abstract

Multilayer assemblies of two crown-type heteropolyanions (HPA) $[\text{Cu}_{20}\text{Cl}(\text{OH})_{24}(\text{H}_2\text{O})_{12}(\text{P}_8\text{W}_{48}\text{O}_{184})]^{25-}$ and $\text{Ni}_4(\text{P}_8\text{W}_{48}\text{O}_{148})(\text{WO}_2)]^{28-}$ have been immobilized onto glassy carbon electrode surfaces via the layer-by-layer (LBL) technique employing polycation-stabilized silver nanoparticles (AgNP) as the cationic layer within the resulting thin films characterized by electrochemical and physical methods. The redox behaviours of both HPA monitored during LBL assembly with cyclic voltammetry and impedance spectroscopy revealed significant changes by immobilization. The presence of AgNPs led to retention of film porosity and electronic conductivity, which has been shown with impedance and voltammetric studies of film permeabilities towards reversible redox probes. The resulting films have been characterized by physical methods. Finally, the electrocatalytic performance of obtained films to nitrite and nitrate electrocatalytic reduction have been comparatively studied for both catalysts. Nickel atoms entrapped inside HPA showed higher specific activity for reduction.

Keywords: heteropolyanion, crown-type, catalysis, nitrite, silver nanoparticles

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Introduction

Heteropolyanions (HPAs) are a class of inorganic nanoclusters which show wide ranging diversity in both their structure and composition whilst possessing stable redox states ^{1, 2}. They have the ability to undergo reversible multi-electron redox processes which has made them ideal candidates for a range of catalytic reactions ³⁻⁵. In addition, HPAs have received a lot of attention because of their versatility in their structures and potential applications in electrochemistry, magnetism ⁶, photochromism ⁷ and many other applications in material and fundamental science. For the majority of these applications it is important that the HPA can be immobilised onto a range of surfaces resulting in stable and accessible thin films, in which the inherent solution phase properties of the HPA are maintained in the solid state. Various techniques have been employed to surface immobilise HPAs, including, polymeric films ⁸⁻¹¹, electrochemical deposition ⁴, adsorption ^{12, 13}, Langmuir-Blodgett films ¹⁴, sol-gel films ^{15, 16}, self assembled monolayers ¹⁷, layer-by-layer assembly ¹⁸⁻²⁰. Layer-by-layer is a rapid and simple technique to fabricate well-organized molecular layered structures and to obtain functional materials with precisely controlled thickness and uniformity.

The synthesis and design of structures with dimensions ranging between 1-100 nm is an important field of nanotechnology applications in various fields like optical, magnetic, catalytic, thermal and electrochemical properties, which mainly depend on large extent on the particle size, shape, dimensions and the environment ²¹⁻²⁵. In particular silver nanoparticles (AgNPs) are of broad attention because of their prospective properties (e.g., size and shape depending electrical, magnetic and optical properties), which can be incorporated into applications regarding to antimicrobial applications, catalysis, biosensing materials, composites, fibers, electronic components, superconducting materials and plasmonic applications ^{24, 26-29}.

Nitrite has an important role regarding both several biological and the environmental issues due to its extensive usage in various fields of industry, medicine and technology ^{30, 31}. Nitrite ions are known to react with amines forming nitrosamines which are known to be carcinogenic ³². Nitrite in the blood can inhibit the oxygen intake of the body by oxidizing Fe^{2+} to Fe^{3+} of the haemoglobin, known as methemoglobinemia and mostly cause in infants. Electrochemical methods have been employed previously for the determination of nitrite ³³.

On the contrary to nitrite reduction, which is catalyzed by wide variety of HPA, only a few HPA multi-substituted with transitional metal ions (Cu^{2+} , Ni^{2+} and Fe^{3+}) demonstrated the

activity towards nitrate electrochemical reduction³⁴⁻³⁷. The accumulation of transitional ion centers within HPA is favorable to nitrate reduction activity of HPA³⁵. Cu₂₀-substituted crown-type HPA has been immobilized with water-insoluble ionic liquid maintaining nitrate reduction activity³⁶. To our knowledge, there is no examples of immobilization of other types of multi-substituted nitrate-reducing HPA.

In this article, we report the electrode surface immobilization of two crown-type HPAs (Cu₂₀-tungstophosphate and Ni₁₄-tungstophosphate) with LBL assembly with polymer-stabilized AgNPs as cationic moiety. The growth and characterization of the developed films were carried out by electrochemical techniques (cyclic voltammetry and electrochemical impedance spectroscopy) as well as physical methods of surface analysis. The ferro/ferricyanide couple has been used as a probe to study the conductivity and the porosity of LBL films. The employment of stabilized AgNPs sufficiently increases the conductivity of films, which led to sufficient enhancement of electrocatalytic properties of modified electrodes showed on nitrite reduction as a model system.

Experimental

Materials

Potassium ferricyanide, potassium ferrocyanide, hexaammineruthenium(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 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 the electrolyte and buffer solutions. The pure crown HPAs, Cu₂₀-tungstophosphate [Cu₂₀Cl(OH)₂₄(H₂O)₁₂(P₈W₄₈O₁₈₄)]²⁵⁻ (Cu₂₀TP), and Ni₁₄-tungstophosphate [Ni₁₄(P₈W₄₈O₁₄₈)(WO₂)]²⁸⁻ (Ni₁₄TP) were synthesised and characterised according to the literature^{38, 39}. The following buffer solutions have been employed for the electrochemical investigations: 0.1 M Na₂SO₄ (pH 2 – 3), 0.1 M Na₂SO₄ + 20 mM CH₃COOH (pH 3.5 – 5), 0.1M Na₂SO₄ + 20 mM NaH₂PO₄ (pH 5.5 – 7). The pH of the solutions was adjusted with either 0.1 M NaOH or 0.1 M H₂SO₄.

Preparation of PEI-stabilized silver nanoparticles (AgNPs)

A mixture of 100 ml of a 10 mM solution of AgNO_3 and 3 ml of a 2% (W/W) PEI solution was heated for 15 minutes with constant stirring which yielded a brown colloidal solution without precipitation ⁴⁰.

Layer-by-layer (LBL) assembly

A freshly polished GCE was immersed in the 8% (v/v) PDDA solution for one hour for initial surface modification. The electrode was then rinsed thoroughly with deionised water and dipped in a 3.4 mM solution of Ni_4TP 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/ Ni_4TP modified electrodes which were then dipped in a 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. Initial GCE surface modification with PDDA was not carried out for the Cu_{20}TP -based assembly due to the possibility of direct deposition of Cu_{20}TP onto the electrode surface. The outerlayer of the multilayer assembly was chosen so as to be either anionic or cationic in nature.

Electrochemical procedures

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 (3M 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 $0.05 \mu\text{m}$ 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 the electrochemical experiments.

The studies of electrocatalytic performances have been carried out by cyclic voltammetry (scan rate 10 mV/s) at LBL-film modified GCE in stationary pH 4.5 buffer before and after additions of sodium nitrite or sodium nitrate (0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM, 1 mM, 3 mM, 5mM and 7 mM).

Electrochemical Impedance Spectroscopy (EIS)

The EIS experiments were carried out in a 10 mM potassium ferricyanide and 10 mM potassium ferrocyanide 0.1 M KCl solution at an applied potential of +230 mV (versus Ag/AgCl) from 0.1 to 10^5 Hz with a voltage amplitude of 10 mV.

Instrumentation of physical methods

UV-Vis spectra were recorded on a UV-1800 SHIMADZU Spectrophotometer in conjunction with quartz cells with path lengths of 1 cm. Transmission electron microscopy (TEM) images were taken on a JOEL JEM-2100F transmission electron microscope. 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 K α radiation of energy 1486.58 eV. High resolution spectra were taken at fixed pass energy of 20eV. Analysis with atomic force microscopy (AFM) was performed using a NT-MDT SPM Solver P47HPRO instrument operating in tapping mode and in air. Root-Mean-Square (RMS) roughness values were obtained from 3×3 cm² images after a plane fitting procedure. Micrographs were collected in different sample regions in order to check the surface homogeneity. 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.

Results and Discussion

1. Characterization of AgNPs by UV-vis spectroscopy and TEM

PEI has been used for the synthesis of the AgNPs^{41, 42} with the UV-Vis spectrum (Fig. 1SA) revealing the plasma resonance peak at 408 nm, which is typical for the plasmon absorbance

of spherical shaped Ag-NPs ⁴³. The TEM survey (Fig. 1SB) also shows the near spherical shape of the AgNPs. It can be seen that a mixture of particles exist comprising particles of larger (around 10 nm) and smaller diameters (1-4 nm). Particles were measured using STEM-DF with the average diameter of 500 particles being calculated as 1.69 ($\pm$ 0.49) nm.

2. Electrochemical Properties of Cu₂₀TP and Ni₄TP

2.1 Voltammetry studies

Cyclic voltammetry has been utilized to monitor the growth of the LBL assemblies onto the carbon electrode surfaces for both the Ni₄TP/AgNP (Fig. 1A) and Cu₂₀TP/AgNP (Fig. 1B) multilayers. What is apparent is that the various redox processes assigned to either the POM species or the cationic silver nanoparticles are distinguishable during the construction of each assembly. Two well defined redox processes, labelled as I and II, with $E_{1/2}$ values of -0.6 V and -0.7V, and corresponding ΔE_p values of 80 and 60 mV, respectively, are apparent for the Ni₄TP-based film. The identical two redox processes with $E_{1/2}$ values of -0.58 V and -0.71 V and ΔE_p values of 60 mV, respectively, are observed for the Cu₂₀TP-based films. These two redox processes, I and II, represent the two consecutive eight-electron redox-processes associated with each POM's tungsten-oxo (W-O) framework ⁴⁴.

An increase in the anodic peak currents for the W-O II redox process with increasing layer number, for both films, illustrates the facile construction of the layers. The voltammograms obtained with first layers of both HPA (Inset 1 of Fig. 1) have been characterized with irreversible silver oxidation (-0.2 - 0.3 V) and with reversible redox processes of W-O I and II framework.

Significant changes in voltammetric responses of both HPA are observed with immobilization. The free HPA in solution (pH 2) showed a suppressed W-O redox reactions characterized by divided redox peaks for W-O I and broad redox peak couple for W-O II in comparison with immobilized compounds within LBL films (pure buffer pH 4.5). The suppression of irreversible redox process associated with the copper centres of Cu₂₀TP (Inset 2 of Fig. 1) has been observed with immobilization within LBL film ($E_{1/2}$ of -0.04 V, ΔE of 0.15 V).

The rise of redox peak currents and decrease of peak-to-peak separations for W-O I and II redox processes of both Ni₄TP and Cu₂₀TP showed thin-film behaviour and enhancement of

redox reactions due to immobilization into the highly conductive microenvironment of LBL film, which has been confirmed with the linear dependencies of peak currents on the scan rate (Fig. S2 for Ni₄TP-based LBL film).

The study of electrode kinetics of the W-O I and II redox processes has been undertaken in accordance with the Laviron approach^{45, 46}, wherein the peak-to-peak separations (ΔE_p) is higher than 200/ n mV where equation (1) applies:

$$\log k = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log\left(\frac{RT}{nF\nu}\right) - \frac{\alpha(1 - \alpha)nF\Delta E_p}{2.3RT} \quad (1)$$

where $\Delta E_p = E_{PA} - E_{PC}$ (E_{PA} and E_{PC} are the anodic and cathodic peak potentials respectively), α is the transfer coefficient, n is the number of transferred electrons per one redox cycle ($n = 8$ for both W-O I and II)⁴⁴, ν is the scan rate, T is temperature, R is Boltzmann constant (8.314 J mol⁻¹ K⁻¹), F is Faraday constant (96485 C mol⁻¹) and k is the heterogeneous electron transfer rate constant. If $\alpha = 0.5$, then equation (1) gives the average values of the heterogeneous electron transfer rate constants of 0.2 cm s⁻¹ and 0.5 cm s⁻¹ for the W-O I redox process for the Ni₄TP- and Cu₂₀TP-based LBL films, respectively.

The consistent growth in the redox currents with layer number illustrates the absence of a terminal layer effect. Instead of assembly with organic cationic moiety (e.g. Methylene Blue)⁴⁷ LBL deposition with AgNPs leads to formation of terminal layer, which does not affect the counter ions transfer through the film/solution interface during Faradaic processes. However, the redox couple associated with AgNPs does not exhibit a linear growth in redox currents with layer number this being probably due to the strong masking effect of the W-O I and II redox processes at the same potential³³.

The surface coverage of the Ni₄TP-based LBL film composed of 8 layers was assessed from the integral charge of the W-O I anodic peak by the employing the relationship $\Gamma = \frac{Q}{nFA}$, where Q (C) is the charge assessed from integration of peak of current obtained at slow scan rate ensuring a full conversion of film (5 mV/s), A (cm²) is the electrode surface area, F is Faraday constant (96485 C mol⁻¹) and n is the number of transferred electrons per one redox cycle ($n = 8$ for both W-O I and II of the crown-type heteropolyanions P₈W₄₈O₁₈₄)⁴⁴. The surface coverage was found to be 0.1 nmol cm⁻². A doubling of the layer number in the assembly led to a 1.8 increase in the amount of immobilised redox active material on the

electrode surface. Integration of corresponding cathodic peak showed a 1.8 times higher value. Almost the same mass load has been observed for Cu₂₀TP based LBL films.

It is well known that the POM's W-O based redox processes, both in the solution and immobilised phases, involve protons⁴⁸⁻⁵¹. The role of pH of the contacting electrolyte upon the redox activity of both POM based multilayers was investigated. It can be seen from Fig. S3 that with increasing pH there is a cathodic shift in the potentials associated with the Ni₄TP-POM's W-O I and II redox processes, with this also being observed for the Cu₂₀TP-based LBL films. By studying the effect of pH upon the measured $E_{1/2}$ values for the W-O redox processes across a broad range of pH values it was possible to ascertain the number of protons involved in each W-O based redox process for the POM based multilayers. From the slopes of the pH versus $E_{1/2}$ plots, namely 80 and 75 mV per pH unit for the W-O processes, I and II, respectively, for both Ni₄TP- and Cu₂₀TP-based LBL films. It can be concluded that each redox process involves not only the addition of 8 electrons but also 8 protons^{47, 52}.

2.2 EIS studies

EIS has been employed to further study the growth of each POM based multilayer assembly. Figures 2A and 2B show the resulting impedance spectra obtained during the construction of the Ni₄TP- and Cu₂₀TP-AgNP LBL films, respectively, in the form of Nyquist plots. The Randles equivalent circuit developed previously⁴⁷ has been employed here to allow interpretation of these impedance spectra. This equivalent circuit consists of a double layer capacitance in series with a solution resistance and in parallel with a diffusional branch, i.e. charge transfer resistance and Warburg impedance. Due to the non-uniform distribution of interfacial properties at the electrode surface the constant phase element substituted double layer capacitance in the equivalent circuit. Fitting of the experimental data observed in Figures 2A and 2B confirmed the reproducible switching behaviour of the measured charge transfer resistance (R_{CT}) values. It can be seen from Figure 2C that with the deposition of each AgNP layer within both assemblies there is a decrease in the measured R_{CT} values. This is probably due to the several reasons. Firstly, metal nanoparticles are conductive, which might facilitate the electronic communication between the probe molecules and the electrode. Secondly, there might be electrostatic attraction between the cationic outer nanoparticles and the negatively charged ferricyanide/ferrocyanide redox probe. Thirdly, in contrast to organic cations (e.g. Methylene Blue)⁴⁷, the high charge density of AgNP can cause the strong

electrostatic interactions with HPA leading to the non-uniform and defective assembly. For the Ni₄TP-AgNP LBL films, the R_{CT} values are seen to be higher than those for the Cu₂₀TP-AgNP LBL films probably due to the presence of the initial PDDA layer on the electrode surface for the Ni₄TP-AgNP LBL films. In addition, it can be seen that with the deposition of each POM layer there is an increase in the R_{CT} values for each multilayer system, again probably due to the presence of repulsive forces between the outer POM layer and the anionic ferricyanide/ferrocyanide redox probe.

2.3 Permeability studies

The porosities of each multilayer assembly was investigated by studying the effect of the presence of the multilayer film immobilised on the carbon working electrodes on the redox behaviour of two reversible mono-electronic redox probes, namely, $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ and $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Upon interaction with the modified electrodes the redox probes could diffuse through the multilayer films and react at the underlying electrode or undergo reaction at the film/solution interface through mediated electron transfer by the redox active sites within each multilayer film ⁴⁹. It can be seen from Figure 3 that a Ni₄TP-AgNP LBL film composed of either 8 or 16 layers with an outer POM layer maintains the distorted voltammetry signal of the $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ redox process. This is in contrast to other POM based multilayer systems, where there is an absence of nanoparticles, which leads to reduced film porosities ⁴⁷. Therefore, the metal nanoparticles are seen here to mediate the probe redox reaction or, alternatively, create a disorganized electrode material. Again, there appears to be a high level porosity of the Ni₄TP -based LBL films towards the anionic redox probe (Fig. S4). These results appear to be in agreement with the low R_{CT} values obtained during the EIS experiments discussed earlier. Similar behaviour has been observed for the Cu₂₀TP -based LBL films.

2.4 Electrocatalysis of nitrite and nitrate reduction

The reduction of nitrite and nitrate at a bare carbon electrode requires a large over-potentials. HPA have been previously shown to be effective electrocatalysts for the reduction of nitrite ^{50, 53-56} as a standard reaction for the assessment of HPA electrocatalytic performance ⁵⁷. On the contrary, only a few examples of transitional metal ion-substituted HPA demonstrated the

electrocatalytic activity towards nitrate reduction ³⁴⁻³⁷. The accumulation of transitional ion centers within HPA 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 ³⁵. The favorable effect on nitrate catalysis of accumulation of substituent ion within the same molecule has been shown for sandwich-type Cu^{2+} - ⁵⁸ and Ni^{2+} -multisubstituted HPA ^{58, 59} in comparison with monosubstituted derivatives. Nitrate is hardly reduced to nitrite, while the nitrite reduction to nitric oxide (NO) ⁶⁰ and to further reduced products down to ammonia ⁵⁷ is facilitated with the addition of transitional metal ions into the W-O cage. However, the nitrate electrocatalysis attributes not all transition metal multisubstituted HPA ⁶¹.

Here the abilities of the developed Ni_4TP - and Cu_{20}TP -based LBL films to catalyse the reduction of nitrite and nitrate has been comparatively investigated. Due to the inherent instability of HNO_2 (pK_a 3.3), via a disproportion reaction ⁴⁹, the electrocatalytic reduction of nitrite has been studied at pH 4.5. Figures 4A and 4B illustrates the series of cyclic voltammograms obtained for electrodes modified with Ni_4TP - and Cu_{20}TP -AgNP LBL films in the absence and the presence of nitrite or nitrate. It can be seen that the cathodic peak currents for both the POM's W-O redox processes, I and II, increase with the additions of nitrite or nitrate accompanied by a decrease in the currents associated with the redox processes anodic counterparts. These results imply that it is the multiply reduced form of the POM that catalyses the reduction of the nitrate to nitrite and subsequently nitrite. The observed electrocatalytic currents are comparable for both catalysts. Having five times smaller amount of entrapped transitional metal ions, Ni_4TP showed electrocatalytic activity similar to Cu_{20}TP , which illustrates higher specific activity of nickel atoms inside HPA. Nitrite reduction generated higher currents on Cu_{20}TP -based film and smaller currents at Ni_4TP -based film in comparison with nitrate, respectively.

The calibration plots developed as a concentration dependencies of catalytic current responses observed at potential of W-O II peak current (-0.72 V) showed the consistent increases of catalytic currents upon nitrite or nitrate concentration increase. The sensitivities assessed within the linear range from 0.2 mM to 1 mM (dynamic range from 0.2 mM to 7 mM) for Cu_{20}TP -based film were 10 % and 15 % higher than for Ni_4TP films for nitrite and nitrate reduction, respectively. The nitrite reduction revealed 2 % and 10 % higher sensitivities in comparison with nitrate for Ni_4TP - and Cu_{20}TP -based films, respectively.

These observations demonstrate the easier reduction of nitrite in comparison with nitrate reduction process.

The effect of LBL film thickness upon the electrocatalytic performance has been assessed also for both catalysts (Fig. S5). It can be seen that doubling the number of layers within the assembly leads to an increase in the measured catalytic currents.

The limits of detection assessed as $3 \times \text{SD} / \text{sensitivity}$, were of 14 μM and 13 μM for nitrite detection at Ni_4TP - and Cu_{20}TP -based films, respectively. Both systems showed the limits of detection of nitrate as 15 μM . Both systems showed the reproducibility of 90%. Table 1 shows the summarised data of sensitivity values obtained at different film-modified electrodes for electrocatalytic reduction of nitrite. From this it can be concluded, that AgNPs sufficiently intensify the electrocatalytic performance of the studied LBL films both as outer layers and as cationic moieties within the assembly. Ni_4TP -based films revealed higher sensitivities than the Cu_{20}TP -based films. The comparison with literature data showed that the Ni_4TP -AgNP LBL film has one of the highest sensitivities towards the reduction of nitrite.

The sensitivities of developed LBL film-modified electrodes towards nitrate reduction are comparable with the same characteristics deduced for Cu_{20}TP immobilized within water-insoluble ionic liquid ³⁶.

The developed films do not showed the response to chloride anion illustrating the good stability of multi-substituted HPA. Both electrocatalytic systems revealed a good operational stability over 10 days of discontinuous measurements (60 % and 80 % retention of electrocatalytic activity to nitrate for Ni_4TP - and Cu_{20}TP -based films).

3. Characterization with physical methods

The surface roughness and morphology of the films of varying thicknesses, have been studied with AFM (Fig. 5). The uniform distribution of globular aggregates has been observed at PDDA-modified surfaces (Fig. 5A). Minor increases in the surface roughness has been observed with modification (RMS increase from 4 nm (blank slide) to 8 nm). Formation of Ni_4TP - and Cu_{20}TP -based LBL films composed of 16 layers led to appearance of spherical

aggregates of quasi-columnar habit (Fig. 5B and 5C) accompanied with roughness increases (RMS increase up to 33 nm).

The effect of the outer layer on the surface morphology has been surveyed with SEM (Fig. 6). The presence of spherical aggregates distributed uniformly over smooth and flat matrix has been observed after the formation of all LBL films. A Ni₄TP- based film composed of 16 layers with an outer HPA layer (Fig. 6A) was characterised by spherical aggregates (with a size diameter ranging from 25 to 60 nm) wrapped up in a smooth and flat matrix. The presence of a second aggregate domain characterized by smaller particle sizes ranging from 10 to 3nm have been identified at Ni₄TP- based films with AgNPs as the outer layer (Fig. 6B) probably due to silver clusters. Cu₂₀TP-based LBL films showed the same trend of surface morphology. XPS of Ni₄TP- and Cu₂₀TP-AgNPs LBL films formed on ITO-modified glass slides showed the presence of all related elements and confirm the LBL assembly of films (Fig. S6, Table S1).

Conclusion

Two crown-type heteropolyanions ([Ni₄(P₈W₄₈O₁₄₈)(WO₂)]²⁸⁻ and [Cu₂₀P₈W₄₈O₁₄₈]²⁵⁻) have been successfully immobilized via the layer-by-layer technique with silver nanoparticles stabilized by a cationic polymer on carbon electrode surfaces. The films have been characterized by electrochemical and physical methods. The employment of AgNPs increased the conductivity and porosity of the films. The electrocatalytic performance of developed films towards reduction of nitrite and nitrate showed higher specific activity of nickel atoms entrapped within multi-substituted HPA.

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Table 1. Analytical characteristics of different electrocatalytical systems based on HPA towards nitrite reduction.

Cathionic moiety	Assembly number	Terminal layer	Sensitivity mA/(M cm ²)
Ni₄TP-based films (this work)			
AgNPs	16	Ni ₄ TP	58.7
AgNPs	8	AgNPs	51.9
AgNPs	8	Ni ₄ TP	26.9
PEI	8	Ni ₄ TP	23.3
Cu₂₀TP-based films (this work)			
AgNPs	16	Cu ₂₀ TP	65.1
AgNPs	8	Cu ₂₀ TP	33.4
PEI	16	Cu ₂₀ TP	28.5
K ₅ [SiW ₁₁ Fe(H ₂ O)O ₃₉]-PEI LBL film 14 assembly layers, pH 4 ⁶²			6
Li ₄ K ₁₆ [P ₈ W ₄₈ O ₁₈₄ Fe ₁₆ (OH) ₂₈ (H ₂ O) ₄]-Ru dendrimer LBL film, 11-21 assembly layers, pH 4.5 ⁶¹			22-38
K ₇ [H ₄ PW ₁₈ O ₆₂]-PAH LBL film 10 assembly layers, pH 1.2 ⁶³			0.5
K ₆ P ₂ W ₁₈ O ₆₂ -PAMAM LBL film 20 assembly layers, pH 1.1 ⁶⁴			2.9
[SiW ₁₂ O ₄₀]-[Ru(bipy) ₃] ₂ -modified GCE, pH 1 ⁶⁰			70
[SiW ₁₂ O ₄₀] ⁴⁻ -Nile blue composite carbon paste electrode, pH 1 ⁶⁵			178
H ₆ P ₂ Mo ₁₈ O ₆₂ -based composite with ordered mesoporous carbon, pH 1 ⁶⁶			41
W/WO ₃ electrode ⁶⁷			370
(Bu ₄ N) ₇ SiW ₉ O ₃₇ (C ₅ H ₅ -Ti) ₃ -doped composite ⁶⁸			9.5

Figure legends

Figure 1. LBL assembly of Ni₄TP- (A) and Cu₂₀TP-based (B) films monitored by voltammetry. Consecutive cyclic voltammograms obtained at GCE electrode modified with LBL films at different assembly stages in pH 4.5. Black curves: voltammetric responses of appropriated solutions HPAs (1 mM, pH2); **inset 1:** voltammetric response of GCE modified with first layers of HPA (red and blue curves: Ni₄TP- and Cu₂₀TP-based films, respectively); **inset 2:** voltammetric response of Cu₂₀TP solution in large current scale. Scan rate 100 mVs⁻¹.

Figure 2. LBL assembly of Ni₄TP- (A) and Cu₂₀TP-based (B) films monitored by impedance spectroscopy. Consecutive impedance spectra presented in Nyquist plots have been recorded at electrodes modified with LBL films at different assembly stages: green dots - bare GCE; cyan or blue dots – film-modified electrodes with HPAs terminal layers; red spectra - film-modified electrodes with AgNPs terminal layers; black dots – PDDA-modified electrode; solid black lines: curves obtained by fitting (0.1 M KCl, 10 mM K₃Fe(CN)₆, 10 mM K₄Fe(CN)₆, 0.23 V measurement potential, 10 mV amplitude). C: the dependence of charge transfer resistance on the assembly number.

Figure 3. Permeability of Ni₄TP-AgNP LBL films to positively-charged redox probe. Cyclic voltammetry have been obtained at electrodes modified with films of 8 (red curve) and 16 (black curve) as numbers of assembly. Dashed line represents the response of redox probe (1 mM hexaammineruthenim(III) chloride) on bare GCE (pH 5, scan rate 50 mV/s).

Figure 4. Nitrite and nitrate electrocatalytic reduction on Ni₄TP- (A) and Cu₂₀TP-based (B) LBL film-modified electrodes. Cyclic voltammograms have been obtained at GCE modified with LBL films of 16 numbers of assembly with HPA as a terminal layer at absence (black curves) and after additions of 5 mM sodium nitrite (red curves) or sodium nitrate (blue curves) pH 4.5, scan rate 10 mV/s; **C:** calibration plots for the nitrite (▲, ●) and nitrate (△, ○) detection obtained in potential of W-O II cathodic peak (-0.72 V) at electrodes modified

with 16 layers of assembly with Ni₄TP (green symbols) or Cu₂₀TP (blue symbols) as a terminal layers.

Figure 5. Evolution of topography observed with AFM during the LBL film assembly. **A**: PDDA-modified ITO glass slide; **B** and **C**: slides modified with Ni₄TP- (**B**) and Cu₂₀TP-based (**C**) films of 16 assembly layers with HPAs as a terminal layers.

Figure 6. The effect of terminal layer. The SEM images of ITO glass slides modified with Ni₄TP-AgNP LBL film with HPA (**A**) and AgNPs (**B**) terminal layers both reported at lower and higher magnification level.

Figure 1.

Figure 2.

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Figure 6.

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SUPPORTING INFORMATION

Enhancement of Nitrite and Nitrate Electrocatalytic Reduction through the Employment of Self-Assembled Layers of Nickel and Copper-Substituted Crown-Type Heteropolyanions

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Table S1. Relative composition of LBL films analysed by XPS

	Atomic %						
	N	P	C	W	Ag	Ni	Cu
Ni ₄ TP- AgNPs film of 16 assembly layers	7.6	2.0	39.8	9.5	1.5	0.1	---
Cu ₂₀ TP-AgNPs film of 8 assembly layers	6	1.9	42.3	8.4	2.4	---	0.2

Figure S1. **A:** UV-Vis spectrum of AgNPs. **B:** Typical TEM image of AgNPs.

Figure S2. The scan rate dependence of voltammetric response of electrode modified with Ni₄TP-AgNP LBL film of 16 assembly layers (pH 2). Inset: the dependence of W-O I cathodic peak current on a scan rate.

Figure S3. pH dependence of voltammetric response of electrode modified with Ni₄TP-AgNP LBL film of 16 layers of assembly. Black curve – pH2.5, green – pH 3, red – pH 3.5 and blue – pH 5.5. Inset: the dependences of formal redox potentials on pH for W-O I (■) and W-O II (□) redox processes.

Figure S4. Permeability of Ni₄TP-AgNP LBL films towards negatively-charged redox probe. Cyclic voltammetry have been obtained at at bare GCE (dotted line) and at electrodes modified with LBL films of 6 (solid line, HPA as a terminal layer) and 7 (dashed line, AgNP as a terminal layer) (0.1 M KCl, 10 mM K₃[Fe(CN)₆], scan rate 100 mV/s).

Figure S5. Effect of assembly number on the electrocatalytic reduction of nitrite on Ni_4TP - (A and B) and Cu_{20}TP -based (C and D) LBL film-modified electrodes. Cyclic voltammograms have been obtained at GCE modified with LBL films of 8 (A and C) and 16 (B and D) numbers of assembly with HPA as a terminal layer at absence (solid

lines) and after additions of sodium nitrite (dashed lines): 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM, 1 mM and 2 mM (pH 5, scan rate 50 mV/s).

Figure S6. Survey spectrum of Ni₄TP- AgNPs film of 16 assembly layers formed onto ITO coated glass slide.