Facile fabrication of a Prussian Blue film by direct aerosol deposition on a Pt electrode†

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A facile aerosol deposition approach, which was simulated as feasible by density functional theory (DFT), was applied to synthesize a Prussian Blue (PB) film directly on a Pt electrode surface.
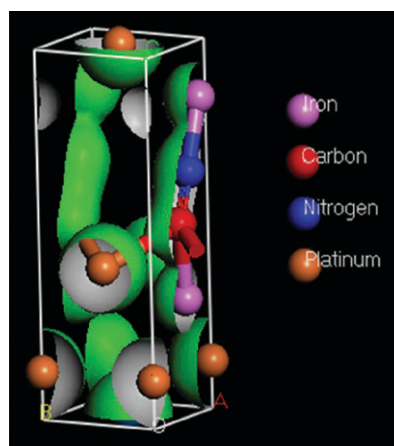
Prussian Blue (PB) is an old but important metal hexa-cyanoferrate. Since it was discovered in the early 1700s, many researchers have been interested in its special properties due to the different valences of the transitional metal Fe. Many research groups have undertaken a huge amount of work in the fields of magnetic properties, optical properties, electron transfer and biosensors.[1–5] PB can reduce the overpotential of H_2O_2 reduction to avoid interference from other substances, such as ascorbic acid,[6] and PB-based biosensors have advantages for selectivity and accuracy. During the last century, preparation methods for PB-modified electrodes were discovered and applied. Electrochemical deposition and self-assembly are the traditional, and still current, approaches to fabricating PB-modified electrodes.[7–9] However, these approaches have their own limits, as electrochemical deposition may not be easily used in large-scale production. In our previous work, we studied the preparation of PB-modified electrodes by a self-assembly approach.[10] This method requires the adsorption of a layer of polyelectrolyte to increase the electrostatic charge for attracting ferricyanide anions, $[Fe(CN)_6]^{4-}$, the poly-electrolyte layer possibly increasing the distance between the PB outer layer and the electrode surface, resulting in a decreased electron transfer rate. Consequently, we have developed here a novel and facile method for directly depositing PB on a Pt surface.

Firstly, we simulated the performance of PB adsorbed onto a Pt surface by density functional theory (DFT) using the Cambridge sequential total energy package (CASTEP). The Perdew–Burke–Ernzerhof functional (PBE) of the gradient-corrected functional was chosen as the exchange-correlation functional. The partial density of the states (PDOS), bond population and electron density difference were then calculated (ESI, S1†). Fig. 1 is the terminative optimization result of the Fe–C–N–Fe unit freely adsorbed onto the Pt(110) surface. The electron density isosurface is coloured in green,

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and the electron clouds of Fe, C and N are superimposed. It can be seen that the electron cloud of the Pt does not overlap with that of the C atom. Comparing the PDOS of C in PB crystals and PB adsorbed onto a Pt (110) surface (ESI, Fig. S2†), we found that there was an interaction between the Pt and C atoms; a van der Waals force. The calculated bond population confirmed the length of the C–Pt bond to be 2.19842 Å (ESI, Table S3†).

Based on the above simulation results, an aerosol deposition was adopted to prepare a Pt electrode modified with a PB film. 0.01 M $K_4[Fe(CN)_6]$ and $FeCl_3$ aqueous solutions were added to two ultrasonic nebulizers, respectively. After pre-treatment of the Pt electrode (ESI, S4†), $K_4[Fe(CN)_6]$ was adsorbed on the surface of the Pt by using the aerosol of $K_4[Fe(CN)_6]$ in an air-tight organic glass container at room temperature for 2 h. Subsequently, the $FeCl_3$ aerosol reacted with the $K_4[Fe(CN)_6]$ to form a PB film. Finally, the prepared electrode was washed with de-ionized water and heated at 100 °C for 1 h to dehydrate it.

Cyclic voltammetry (CV) and atomic force microscopy (AFM) characterizations were performed in order to gain information on the growth of the PB film.‡ PB film samples of different deposition times (2, 3, 4, 5, 6 and 7 h) were prepared on the Pt surface. The effect of the deposition time is shown in Fig. 2(a). The amount of PB was also calculated (Fig. 2(b)). The amount of PB on the Pt surface increased with the deposition time; it grew slowly at the beginning of the deposition process because only small amounts of PB existed as growth cores on the Pt electrode surface. The PB particles then grew more quickly than before. However, the growth rate slowed when the time reached 5 and 6 h; the surface of the
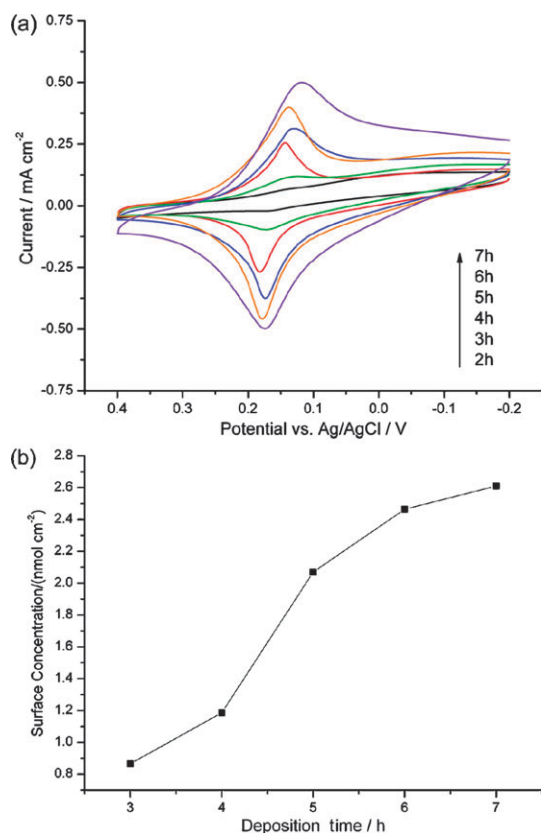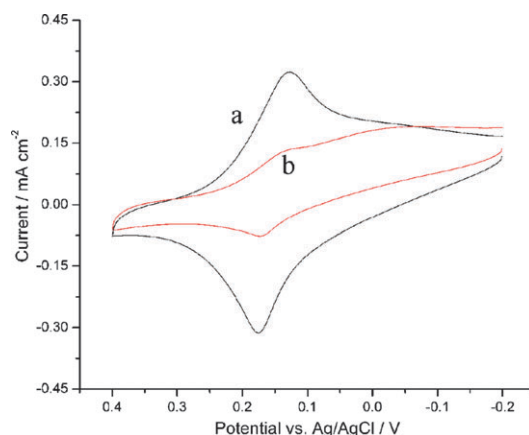

Fig. 1 The simulated electron density isosurface of optimized PB freely adsorbed onto a Pt(110) surface.

Fig. 2 (a) Cyclic voltammograms of PB-modified electrodes deposited for 2, 3, 4, 5, 6 and 7 h. (b) The amount of PB on the electrode surface, calculated from cyclic voltammograms *vs.* deposition time.

Fig. 3 The CV performance of PB-modified electrodes prepared in both deposition orders: (a) $K_4[Fe(CN)_6]$ was deposited first and $FeCl_3$ second; (b) deposited the reverse order.

electrode reaching PB saturation. The film morphology was visualised by AFM (ESI, S5†). From the AFM images, one can observe that the number and size of the PB particles increased with the deposition time. This result corresponds with the observed CV performance. For deposition times of 3, 4 and 5 h, the mean particle sizes were analysed to be *ca.* 84, 85 and 91 nm, respectively, while the observed average heights were *ca.* 17, 36 and 40 nm, respectively.

PB-modified electrodes were also prepared in the reverse deposition order to confirm the contribution of the interaction between the Pt and C atoms on PB deposition. The $FeCl_3$ aerosol was deposited first on the electrode surface in the container. The redox peak of the PB deposited first in the $K_4[Fe(CN)_6]$ aerosol was much higher (Fig. 3). This phenomenon could be explained as follows: when the Fe^{3+} ions cover the Pt surface first, most of the Pt atoms are enveloped. As a result, $[Fe(CN)_6]^{4-}$ ions are hardly able to make contact with the Pt surface. In this case, the formation of van der Waals forces is difficult. Consequently, most of the weakly-bound PB particles are washed away and the adsorbed amount remains small. Accordingly, to prepare the PB modified electrode, we suggest that the $K_4[Fe(CN)_6]$ aerosol is deposited first to form the

van der Waals forces between the Pt and C atoms on the Pt surface.

In summary, a facile aerosol deposition approach has been developed to directly fabricate a PB film on a Pt electrode, and the surface concentration of PB can be controlled by the deposition time. The simulation and experimental results demonstrate that the interaction between Pt and PB is based on van der Waals forces.

Notes and references

‡ All cyclic voltammograms were observed in 0.05 M phosphate buffer (pH = 6.5) containing 0.1 M KCl. The counter and reference electrodes were Pt wire and Ag/AgCl, respectively. The scan rate was 50 mV s^{-1}.

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