Supporting Information for

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

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Supplement 1 (S1). Simulative section

The performance of PB adsorbed on Pt surface was simulated at the level of DFT by Cambridge sequential total energy package (CASTEP). The Perdew–Burke–Ernzerhof functional (PBE) of gradient-corrected functional was chosen as the exchange-correlation functional. The electronic wavefunctions at each k-point were expanded in a plane-wave basis set up to 300eV. The Monkhorst-Pack k-points for the accuracy of the Brillouin zone sampling were set at fine level. Ultrasoft pseudopotential was used to perform with the lowest possible cutoff energy for the plane-wave basis set and the space was the reciprocal space. The SCF tolerance reached 1×10^{-6} eV/atom.

The Pt(110) surface was established through cutting from the Pt crystal and added the vacuum slab 8.00Å thickness. Then the Fe-C-N-Fe structure was added on the surface as the unit molecular for free adsorption. PB crystal was also optimized.

Supplement 2 (S2). Simulated PDOS images of C in a PB crystal and PB adsorbed on Pt surface.

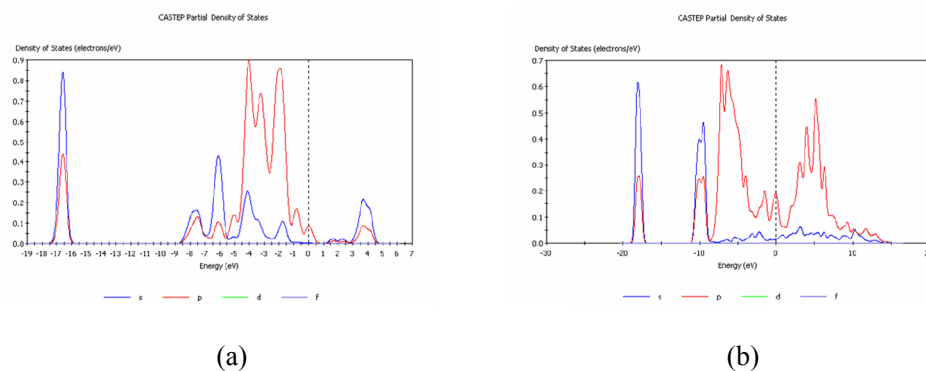(a)   (b)

Fig. S2

Fig. S2. The partial density of states (PDOS) image for C in (a) PB crystal; (b) PB adsorbed on Pt (110) surface. (The colorful lines presented the contributions of different atom orbits.)

PDOS images presented the information of electronic structure. Fig. S2 illustrates the electronic orbit contributions of C atoms to the system of a PB crystal and a PB crystal on Pt (110) surface. The s and p orbits give the main influence to the whole system. The two images of the C atoms are different. Considering the simulative structure, we can conclude that there is an interaction between C and Pt atoms.

Supplement 3 (S3). Table of simulated bond population and length.

Tab. S3

Bond	Population	Length(Å)
C 001 -- N 001	1.49	1.24068
N 001 -- Fe 001	0.67	1.73899
C 001 -- Pt 002	0.36	2.19842
C 001 -- Fe 002	0.35	1.87029
Fe 002 -- Pt 003	0.09	2.55345
Pt 001 -- Pt 003	0.36	2.55642
Fe 002 -- Pt 002	0.35	2.56508
Fe 001 -- Pt 001	0.75	2.59582

Table. S3. Data of simulated bond population and length obtained by Cambridge sequential total

energy package (CASTEP).

Bond population is used to assess the covalent or ionic nature of a bond. The high

value of the bond population indicates a covalent bond, while a low value indicates

other interactions. We defined the Pt atom which was combined with C in Fig. 1 as Pt

002 before simulation. There was the interaction between Pt and C from the Table. It

should be noted that the calculation result did not present the N-Pt bond. It was

concluded that N atoms of PB had no contribution to adsorption.

Supplement 4 (S4). Experimental section.

1. Chemicals and Reagents. $K_4Fe(CN)_6 \cdot 3H_2O$ (Sigma-Aldrich) and $FeCl_3 \cdot 6H_2O$ (Sigma - Aldrich) were of analytical purity and used without further purification. All solutions were prepared with deionized water.

2. Pretreatment of Pt electrode. For keeping the Pt electrode clean, pretreatment was used on the platinum foil surface(7×2 mm^2). The surface of the Pt electrode was polished as mirror using metallographical sand paper, then dipped into the Piranha solution (7:3 mixture of H_2SO_4/H_2O_2. Caution: *The mixture is strongly oxidizing and may detonate upon contact with organic material*) for 30 min and rinsed with water. After ultrasonic washing in water for 30 min, the Pt electrode was clean.

3. Aerosol deposition of PB film on Pt electrode. For the deposition of PB films, two solutions were prepared. Solution 1: 0.01 M K4[Fe(CN)6] + 0.1 M KCl + 0.1 M HCl. Solution 2: 0.01 M FeCl3 + 0.1 M KCl + 0.1 M HCl. The prepared $K_4Fe(CN)_6$ and $FeCl_3$ solutions were respectively filled in two ultrasonic nebulizers (Shanghai Yu Yue Medical Equipment Co., Ltd, China; Size: $240*130*200$ mm^3; Power: 50W; Frequency: 1.7 MHz.). The Pt electrode was fixed in one airtight organic glass container. Then, $K_4Fe(CN)_6$ aerosol was continuously injected into the container for two hours. The average injection rate is 1.1 ml·min^{-1}. Subsequently, $FeCl_3$ aerosol was deposited after the former aerosol exhausted. This process lasted two hours. Finally, the prepared electrodes were cleaned with deionized water and heated at 100 ^{O}C for one hour to dehydrate. The PB film samples of different deposition time (2, 3, 4, 5, 6 and 7 h) were also prepared for characterization. Both of the $K_4Fe(CN)_6$ and $FeCl_3$ aerosols were adsorbed in the same period.

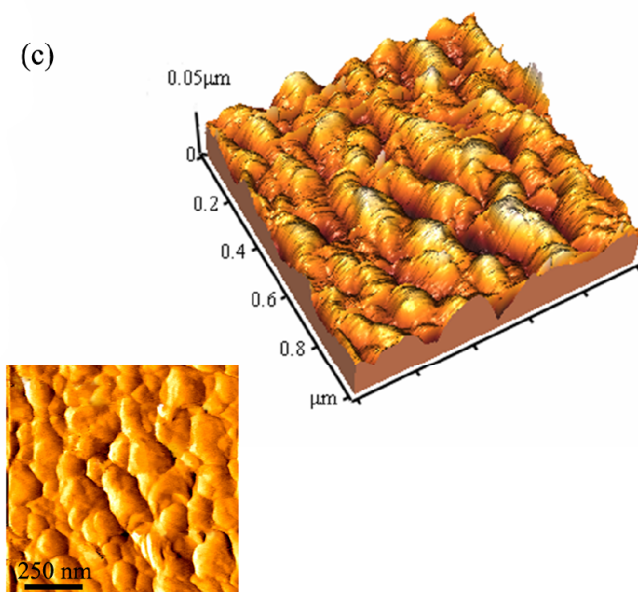## Supplement 5 (S5). AFM images of PB films for different deposition time

(a)

(b)
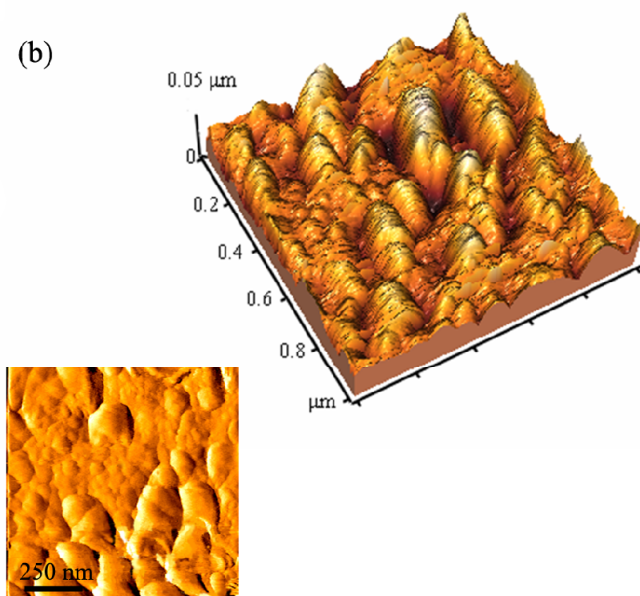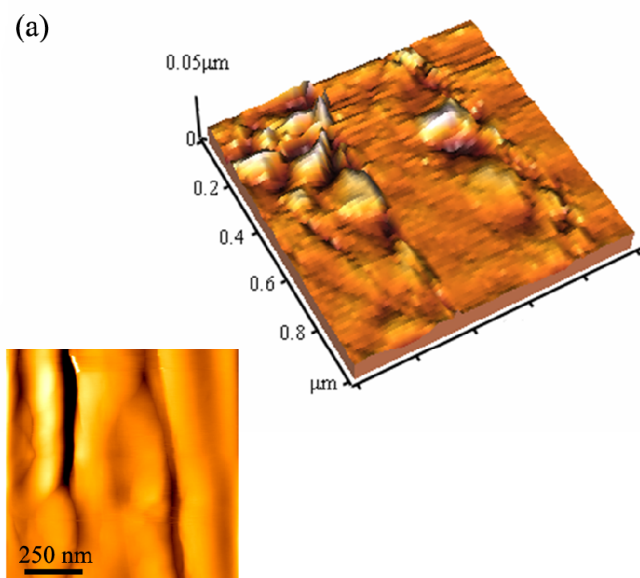
Fig. S5

Fig. S5. AFM 2D and 3D images of PB film which were prepare for 3 h (a), 4 h (b) and 5 h (c)

on the Pt surface

AFM characterization operating in contact mode was used to study the morphology of

PB films which were prepared on the Pt surface using the aerosol deposition approach.

Samples of different total deposition time (3 h, 4 h and 5 h) were compared. From the

2D images, we can find that the amount of PB particles increased with the deposition

time, and the whole Pt surface was covered by PB particles. Meanwhile, the particle

size also increased with the time. For the deposition time of 3, 4 and 5 h the mean

particle sizes were analysed to be ca. 84nm, 85 nm and 91 nm, respectively, while the

observed average heights were ca. 17 nm, 36 nm and 40 nm, respectively.