Dendrimer-carbon nanotube layer-by-layer film as an efficient host matrix for electrogeneration of PtCo electrocatalysts
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In this paper we demonstrate that layer-by-layer (LbL) films of polyamidoamine (PAMAM) dendrimers and single-walled carbon nanotubes (SWCNTs) are efficient for controlling the morphology of electrogenerated cobalt (Co) and the platinum–cobalt (PtCo) alloy. While Co grew to the micrometer scale and poorly covered the ITO substrate, with the LbL matrix it was kept in the nanoscale regime and provided full substrate coverage. Pt-decorated Co nanoparticles were then generated by applying a single potential pulse in a solution containing simultaneously Co and Pt ions. Segregation of Pt and Co deposits was observed in field emission gun (FEG) images, but the PtCo alloy was probably formed to some extent according to X-ray diffraction analysis. The PtCo–LbL hybrid exhibited superior catalytic activity toward H₂O₂ reduction compared to the Pt-modified LbL film, which opens new prospects for applications in biosensing and fuel cells.

1. Introduction

Nanocrystalline materials exhibit significantly different physico-chemical properties from their microcrystalline analogues. As particles become smaller, the dispersion – defined as the ratio between the number of atoms on the surface and the total number of atoms – increases, and nanoparticles can display enhanced catalytic properties owing to a higher density of low coordinated atoms and excess electronic charge. The electro-oxidation of CO over carbon-supported Pt nanoparticles, for instance, depends strongly on the average particle size, with the peak potential in the cyclic voltammogram deviating from the value for bulk Pt as the particle size decreases below ca. 5 nm.

A variety of approaches are used to synthesize nanomaterials, which can be classified into physical (e.g. electron-beam lithography and pulsed laser deposition), chemical (e.g. colloidal technique) and electrochemical deposition methods. The latter is attractive because it is a relatively inexpensive and non-equipment-intensive method, with which fully dense or porous metallic materials can be produced in a single step. In addition, as the electron is a clean reactant, there is no adsorption of residual reducing agent that might hamper the reaction under study. Nanoelectrodeposition can be further assisted by incorporating matrices into the working electrode that can control the shape of the metallic nanostructure or prevent its excessive growth. An example is the electrodeposition of regular arrays of submicrometer-wide copper wires onto a patterned Langmuir–Blodgett (LB) film. The regular amino stripes of the 1,2-dipalmitoyl phosphatidylethanolamine (DPPC), which is the base of the LB film, served as a template for electrodeposition copper using an ultrathin electrochemical deposition method. Layer-by-layer (LbL) films have also been effective as host matrices for electrodeposition of nanostructures.

In a previous work, we showed that the thickness of a cobalt electrodeposits could be regulated by incorporating a dendrimer–carbon nanotube LbL film. In another study, we performed electroreduction of hydrogen peroxide onto a Pt-nanoparticle-modified LbL film, where synergy was achieved between Pt nanoparticles and carbon nanotubes.

In this study we investigated the electrochemical synthesis of PtCo nanostructures using LbL films made with dendrimer–carbon nanotubes as stabilizing matrices. Alloying Pt with Co might enhance the catalytic performance because Co, like ruthenium, is more efficient in breaking down water into adsorbed OH, a required species for the electroreduction of hydrogen peroxide. The results were compared with those for Pt.
and Co nanoparticles. The morphology of the electrodeposits was analyzed by atomic force microscopy (AFM) and field emission gun (FEG) microscopy, while X-ray diffraction (XRD) was used to infer their crystalline phases. The electrocatalytic activity toward hydrogen peroxide reduction of the deposits was investigated by cyclic voltammetry.

2. Experimental

Carboxylic acid functionalized single-walled carbon nanotubes (CNTs), G4 polyamidoamine dendrimer (PAMAM), H₂PtCl₆, CoCl₂ and H₂O₂ were purchased from Aldrich Co. 5-bilayer PAMAM–CNT LbL films were fabricated by immersing an ITO substrate alternately into a 1.0 g L⁻¹ polycationic PAMAM (5 min) solution at pH 4 and 10 mg/10 mL of anionic CNT solution (10 min) at pH 8 adjusted with NaOH. The 5-bilayer LbL film served as a working electrode in a Teflon electrochemical cell (geometric area of 0.3 cm²) with a Pt mesh and Ag/AgCl as counter and reference electrodes, respectively. The Teflon cell was clamped onto the LbL film and filled with a 3 mmol L⁻¹ H₂PtCl₆ + 0.11 mol L⁻¹ CoCl₂ solution for electrogeneration of the PtCo film. After the synthesis, the electrochemical cell was rinsed with deionised water and then filled with the H₂O₂-containing solutions (concentrations ranged from 0.010 mmol L⁻¹ to 10 mmol L⁻¹) for the electrochemical tests. All electrochemical measurements were carried out using a MicroAutolab III potentiostat/galvanostat controlled by the Nova software. Field emission gun microscopy (FEG) was conducted on a FEG-VP Zeiss Supra 35. Room temperature X-ray diffraction (XRD) patterns were recorded on an XRD-6000 Shimadzu diffractometer, using monochromatic Cu-Kα1 radiation (λ = 1.54056 Å). Ex situ AFM images of the PtCo-modified PAMAM–CNT LbL film were acquired at room temperature using a Shimadzu scanning probe microscope (SPM-9600). The resolution in the vertical z-direction for topographic images is 0.01 nm.

3. Results and discussion

3.1 PtCo electrodeposition onto PAMAM–CNT LbL films

Fig. 1A shows representative cyclic voltammograms (CVs) of the 5-bilayer PAMAM–CNT LbL film at 50 mV s⁻¹ in 3 mmol L⁻¹ H₂PtCl₆ + 0.11 mol L⁻¹ CoCl₂ + 0.1 mol L⁻¹ KCl and in a pure supporting electrolyte (KCl). A CV for electrodeposition of PtCo onto bare ITO is also presented for comparison. Upon sweeping the potential from 0.50 V vs. Ag/AgCl toward negative potentials, the cathodic currents between 0.20 V and −0.55 V for bare ITO were higher than those in the supporting electrolyte owing to platinum electrodeposition, as indicated in previous studies. Two cathodic peaks appear which are related to a mixture of kinetically inert Cl⁻–H₂O complexes as a consequence of the hexachloroplatinic acid speciation. Yasin et al. showed multiple cathodic waves in CVs of carbon and gold electrodes in H₂PtCl₆, resulting from reduction of Pt(IV) to Pt(0), with no evidence for Pt(ii) being a stable intermediate at any potential. The Pt(IV) reduction processes onto the LbL film are overlapped and shifted toward more negative potentials (between −0.48 V and −0.82 V). This is probably due to the chelating properties of PAMAM, therefore its interaction with the different Pt species led to higher reduction potentials.

In order to prove that those processes are indeed related only to Pt deposition, we conducted a chronopotentiometry experiment with the LbL film at −0.70 V and analyzed the electrodeposition by FEG microscopy. The image in Fig. 1B indicates densely packed, 10 nm nanoparticles. An EDX analysis revealed the particles to be solely composed of platinum. Cobalt electrodeposition sets in at potentials below −0.65 V vs. Ag/AgCl on bare ITO and at −0.90 V vs. Ag/AgCl on the LbL film (Fig. 1A). Therefore, the LbL film affects Co deposition, which is confirmed by the lower cathodic currents for the LbL film in that potential range. During the back scan the CV exhibited a current crossover (typical for a nucleation-controlled process) and the anodic currents between −0.60 V and 0.0 V vs. Ag/AgCl are correlated with Co dissolution.

3.2 Physical characterization

3.2.1 Pure cobalt electrodeposition onto LbL films. The FEG images in Fig. 2 show the effect of the LbL film on the
shape and size of cobalt electrodeposits. We start the discussion with Co because it is the most affected by the film. Fig. 2A depicts the morphology of Co made at $-0.95$ V vs. Ag/AgCl for 1 min onto bare ITO in 0.11 mol L$^{-1}$ CoCl$_2$ + 0.1 mol L$^{-1}$ KCl, featuring irregularly-shaped Co structures ranging from 500 nm to over 1 $\mu$m grown over a defective Co layer. On the other hand, with the PAMAM/CNT LbL film as a working electrode and keeping the other parameters constant (potential and time), a drastic effect on the particle size and shape occurred. Indeed, Fig. 2B shows nanohexagons aligned with the plane of the image as well as perpendicular to it. This flake-like structure can be better visualized in the topographic AFM image in Fig. 3 with perpendicular (brighter regions that look like needles) and tilted nanohexagons. Furthermore, the Co structures are densely packed and homogenously distributed over the entire surface, in contrast to the deposit produced in the absence of an LbL film. Hence, the LbL film acts effectively as a host matrix for a homogeneous generation of metallic nanostructures.

### 3.2.2 PtCo electrodeposition onto LbL films.

Fig. 4 displays a FEG image of the PtCo electrodeposited produced on a fresh LbL film at a constant potential of $-0.95$ V in 3 mmol L$^{-1}$ H$_2$PtCl$_6$ + 0.11 mol L$^{-1}$ CoCl$_2$ + 0.1 mol L$^{-1}$ KCl for 1 min. This is not surprising because the Co$^{2+}$ concentration is much higher than that of Pt$^{4+}$ and, as the electrodeposition of both metals is controlled by mass transfer, Co is deposited at a much higher rate than Pt due to the greater concentration gradient of the former. This conclusion is corroborated by the results for the LbL film in Fig. 1A, according to which the electrodeposition of Co (between $-0.90$ V and $-1.0$ V) produced a steeper curve than for Pt (between $-0.5$ V and $-0.80$ V). Since a steeper slope means faster reaction, Co is indeed electrodeposited at a much higher rate than Pt.

With the segregation of Pt and Co deposits, one may wonder whether some degree of alloying could have taken place. This possibility was checked by XRD experiments, and the diffractograms for bare ITO and the electrodeposits on LbL films are shown in Fig. 5. The XRD patterns revealed the typical responses of Pt and PtO$_{18}$ and cobalt oxide, CoO [ICSD 43458 and 53057]. Bragg diffraction peaks assigned to CoO appear because Co oxidizes easily under environmental conditions. All diffractograms lacked some characteristic peaks, which can be explained by the existence of a superlattice normal to those diffraction planes. The inset in Fig. 5 shows only one broad
peak (2θ = 39.5) between those of Pt and CoO for PtCo, which suggests a low amount of PtCo alloy might have been formed. The composition determined by EDX was Pt_{25}Co_{75} for the mixture obtained on the LbL film at −0.95 V.

3.3 Catalytic properties of PtCo–LbL film towards H$_2$O$_2$

The detection of H$_2$O$_2$ is relevant for a number of applications. Various oxidative enzymes (e.g., glucose oxidase and xanthine oxidase) are known to produce hydrogen peroxide as a by-product of the reaction they catalyze in the presence of molecular oxygen. H$_2$O$_2$ is also used for sterilization processes and as an important mediator in food, environmental and pharmaceutical analyses. Amperometric biosensors function by measuring the current variation upon addition of the enzyme substrate, which is due to the electrochemical transformation (oxidation or reduction) of the generated H$_2$O$_2$. Sensors based on recording the current from the electrochemical oxidation of the formed hydrogen peroxide are poorly selective as a consequence of the high operational potentials, at which the compounds normally contained in biological fluids (organic acids, neurotransmitters, and drugs) are co-oxidized, thus leading to overestimated analyte levels. Alternatively, reducing electrochemically H$_2$O$_2$ at lower working potentials (usually around 0 V vs. Ag/AgCl), a potential at which interfering species are electrochemically inert, would allow for a much more selective assay of the analyte.

Fig. 6 shows CVs illustrating the superior catalytic activity of the PtCo-modified PAMAM–CNT LbL film in comparison to the individual film constituents. The pristine LbL film is by far the least catalytic material among those studied in this work, with the electroreduction of H$_2$O$_2$ leading to a current peak at −0.77 V. Upon electrodepositing Co onto the PAMAM–CNT LbL film, a decrease of 370 mV was observed in the hydrogen peroxide reduction peak in comparison with the pristine LbL film. Lowering of the potential magnitude implies a decrease in the overpotential ($\eta$), an extra potential over the equilibrium value that must be applied to cause an electrochemical reaction at a certain rate. Hence, low $\eta$ means enhanced electrode kinetics. Obviously, a further catalysis enhancement took place upon incorporation of Pt into the LbL film, as indicated by the decrease of ca. 600 mV in the hydrogen peroxide reduction peak in comparison with the pristine LbL film. A further decrease of 100 mV hydrogen peroxide reduction peak, compared with the Pt-modified LbL film, has been achieved upon alloying Pt with Co (blue curve in Fig. 6).
Pt alloys with the first row transition metals exhibit higher catalytic activity for reactions such as oxygen reduction (ORR)\cite{21,22} and methanol oxidation (MOR).\cite{23,24} The catalytic enhancement in ORR has been ascribed to different factors: (i) Pt lattice contraction due to the introduction of alloying elements and hence reduction in the nearest neighbor distances which in turn brings about a more favorable and optimum Pt–Pt spacing;\cite{25} (ii) an increase of Pt d-electron band vacancies of the thin Pt surface layer caused by the underlying alloy;\cite{26} (iii) greater availability of oxygenated species provided by the less noble metal (cobalt, in our case). For MOR, adding cobalt to Pt leads to enhanced catalysis due to the lowering of the binding in Pt promoting the C–H cleavage at lower overpotentials, while cobalt oxides provide an oxygen source for carbon monoxide oxidation at lower potentials.

Concerning hydrogen peroxide reduction, the enhanced catalysis of PtCo might have arisen from the oxides provided by cobalt as follows: hydrogen peroxide reduction on Pt\cite{28} as well on Cu\cite{29} and stainless steel\cite{30} involves firstly a non-electrochemical dissociative adsorption $2\text{M} + \text{H}_2\text{O}_2 \rightarrow 2\text{M(OH)}_{\text{ads}}$ with a subsequent liberation of Pt sites in an electrochemical step $2\text{Pt(OH)}_{\text{ads}} + \text{H}^+ + 2\text{e}^- \rightarrow 2\text{Pt(H}_2\text{O)}$. As the OH$_{\text{ads}}$ adsorbate accelerates the reaction,\cite{31} any species that further provides OH$_{\text{ads}}$ could actively participate in the H$_2$O$_2$ reduction. In our case, although structural and electronic factors cannot be completely ruled out, it is reasonable to assume that the generation of OH$_{\text{ads}}$ on Co would facilitate hydrogen peroxide catalysis by further supplying oxygenated species and, hence, promote the reaction at lower potentials compared with those observed for the separated materials employed in this work. To our knowledge, this is the first report on the utilization of PtCo for reduction of hydrogen peroxide.

Another interesting feature was the role of the PAMAM–CNT LbL film on the stability of the electrogenerated metals. Fig. 7 shows photographs of just-made Co, Pt and PtCo deposits onto PAMAM–CNT LbL films and bare ITO after being thoroughly rinsed with ultrapure water. The Pt and PtCo deposits onto ITO lacked mechanical stability owing to discontinuities throughout the materials. On the other hand, all the deposits were quite stable onto the LbL film. After conducting H$_2$O$_2$ reduction the deposits onto ITO were barely observable while those onto the LbL film withstood at least ten CV cycles.

4. Conclusions

The use of the PAMAM–CNT LbL film as a matrix for the electrodeposition of PtCo films was decisive to achieve a more controllable morphology for the electrodeposits. Pt-decorated Co nanoparticles were obtained by applying a single potential pulse in a solution containing simultaneously cobalt and platinum ions. In comparison to the Pt-modified LbL film, the PtCo-LbL hybrid displayed a superior electrocatalytic activity toward H$_2$O$_2$ reduction. An important implication of our findings is related to the possible use of PtCo to reduce H$_2$O$_2$ at the cathode of fuel cells. Though PtCo is already used to reduce O$_2$ for a similar purpose, its use for H$_2$O$_2$ with higher efficiency than Pt certainly opens new prospects. Furthermore, the method based on LbL film as a matrix is entirely generic and may be extended to other materials, including AuPt.

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References

18 J. R. McBride, G. W. Graham, C. R. Peters and W. H. Weber, 
20 M.-L. Wu and L.-B. Lai, *Colloids Surf., A*, 2004, 244, 
149–157.
21 F. H. B. Lima, W. H. Lizcano-Valbuena, E. Teixeira-Neto, 
22 U. A. Paulus, A. Wokaun, G. G. Scherer, T. J. Schmidt, 
V. Stamenkovic, V. Radmilovic, N. M. Markovic and 
B*, 2006, 63, 137–149.
2299–2302.
26 T. Toda, H. Igarashi, H. Uchida and M. Watanabe, 
27 K. A. Daube, M. T. Paffett, S. Gottesfeld and C. T. Campbell, 
28 I. Katsounaros, W. B. Schneider, J. C. Meier, U. Benedikt, 
9911–9918.
30 S. Patra and N. Munichandraiah, *J. Chem. Sci.*, 2009, 121, 
675–683.
31 G. Flätgen, S. Wasle, M. Lübke, C. Eickes, G. Radhakrishnan, 