Supporting Information

Template-free growth of regular nano-structured Prussian blue on Platinum surface and its application in biosensor with high sensitivity

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Supplement 1 (S1). Optimization of PB crystal cell.

Convergence tolerance setting: (1) energy tolerance was 10^{-5} eV; (2) maximum force, stress and displacement was set as 0.03 eV, 0.05 GPa and 0.001 Å, respectively. The energy cutoff was adjusted to be 220 eV for reaching convergence.

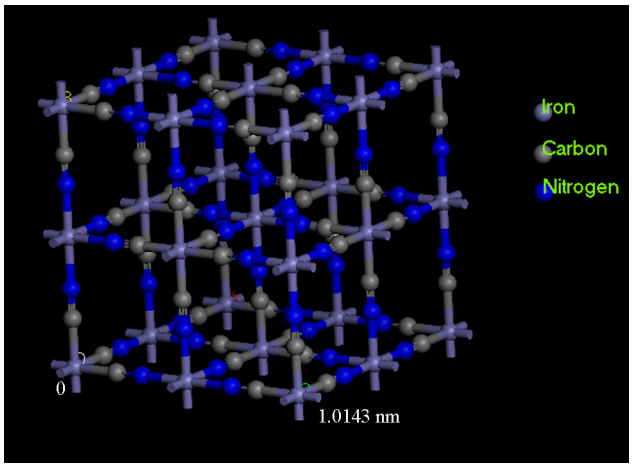

Figure S1. The image of Prussian blue crystal cell after optimization by DFT simulation.

The original unit cell of PB was established before optimization. The structure was set as face-center-cubic type with 1.02 nm lattice size. For keeping the structure stable, we chose a fixed basis size for cell optimization, which depended on the cell size and shape. The setting force can continuously condense the cell till the most stable structure with the lowest energy of all atoms was reached. At the beginning, the energy of original cell was -17136.61 eV. After the 11 BFGS iterations, the energy was decreased to -17139.22 eV and the final structure is shown in Figure S1. The optimized cell lattice was calculated to be 1.0143 nm

Fractional Coordinates and Energies of optimized structure of PB:

Original structure:
Initial energy: -1.71366132E+004 eV

Element	Fractional coordinates of atoms		
	x	y	z
C	0.190196	0.000000	0.000000
C	0.000000	0.190196	0.000000
C	0.000000	0.000000	0.190196
C	0.809804	0.000000	0.000000
C	0.000000	0.809804	0.000000
C	0.000000	0.000000	0.809804
C	0.309804	0.000000	0.500000
C	0.690196	0.000000	0.500000
C	0.000000	0.309804	0.500000
C	0.000000	0.690196	0.500000
C	0.190196	0.500000	0.500000
C	0.809804	0.500000	0.500000
C	0.500000	0.190196	0.500000
C	0.500000	0.809804	0.500000
C	0.309804	0.500000	0.000000
C	0.690196	0.500000	0.000000
C	0.500000	0.309804	0.000000
C	0.500000	0.690196	0.000000
C	0.000000	0.500000	0.309804
C	0.000000	0.500000	0.690196
C	0.500000	0.000000	0.309804
C	0.500000	0.000000	0.690196
C	0.500000	0.500000	0.190196
C	0.500000	0.500000	0.809804
N	0.302941	0.000000	0.000000
N	0.000000	0.302941	0.000000
N	0.000000	0.000000	0.302941
N	0.697059	0.000000	0.000000
N	0.000000	0.697059	0.000000
N	0.000000	0.000000	0.697059
N	0.197059	0.000000	0.500000
N	0.802941	0.000000	0.500000
N	0.000000	0.197059	0.500000
N	0.000000	0.802941	0.500000
N	0.302941	0.500000	0.500000
N	0.697059	0.500000	0.500000
N	0.500000	0.302941	0.500000
N	0.500000	0.697059	0.500000
N	0.197059	0.500000	0.000000
N	0.802941	0.500000	0.000000
N	0.500000	0.197059	0.000000
N	0.500000	0.802941	0.000000
N	0.000000	0.500000	0.197059
N	0.000000	0.500000	0.802941
N	0.500000	0.000000	0.197059
N	0.500000	0.000000	0.802941
N	0.500000	0.500000	0.302941
N	0.500000	0.500000	0.697059
Fe	0.000000	0.000000	0.000000
Fe	0.500000	0.000000	0.000000
Fe	0.000000	0.500000	0.000000
Fe	0.000000	0.000000	0.500000
Fe	0.500000	0.000000	0.500000
Fe	0.000000	0.500000	0.500000
Fe	0.500000	0.500000	0.500000
Fe	0.500000	0.500000	0.000000

Iteration 1:
Energy: -1.71371273E+004 eV

Element	Fractional coordinates of atoms		
	x	y	z
C	0.188357	0.000000	0.000000
C	0.000000	0.188357	0.000000
C	0.000000	0.000000	0.188357
C	0.811643	0.000000	0.000000
C	0.000000	0.811643	0.000000
C	0.000000	0.000000	0.811643
C	0.311466	0.000000	0.500000
C	0.688533	0.000000	0.500000
C	0.000000	0.311466	0.500000
C	0.000000	0.688534	0.500000
C	0.188369	0.500000	0.500000
C	0.811631	0.500000	0.500000
C	0.500000	0.188369	0.500000
C	0.500000	0.811631	0.500000

C	0.311466	0.500000	0.000000	N	0.500000	0.305112	0.500000
C	0.688534	0.500000	0.000000	N	0.500000	0.694888	0.500000
C	0.500000	0.311466	0.000000	N	0.194863	0.500000	0.000000
C	0.500000	0.688534	0.000000	N	0.805137	0.500000	0.000000
C	0.000000	0.500000	0.311466	N	0.500000	0.194863	0.000000
C	0.000000	0.500000	0.688534	N	0.500000	0.805137	0.000000
C	0.500000	0.000000	0.311467	N	0.000000	0.500000	0.194863
C	0.500000	0.000000	0.688533	N	0.000000	0.500000	0.805137
C	0.500000	0.500000	0.188369	N	0.500000	0.000000	0.194863
C	0.500000	0.500000	0.811631	N	0.500000	0.000000	0.805137
N	0.305116	0.000000	0.000000	N	0.500000	0.500000	0.305113
N	0.000000	0.305115	0.000000	N	0.500000	0.500000	0.694888
N	0.000000	0.000000	0.305115	Fe	0.000000	0.000000	0.000000
N	0.694884	0.000000	0.000000	Fe	0.500000	0.000000	0.000000
N	0.000000	0.694885	0.000000	Fe	0.000000	0.500000	0.000000
N	0.000000	0.000000	0.694885	Fe	0.000000	0.000000	0.500000
N	0.194863	0.000000	0.500000	Fe	0.500000	0.000000	0.500000
N	0.805137	0.000000	0.500000	Fe	0.000000	0.500000	0.500000
N	0.000000	0.194863	0.500000	Fe	0.500000	0.500000	0.500000
N	0.000000	0.805137	0.500000	Fe	0.500000	0.500000	0.000000
N	0.305112	0.500000	0.500000				
N	0.694888	0.500000	0.500000				

Iteration 2:
Energy: -1.71374495E+004 eV

Element	Fractional coordinates of atoms			C	0.500000	0.310809	0.000000
	x	y	z	C	0.500000	0.689191	0.000000
C	0.189028	0.000000	0.000000	C	0.000000	0.500000	0.310809
C	0.000000	0.189027	0.000000	C	0.000000	0.500000	0.689191
C	0.000000	0.000000	0.189028	C	0.500000	0.000000	0.310809
C	0.810972	0.000000	0.000000	C	0.500000	0.000000	0.689191
C	0.000000	0.810973	0.000000	C	0.500000	0.500000	0.189026
C	0.000000	0.000000	0.810972	C	0.500000	0.500000	0.810974
C	0.310809	0.000000	0.500000	N	0.304727	0.000000	0.000000
C	0.689191	0.000000	0.500000	N	0.000000	0.304729	0.000000
C	0.000000	0.310809	0.500000	N	0.000000	0.000000	0.304728
C	0.000000	0.689191	0.500000	N	0.695273	0.000000	0.000000
C	0.189026	0.500000	0.500000	N	0.000000	0.695271	0.000000
C	0.810974	0.500000	0.500000	N	0.000000	0.000000	0.695272
C	0.500000	0.189025	0.500000	N	0.195165	0.000000	0.500000
C	0.500000	0.810975	0.500000	N	0.804835	0.000000	0.500000
C	0.310809	0.500000	0.000000	N	0.000000	0.195164	0.500000
C	0.689191	0.500000	0.000000	N	0.000000	0.804836	0.500000

N	0.304729	0.500000	0.500000	N	0.500000	0.000000	0.804836
N	0.695271	0.500000	0.500000	N	0.500000	0.500000	0.304729
N	0.500000	0.304730	0.500000	N	0.500000	0.500000	0.695271
N	0.500000	0.695270	0.500000	Fe	0.000000	0.000000	0.000000
N	0.195165	0.500000	0.000000	Fe	0.500000	0.000000	0.000000
N	0.804835	0.500000	0.000000	Fe	0.000000	0.500000	0.000000
N	0.500000	0.195164	0.000000	Fe	0.000000	0.000000	0.500000
N	0.500000	0.804836	0.000000	Fe	0.500000	0.000000	0.500000
N	0.000000	0.500000	0.195164	Fe	0.000000	0.500000	0.500000
N	0.000000	0.500000	0.804836	Fe	0.500000	0.500000	0.500000
N	0.500000	0.000000	0.195164	Fe	0.500000	0.500000	0.000000

Iteration 3:
Energy: -1.71381462E+004 eV

Element	Fractional coordinates of atoms			N	0.694952	0.000000	0.000000
	x	y	z	N	0.000000	0.694955	0.000000
C	0.189829	0.000000	0.000000	N	0.000000	0.000000	0.694952
C	0.000000	0.189833	0.000000	N	0.194639	0.000000	0.500000
C	0.000000	0.000000	0.189829	N	0.805361	0.000000	0.500000
C	0.810171	0.000000	0.000000	N	0.000000	0.194639	0.500000
C	0.000000	0.810167	0.000000	N	0.000000	0.805361	0.500000
C	0.000000	0.000000	0.810172	N	0.305037	0.500000	0.500000
C	0.309791	0.000000	0.500000	N	0.694963	0.500000	0.500000
C	0.690209	0.000000	0.500000	N	0.500000	0.305032	0.500000
C	0.000000	0.309789	0.500000	N	0.500000	0.694968	0.500000
C	0.000000	0.690211	0.500000	N	0.194639	0.500000	0.000000
C	0.189826	0.500000	0.500000	N	0.805361	0.500000	0.000000
C	0.810174	0.500000	0.500000	N	0.500000	0.194640	0.000000
C	0.500000	0.189830	0.500000	N	0.500000	0.805360	0.000000
C	0.500000	0.810170	0.500000	N	0.000000	0.500000	0.194638
C	0.309790	0.500000	0.000000	N	0.000000	0.500000	0.805362
C	0.690210	0.500000	0.000000	N	0.500000	0.000000	0.194639
C	0.500000	0.309788	0.000000	N	0.500000	0.000000	0.805361
C	0.500000	0.690212	0.000000	N	0.500000	0.500000	0.305036
C	0.000000	0.500000	0.309789	N	0.500000	0.500000	0.694964
C	0.000000	0.500000	0.690211	Fe	0.000000	0.000000	0.000000
C	0.500000	0.000000	0.309788	Fe	0.500000	0.000000	0.000000
C	0.500000	0.000000	0.690211	Fe	0.000000	0.500000	0.000000
C	0.500000	0.500000	0.189827	Fe	0.000000	0.000000	0.500000
C	0.500000	0.500000	0.810173	Fe	0.500000	0.000000	0.500000
N	0.305048	0.000000	0.000000	Fe	0.000000	0.500000	0.500000
N	0.000000	0.305045	0.000000	Fe	0.500000	0.500000	0.500000
N	0.000000	0.000000	0.305048	Fe	0.500000	0.500000	0.000000

Iteration 4:
Energy: -1.71391239E+004 eV

Element	Fractional coordinates of atoms		
	x	y	z
C	0.191725	0.000000	0.000000
C	0.000000	0.191725	0.000000
C	0.000000	0.000000	0.191723
C	0.808275	0.000000	0.000000
C	0.000000	0.808275	0.000000
C	0.000000	0.000000	0.808277
C	0.307024	0.000000	0.500000
C	0.692976	0.000000	0.500000
C	0.000000	0.307023	0.500000
C	0.000000	0.692977	0.500000
C	0.191714	0.500000	0.500000
C	0.808286	0.500000	0.500000
C	0.500000	0.191708	0.500000
C	0.500000	0.808292	0.500000
C	0.307017	0.500000	0.000000
C	0.692983	0.500000	0.000000
C	0.500000	0.307022	0.000000
C	0.500000	0.692978	0.000000
C	0.000000	0.500000	0.307016
C	0.000000	0.500000	0.692984
C	0.500000	0.000000	0.307022
C	0.500000	0.000000	0.692978
C	0.500000	0.500000	0.191714
C	0.500000	0.500000	0.808286
N	0.307154	0.000000	0.000000
N	0.000000	0.307157	0.000000
N	0.000000	0.000000	0.307153
N	0.692846	0.000000	0.000000
N	0.000000	0.692843	0.000000
N	0.000000	0.000000	0.692847
N	0.191715	0.000000	0.500000
N	0.808285	0.000000	0.500000
N	0.000000	0.191710	0.500000
N	0.000000	0.808290	0.500000
N	0.307132	0.500000	0.500000
N	0.692868	0.500000	0.500000
N	0.500000	0.307135	0.500000
N	0.500000	0.692865	0.500000
N	0.191711	0.500000	0.000000
N	0.808289	0.500000	0.000000
N	0.500000	0.191707	0.000000
N	0.500000	0.808293	0.000000
N	0.000000	0.500000	0.191710
N	0.000000	0.500000	0.808290
N	0.500000	0.000000	0.191711
N	0.500000	0.000000	0.808289
N	0.500000	0.500000	0.307135
N	0.500000	0.500000	0.692865
Fe	0.000000	0.000000	0.000000
Fe	0.500000	0.000000	0.000000
Fe	0.000000	0.500000	0.000000
Fe	0.000000	0.000000	0.500000
Fe	0.500000	0.000000	0.500000
Fe	0.000000	0.500000	0.500000
Fe	0.500000	0.500000	0.500000
Fe	0.500000	0.500000	0.000000

Iteration 5:
Energy: -1.71392093E+004 eV

Element	Fractional coordinates of atoms		
	x	y	z
C	0.191632	0.000000	0.000000
C	0.000000	0.191634	0.000000
C	0.000000	0.000000	0.191631
C	0.808368	0.000000	0.000000
C	0.000000	0.808366	0.000000
C	0.000000	0.000000	0.808369
C	0.306982	0.000000	0.500000
C	0.693018	0.000000	0.500000
C	0.000000	0.306978	0.500000
C	0.000000	0.693022	0.500000
C	0.191624	0.500000	0.500000
C	0.808376	0.500000	0.500000
C	0.500000	0.191624	0.500000
C	0.500000	0.808376	0.500000

C	0.306976	0.500000	0.000000	N	0.692371	0.500000	0.500000
C	0.693024	0.500000	0.000000	N	0.500000	0.307627	0.500000
C	0.500000	0.306976	0.000000	N	0.500000	0.692373	0.500000
C	0.500000	0.693024	0.000000	N	0.191088	0.500000	0.000000
C	0.000000	0.500000	0.306975	N	0.808912	0.500000	0.000000
C	0.000000	0.500000	0.693025	N	0.500000	0.191090	0.000000
C	0.500000	0.000000	0.306978	N	0.500000	0.808910	0.000000
C	0.500000	0.000000	0.693022	N	0.000000	0.500000	0.191088
C	0.500000	0.500000	0.191626	N	0.000000	0.500000	0.808912
C	0.500000	0.500000	0.808374	N	0.500000	0.000000	0.191092
N	0.307641	0.000000	0.000000	N	0.500000	0.000000	0.808908
N	0.000000	0.307641	0.000000	N	0.500000	0.500000	0.307630
N	0.000000	0.000000	0.307639	N	0.500000	0.500000	0.692370
N	0.692359	0.000000	0.000000	Fe	0.000000	0.000000	0.000000
N	0.000000	0.692359	0.000000	Fe	0.500000	0.000000	0.000000
N	0.000000	0.000000	0.692361	Fe	0.000000	0.500000	0.000000
N	0.191094	0.000000	0.500000	Fe	0.000000	0.000000	0.500000
N	0.808906	0.000000	0.500000	Fe	0.500000	0.000000	0.500000
N	0.000000	0.191091	0.500000	Fe	0.000000	0.500000	0.500000
N	0.000000	0.808909	0.500000	Fe	0.500000	0.500000	0.500000
N	0.307629	0.500000	0.500000	Fe	0.500000	0.500000	0.000000

Iteration 6:
Energy: -1.71392179E+004 eV

Element	Fractional coordinates of atoms			C	0.500000	0.692838	0.000000
	x	y	z	C	0.000000	0.500000	0.307160
C	0.191409	0.000000	0.000000	C	0.000000	0.500000	0.692840
C	0.000000	0.191409	0.000000	C	0.500000	0.000000	0.307165
C	0.000000	0.000000	0.191407	C	0.500000	0.000000	0.692835
C	0.808591	0.000000	0.000000	C	0.500000	0.500000	0.191412
C	0.000000	0.808591	0.000000	C	0.500000	0.500000	0.808588
C	0.000000	0.000000	0.808594	N	0.307649	0.000000	0.000000
C	0.307167	0.000000	0.500000	N	0.000000	0.307646	0.000000
C	0.692833	0.000000	0.500000	N	0.000000	0.000000	0.307646
C	0.000000	0.307164	0.500000	N	0.692351	0.000000	0.000000
C	0.000000	0.692836	0.500000	N	0.000000	0.692354	0.000000
C	0.191411	0.500000	0.500000	N	0.000000	0.000000	0.692354
C	0.808589	0.500000	0.500000	N	0.191073	0.000000	0.500000
C	0.500000	0.191409	0.500000	N	0.808927	0.000000	0.500000
C	0.500000	0.808591	0.500000	N	0.000000	0.191069	0.500000
C	0.307160	0.500000	0.000000	N	0.000000	0.808931	0.500000
C	0.692840	0.500000	0.000000	N	0.307650	0.500000	0.500000
C	0.500000	0.307162	0.000000	N	0.692350	0.500000	0.500000

N	0.500000	0.307649	0.500000	N	0.500000	0.500000	0.307650
N	0.500000	0.692351	0.500000	N	0.500000	0.500000	0.692350
N	0.191071	0.500000	0.000000	Fe	0.000000	0.000000	0.000000
N	0.808929	0.500000	0.000000	Fe	0.500000	0.000000	0.000000
N	0.500000	0.191067	0.000000	Fe	0.000000	0.500000	0.000000
N	0.500000	0.808933	0.000000	Fe	0.000000	0.000000	0.500000
N	0.000000	0.500000	0.191071	Fe	0.500000	0.000000	0.500000
N	0.000000	0.500000	0.808929	Fe	0.000000	0.500000	0.500000
N	0.500000	0.000000	0.191070	Fe	0.500000	0.500000	0.500000
N	0.500000	0.000000	0.808930	Fe	0.500000	0.500000	0.000000

Iteration 7:
Energy: -1.71392191E+004 eV

Element	Fractional coordinates of atoms			N	0.692305	0.000000	0.000000
	x	y	z	N	0.000000	0.692307	0.000000
C	0.191409	0.000000	0.000000	N	0.000000	0.000000	0.692307
C	0.000000	0.191407	0.000000	N	0.190957	0.000000	0.500000
C	0.000000	0.000000	0.191406	N	0.809043	0.000000	0.500000
C	0.808591	0.000000	0.000000	N	0.000000	0.190953	0.500000
C	0.000000	0.808593	0.000000	N	0.000000	0.809047	0.500000
C	0.000000	0.000000	0.808594	N	0.307704	0.500000	0.500000
C	0.307096	0.000000	0.500000	N	0.692296	0.500000	0.500000
C	0.692904	0.000000	0.500000	N	0.500000	0.307702	0.500000
C	0.000000	0.307093	0.500000	N	0.500000	0.692298	0.500000
C	0.000000	0.692907	0.500000	N	0.190954	0.500000	0.000000
C	0.191422	0.500000	0.500000	N	0.809046	0.500000	0.000000
C	0.808578	0.500000	0.500000	N	0.500000	0.190953	0.000000
C	0.500000	0.191420	0.500000	N	0.500000	0.809047	0.000000
C	0.500000	0.808580	0.500000	N	0.000000	0.500000	0.190952
C	0.307092	0.500000	0.000000	N	0.000000	0.500000	0.809048
C	0.692908	0.500000	0.000000	N	0.500000	0.000000	0.190955
C	0.500000	0.307091	0.000000	N	0.500000	0.000000	0.809045
C	0.500000	0.692909	0.000000	N	0.500000	0.500000	0.307704
C	0.000000	0.500000	0.307092	N	0.500000	0.500000	0.692296
C	0.000000	0.500000	0.692908	Fe	0.000000	0.000000	0.000000
C	0.500000	0.000000	0.307093	Fe	0.500000	0.000000	0.000000
C	0.500000	0.000000	0.692907	Fe	0.000000	0.500000	0.000000
C	0.500000	0.500000	0.191422	Fe	0.000000	0.000000	0.500000
C	0.500000	0.500000	0.808578	Fe	0.500000	0.000000	0.500000
N	0.307695	0.000000	0.000000	Fe	0.000000	0.500000	0.500000
N	0.000000	0.307693	0.000000	Fe	0.500000	0.500000	0.500000
N	0.000000	0.000000	0.307693	Fe	0.500000	0.500000	0.000000

Iteration 8:
Energy: -1.71392209E+004 eV

Element	Fractional coordinates of atoms		
	x	y	z
C	0.191104	0.000000	0.000000
C	0.000000	0.191099	0.000000
C	0.000000	0.000000	0.191102
C	0.808896	0.000000	0.000000
C	0.000000	0.808901	0.000000
C	0.000000	0.000000	0.808898
C	0.307265	0.000000	0.500000
C	0.692735	0.000000	0.500000
C	0.000000	0.307262	0.500000
C	0.000000	0.692738	0.500000
C	0.191164	0.500000	0.500000
C	0.808836	0.500000	0.500000
C	0.500000	0.191165	0.500000
C	0.500000	0.808835	0.500000
C	0.307268	0.500000	0.000000
C	0.692732	0.500000	0.000000
C	0.500000	0.307261	0.000000
C	0.500000	0.692739	0.000000
C	0.000000	0.500000	0.307267
C	0.000000	0.500000	0.692733
C	0.500000	0.000000	0.307263
C	0.500000	0.000000	0.692737
C	0.500000	0.500000	0.191164
C	0.500000	0.500000	0.808836
N	0.307390	0.000000	0.000000
N	0.000000	0.307390	0.000000
N	0.000000	0.000000	0.307387
N	0.692610	0.000000	0.000000
N	0.000000	0.692610	0.000000
N	0.000000	0.000000	0.692613
N	0.191104	0.000000	0.500000
N	0.808896	0.000000	0.500000
N	0.000000	0.191101	0.500000
N	0.000000	0.808899	0.500000
N	0.307446	0.500000	0.500000
N	0.692554	0.500000	0.500000
N	0.500000	0.307443	0.500000
N	0.500000	0.692557	0.500000
N	0.191098	0.500000	0.000000
N	0.808902	0.500000	0.000000
N	0.500000	0.191102	0.000000
N	0.500000	0.808898	0.000000
N	0.000000	0.500000	0.191096
N	0.000000	0.500000	0.808904
N	0.500000	0.000000	0.191104
N	0.500000	0.000000	0.808896
N	0.500000	0.500000	0.307445
N	0.500000	0.500000	0.692555
Fe	0.000000	0.000000	0.000000
Fe	0.500000	0.000000	0.000000
Fe	0.000000	0.500000	0.000000
Fe	0.000000	0.000000	0.500000
Fe	0.500000	0.000000	0.500000
Fe	0.000000	0.500000	0.500000
Fe	0.500000	0.500000	0.500000
Fe	0.500000	0.500000	0.000000

Iteration 9:
Energy: -1.71392200E+004 eV

Element	Fractional coordinates of atoms		
	x	y	z
C	0.191157	0.000000	0.000000
C	0.000000	0.191160	0.000000
C	0.000000	0.000000	0.191155
C	0.808843	0.000000	0.000000
C	0.000000	0.808840	0.000000
C	0.000000	0.000000	0.808845
C	0.307181	0.000000	0.500000
C	0.692819	0.000000	0.500000
C	0.000000	0.307179	0.500000
C	0.000000	0.692821	0.500000
C	0.191212	0.500000	0.500000
C	0.808788	0.500000	0.500000
C	0.500000	0.191208	0.500000
C	0.500000	0.808792	0.500000

C	0.307170	0.500000	0.000000	N	0.692500	0.500000	0.500000
C	0.692830	0.500000	0.000000	N	0.500000	0.307501	0.500000
C	0.500000	0.307178	0.000000	N	0.500000	0.692499	0.500000
C	0.500000	0.692822	0.000000	N	0.191057	0.500000	0.000000
C	0.000000	0.500000	0.307170	N	0.808943	0.500000	0.000000
C	0.000000	0.500000	0.692830	N	0.500000	0.191046	0.000000
C	0.500000	0.000000	0.307180	N	0.500000	0.808954	0.000000
C	0.500000	0.000000	0.692820	N	0.000000	0.500000	0.191057
C	0.500000	0.500000	0.191211	N	0.000000	0.500000	0.808943
C	0.500000	0.500000	0.808789	N	0.500000	0.000000	0.191049
N	0.307439	0.000000	0.000000	N	0.500000	0.000000	0.808951
N	0.000000	0.307432	0.000000	N	0.500000	0.500000	0.307500
N	0.000000	0.000000	0.307437	N	0.500000	0.500000	0.692500
N	0.692561	0.000000	0.000000	Fe	0.000000	0.000000	0.000000
N	0.000000	0.692568	0.000000	Fe	0.500000	0.000000	0.000000
N	0.000000	0.000000	0.692563	Fe	0.000000	0.500000	0.000000
N	0.191051	0.000000	0.500000	Fe	0.000000	0.000000	0.500000
N	0.808949	0.000000	0.500000	Fe	0.500000	0.000000	0.500000
N	0.000000	0.191048	0.500000	Fe	0.000000	0.500000	0.500000
N	0.000000	0.808952	0.500000	Fe	0.500000	0.500000	0.500000
N	0.307500	0.500000	0.500000	Fe	0.500000	0.500000	0.000000

Iteration 10:
Energy: -1.71392215E+004 eV

Element	Fractional coordinates of atoms			C	0.500000	0.692824	0.000000
	x	y	z	C	0.000000	0.500000	0.307176
C	0.191035	0.000000	0.000000	C	0.000000	0.500000	0.692824
C	0.000000	0.191035	0.000000	C	0.500000	0.000000	0.307177
C	0.000000	0.000000	0.191035	C	0.500000	0.000000	0.692823
C	0.808965	0.000000	0.000000	C	0.500000	0.500000	0.191124
C	0.000000	0.808965	0.000000	C	0.500000	0.500000	0.808876
C	0.000000	0.000000	0.808965	N	0.307317	0.000000	0.000000
C	0.307178	0.000000	0.500000	N	0.000000	0.307309	0.000000
C	0.692822	0.000000	0.500000	N	0.000000	0.000000	0.307309
C	0.000000	0.307172	0.500000	N	0.692683	0.000000	0.000000
C	0.000000	0.692828	0.500000	N	0.000000	0.692691	0.000000
C	0.191129	0.500000	0.500000	N	0.000000	0.000000	0.692691
C	0.808871	0.500000	0.500000	N	0.191036	0.000000	0.500000
C	0.500000	0.191127	0.500000	N	0.808964	0.000000	0.500000
C	0.500000	0.808873	0.500000	N	0.000000	0.191033	0.500000
C	0.307179	0.500000	0.000000	N	0.000000	0.808967	0.500000
C	0.692820	0.500000	0.000000	N	0.307402	0.500000	0.500000
C	0.500000	0.307176	0.000000	N	0.692598	0.500000	0.500000

N	0.500000	0.307394	0.500000	N	0.500000	0.500000	0.307396
N	0.500000	0.692606	0.500000	N	0.500000	0.500000	0.692604
N	0.191033	0.500000	0.000000	Fe	0.000000	0.000000	0.000000
N	0.808967	0.500000	0.000000	Fe	0.500000	0.000000	0.000000
N	0.500000	0.191030	0.000000	Fe	0.000000	0.500000	0.000000
N	0.500000	0.808970	0.000000	Fe	0.000000	0.000000	0.500000
N	0.000000	0.500000	0.191033	Fe	0.500000	0.000000	0.500000
N	0.000000	0.500000	0.808967	Fe	0.000000	0.500000	0.500000
N	0.500000	0.000000	0.191033	Fe	0.500000	0.500000	0.500000
N	0.500000	0.000000	0.808967	Fe	0.500000	0.500000	0.000000

Iteration 11:
Energy: -1.71392215E+004 eV

Element	Fractional coordinates of atoms			N	0.000000	0.692721	0.000000
	x	y	z	N	0.000000	0.000000	0.692722
C	0.191011	0.000000	0.000000	N	0.190979	0.000000	0.500000
C	0.000000	0.191005	0.000000	N	0.809021	0.000000	0.500000
C	0.000000	0.000000	0.191007	N	0.000000	0.190973	0.500000
C	0.808989	0.000000	0.000000	N	0.000000	0.809027	0.500000
C	0.000000	0.808995	0.000000	N	0.307388	0.500000	0.500000
C	0.000000	0.000000	0.808993	N	0.692612	0.500000	0.500000
C	0.307116	0.000000	0.500000	N	0.500000	0.307380	0.500000
C	0.692884	0.000000	0.500000	N	0.500000	0.692620	0.500000
C	0.000000	0.307111	0.500000	N	0.190975	0.500000	0.000000
C	0.000000	0.692889	0.500000	N	0.809024	0.500000	0.000000
C	0.191118	0.500000	0.500000	N	0.500000	0.190972	0.000000
C	0.808882	0.500000	0.500000	N	0.500000	0.809027	0.000000
C	0.500000	0.191112	0.500000	N	0.000000	0.500000	0.190972
C	0.500000	0.808888	0.500000	N	0.000000	0.500000	0.809028
C	0.307119	0.500000	0.000000	N	0.500000	0.000000	0.190975
C	0.692881	0.500000	0.000000	N	0.500000	0.000000	0.809025
C	0.500000	0.307112	0.000000	N	0.500000	0.500000	0.307382
C	0.500000	0.692888	0.000000	N	0.500000	0.500000	0.692618
C	0.000000	0.500000	0.307117	Fe	0.000000	0.000000	0.000000
C	0.000000	0.500000	0.692883	Fe	0.500000	0.000000	0.000000
C	0.500000	0.000000	0.307114	Fe	0.000000	0.500000	0.000000
C	0.500000	0.000000	0.692886	Fe	0.000000	0.000000	0.500000
C	0.500000	0.500000	0.191110	Fe	0.500000	0.000000	0.500000
C	0.500000	0.500000	0.808890	Fe	0.000000	0.500000	0.500000
N	0.307283	0.000000	0.000000	Fe	0.500000	0.500000	0.500000
N	0.000000	0.307279	0.000000	Fe	0.500000	0.500000	0.000000
N	0.000000	0.000000	0.307278				
N	0.692717	0.000000	0.000000				

Supplement 2 (S2). The comparison of responses to H_2O_2 between bare Pt electrode and nano-cubic PB modified electrode.

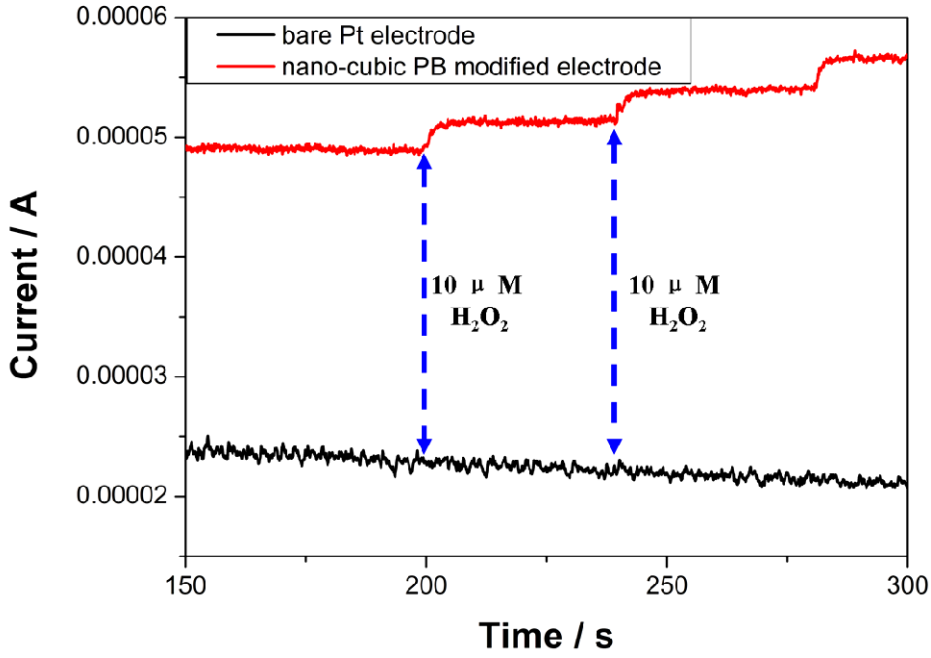

Fig. S2 The comparison of responses to H_2O_2 between bare Pt electrode and nano-cubic PB modified electrode prepared at 35 ˚C and 6 h. The detection potential was -0.05V.

In order to demonstrate the electrocatalytic ability of PB, we compared the performances between the bare Pt electrode and that modified by our material. According to the Fig. S2, we can find the baseline was unstable for the bare Pt electrode after the some period and the signal noise was bigger than the PB modified electrode. This indicated our material can maintain the stable detection environment. When we began to add the 10μM H_2O_2 into the buffer solution, the obvious response current was presented for the PB modified electrode. On the contrary, the bare Pt electrode didn't exhibit any increase of current. The results showed that the amperometric response of PB modified electrode is obviously higher than that of Pt electrode, and the detection stability was better than bare Pt electrode under -0.05V. That is, that catalytic activity of PB toward H_2O_2 reduction is superior to that of

Platinum. Consequently, the performance was mainly depended on our nano-cubic PB. Combining the sensitivity comparison in our paper, our material has the merits of highest reported performance, low detection potential and excellent anti-interference.

Supplement 3 (S3). Comparison of the sensitivities of other PB-based modified electrodes to H_2O_2 detection.

Table S3. Comparison of the sensitivities of the PB-based modified electrodes to H_2O_2 detection

Electrode modifier	Prepared approach	Applied potential (V) vs. Ag/ AgCl	Sensitivity ($mA\ M^{-1}cm^{-2}$)	Reference
Only PB modification	Aerosol deposition	-0.05	1163	This work
	Self-assembly	-0.1 (vs. SCE)	754.6	[1]
		-0.05	625	[2]
	Electrodeposition	-0.05	250	[3]
		-0.20	58.1	[4]
	Chemical deposition	-0.05	1076	[5]
PB/Al_{13}	Self-assembly	-0.1	886	[6]
PB/PAMAM/3-MPA	Chemical deposition	-0.2 (vs. SCE)	765	[7]
MWCNT/PVP/PB		0.1	1300	[8]
PB/[Bmim][Cl]	Electrodeposition	0	225.23	[9]
PB/polymer		0	1000	[10]
PB/poly(1,2-DAB)		0	300	[11]

Up to date, the common preparation approaches of PB modified electrode are self-assembly, electrodeposition and chemical deposition. Table S3 lists sensitivities of the PB-based modified electrodes prepared by other groups reported in recent years. For the convenient comparison, we classified all the work into two parts: one is only deposition of a layer of PB on the substrate; the other is doping of extra substances for performance improvement. Among the electrodes only modified by PB film, our electrode exhibited the best performance. Generally, combination of some substances that are well conductive is an effective method to enhance the electrode performance. However, the sensitivity of our electrode even exceeded those works, which doped with some materials. In Table S3, although the performance of electrode modified by MWCNT/PVP/PB[8] is better than ours, the detection potential is much higher. Accordingly, our electrode has the advantage in low detection potential, which is more important to avoid the interference for real application.

We believe that the sensitivity of our electrode can be further improved with the doping of electron conductors, and this preparation approach can be a promising path for the construction of biosensors with high performance under low potential.

Supplement 4 (S4). Equivalent circuit for AC impedance experiment.

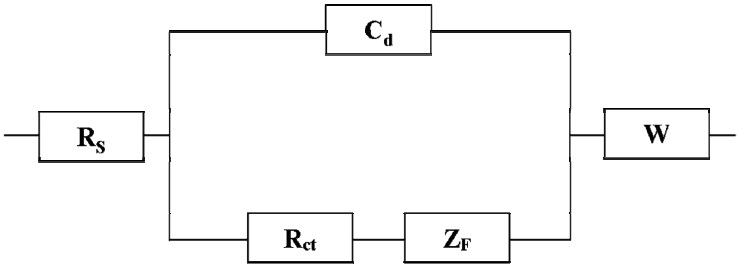

Figure S4. The image of equivalent circuit. C_d and R_{ct} are the double layer capacitance and the charge transfer resistance at the Pt/PB interface. R_s is the ohmic resistance of solution plus a Pt. Z_F is the film associated impedance. W is the Warburg impedance for balance of the buffer solution diffusion under the low frequencies.

In order to know the real electron transfer resistance, the equivalent circuit was constructed for AC impedance experiment. Three samples of PB modified electrodes, one prepared by self-assembly (30 layers of PB) and the other two by aerosol deposition approach (at 25 and 35 ˚C, respectively), were fabricated for comparison. In Figure S4, R_{ct} represents the charge transfer resistance at the Pt/PB interface. Electrons transferred from the solution to the PB film, then reached the interface between Pt and PB. Under the same potential, the lower resistance indicated the more electrons passed the layer of PB film. Accordingly, by comparing the three R_{ct} values of samples, we can find which structure of PB film can improve the electron migration through the film layer.

Supplement 5 (S5). DFT simulation of band structure.

The Pt (110) surface was established through cutting from the Pt crystal and added the vacuum slab with 8.0 Å thickness. The Fe-C-N-Fe structure was added on the surface as the unit molecule for free adsorption of energy. The band structures of adsorption model and PB crystal were both chosen to be simulated.

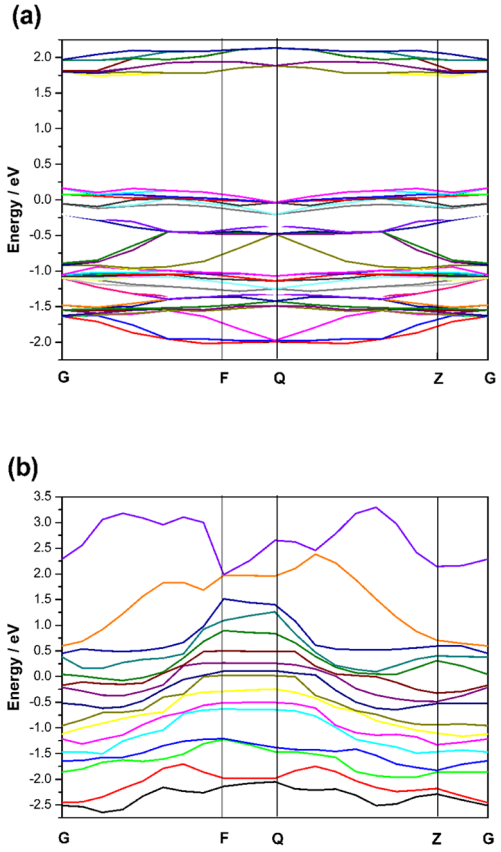

Figure S5. The simulative images of partial band structures for (a) PB crystal; (b) PB adsorbed on the Pt surface.

Figure S5(a) showed the results of simulative band structure for PB. The structure of energy band can be used to analyze the metallicity. The edge between lowest unoccupied orbital (LUMO) and the highest occupied orbital (HOMO) is called as the energy or band gap.[12-13] A material with narrow band gap or none is referred to as a

semiconductor or metal, respectively.[14] The bands in the image were clearly classified to two groups: conduction bands and valence bands. The energy gap between the highest valence band edge (~HOMO) and the lowest conduction band edge (~LUMO) was calculated to be 1.58 eV. This value stands in the range of semi-conduction. Although it is not the insulator, conduction of the electrons should require the extra energy to excite for free transfer. The barrier of electron transfer exists. However, when the PB was deposited on the Pt electrode, it can rapidly respond to the H_2O_2 at the low potential. Comparing with the PB band structure, the band structure of PB adsorbed on Pt was obviously showed that there is no gap (Figure S5(b)). This was due to the supplement of the electron orbits from the Pt to occupy the range of band gap. If no distinction exists between valence and conduction bands, the properties for this structure were as the metal. Valence electrons can freely transfer onto the conduction band. Before the deposition of PB on Pt surface, the electrons on PB valence bands are the only donation to excite. However, the electrons from the Pt bands can also help to contribute the free electrons to the system. Accordingly, the barrier can be reduced to promote the electron transfer. This is why the electrons of the iron atoms can be continuously provided to catalyze the reduction of H_2O_2 under the low potential.

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