Electronic Supplementary Material (ESI) for Nanoscale. This journal is © The Royal Society of Chemistry 2019

> Electronic Supplementary Material (ESI) for Nanoscale. This journal is © The Royal Society of Chemistry 2019

A layer-by-layer strategy for the scalable preparation of uniform electrocatalyst interfaces with high structural tunability: A case study of the CoNP/N-P-graphene catalyst complex

Limei Lu, Yihe Zhang*, Xuelian Yu, Yi Zhang, Zequn Ma, Qi An*

Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing, 100083, China. *Corresponding authors.

E-mail addresses: Y. H. Zhang. (zyh@cugb.edu.cn), Q. An (an@cugb.edu.cn).

Supplementary Note 1: Experimental Section

1.1 Materials

The chemicals are all analytical grade and used without further purification. Bulk crystals of Black Phosphorus was purchased from Smart Elements (Austria). Polyethylenimine (PEI, MW 700,000) and Poly(acrylic acid) (PAA, MW 100,000) were provided by Alfa Aesar. K₃[Co(CN)₆]₂ was obtained from Macklin. N-Methyl-2-Pyrrolidone was purchased from local commercial sources. Single-walled Carbon nanotube paper (XFZ12-1) and Carbon Nanotube sponges (XFCN01) were purchased from Nanjing/Jiangsu XFNANO Materials Tech Co.,Ltd, China. Co(CH₃COO)₂·4H₂O and Polyvinylpyrrolidone (PVP, K30MW=30,000) were bought from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China).

1.2 Materials synthesis

1.2.1 Exfoliation of BP

Liquid exfoliation was used to obtain BP nanosheets. First, mill bulk BP in an agate mortar to obtain BP fine powder. Second, 20 mg BP powder was added into 20 mL NMP, followed by ultrasonication for four hours using a probe sonicator (600 W, 6% power) in ice bath. The temperature of the mixture should be kept under 25 °C. After ultrasonication, the dispersion liquid was centrifuged twice at 4000 rpm for 20 min to remove bulk BP and the supernatant was collected (0.2 mg mL⁻¹).

1.2.2 Synthesis of [(PEI/PAA)-(PEI/BP/PAA)₂]₅ film by Layer-by-Layer assembly

Carbon cloth (CC) (1×3 cm) was pretreated with a mixed solution (V_{H2504}/V_{H202}=7:3) for 30 min, then washed with doubly deionized water. For the assembly of multilayers, firstly, the CC was dipped into PEI solution (1 mg·mL⁻¹, pH=9) for 10 min, and then washed with a copious amount of water. Secondly, the CC was immersed into BP dispersion (0.2 mg·mL⁻¹) for 10 min and washed. Thirdly, the CC was transformed into PAA solution (1 mg·mL⁻¹, pH=6) for 10 min and washed. If BP layer is not required during assembly, the second step was skipped. (Note: every immerse step must follow washing (water for 2 min) and drying (nitrogen flow) steps. Repeat the immerse cycle until the desired number of multilayers are obtained.)

1.2.3 Synthesis of [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs

Solution A: 18.7 mg Co(CH₃COO)₂·4H₂O was dissolved in 10 mL H₂O followed by bath ultrasonication for a few minutes to get a harmonious solution. Solution B: 16.6 mg K_3 [Co(CN)₆]₂ and 0.3 g of polyvinylpyrrolidone (PVP K30) were dissolved in 10 mL H₂O under bath ultrasonication for a few minutes.

First, the as prepared [(PEI/PAA)-(PEI/BP/PAA)₂]₅ film was immersed into solution A for 30 min. Second, the film was dipped into solution B for another 30 min. Recycle the two immersion steps for 4 times. Finally, the sample was annealed at 550 °C for 2 h under nitrogen atmosphere in a tubular furnace.

1.3 Characterization

The thickness and morphology of BP nanosheet was studied with Atomic Force Microscope (AFM, Dimension 3100, Veeco, USA). The structure observation and elemental distribution were studied using a SEM (JSM-IT300), TEM, and HRTEM (Tecnai F20 electron microscopy). The binding energies were characterized by XPS (ThermoFisher Scientifc, using a 1486.6 eV monochromatized AI K α radiation as the X-ray source). The absorbance was monitored using a UV–visible spectrum (Hitachi U-3900H). The Raman spectrum was measured using a Micro-Raman spectroscopy at 532 nm radiation (Horiba). XRD was performed on X-ray diffractometer using Cu K α radiation (Bruker AXS, Germany). The EXAFS spectrum of Co K-edge was conducted at beamline 1W2B of the Beijing Synchrotron Radiation Facility (BSRF).

Electrochemical Measurements

Electrochemical performance was studied on a CHI760D electrochemical workstation using a typical three-electrode system in 0.5 M H₂SO₄. The electrolyte was bubbled with N₂ for 30 min before experiments. The as-prepared samples, a graphite rod, and a Ag/AgCl (3 M KCl) were utilized as the working, counter and reference electrodes, respectively. The potentials were converted to the reversible hydrogen electrode (RHE) potential using E(RHE)=E(Ag/AgCl)+0.059×pH+0.210 V. The surface area of the working electrode immersing in the electrolyte was 2 cm². The LSV curves for HER were conducted at a scan rate of 2 mV s⁻¹ without iR correction.

Supplementary Note 2: Calculation of double-layer capacitance (C_{dl})

The C_{dl} could be calculated by CV plots in the potential ranging from 0.3 to 0.4 V vs. RHE. The scan rates were set to 2, 4, 6 and 8 $\frac{1}{2}$ mV/s. Plot the $\frac{1}{2}$ (j_a-j_c) at 0.35 V against the scan rate, and the fitting slope was C_{dl}.

Supplementary Note 3: Calculation of electrochemically active surface areas (ECSA)

ECSA was calculated according to the equation: ECSA = $R_f \times S$. R_f represent the rough factor, and could be calculated by C_{dl}

 $R_f = \frac{m^2}{the specific capacitance}$, where the specific capacitance of a flat surface is generally identified to be 20~60 μ F cm^{-2 1-6}. S represents the geometric area of electrode (here S=2.0 cm²). The intermediate value of 40 μ F cm⁻² was used in this study to calculate the specific capacitance.

Supplementary Note 4: DFT Computational details

In the DFT simulations, We build a molecular model of a pristine graphene sheet with 10 carbon atoms using Materials Studio shown in Figure 4b. In the graphene structure, some carbon atoms from the rings were replaced by Phosphorus and nitrogen atom. In the purpose of seeking out the thermal stable morphology and realize a conformation with minimum potential energy, we minimize potential energy. In the following electronic structure simulations, the initial status are these minimum energy conformations. The Visualization for Electronic and Structural Analysis(VESTA, series 3)⁷ and Materials Studio are software for visualization and drawing.

DFT calculations were performed in the Vienna ab initio simulation package (VASP). A spin-polarized GGA PBE functional, allelectron plane-wave basis sets with an energy cutoff of 520 eV, and a projector augmented wave (PAW) method were adopted. GO is simulated using a surface model of p (3×3) unit cell periodicity. A (3×3×1) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled. The conjugate gradient algorithm was used in the optimization. The convergence threshold was set at 1×10^{-4} eV in total energy and 0.05 eV/Å in force on each atom.

The free energy change (ΔG) for adsorptions were determined as follows:

 $\Delta G = E_{total}-E_{sur}+\Delta E_{ZPE}-T\Delta S$

where E_{total} is the total energy for the adsorption state, E_{sur} is the energy of pure surface, ΔE_{ZPE} is the zero-point energy change and ΔS is the entropy change. As the vibrational entropy of H* in the adsorbed state is small, the entropy of adsorption of $1/2 H_2$ is SH \approx -0.5S_{0H2}, where S_{0H2} is the entropy of H₂ in the gas phase at the standard conditions. Therefore the overall corrections were taken as in

 $\Delta G_{H^*}=E_{total}-E_{sur}-E_{H2}/2+0.24 \text{ eV}$

where E_{H2} is the energy of H_2 in gas phase.



Figure S1 Tapping-mode AFM image and the corresponding height profiles of BP nanosheets. Insert shows the Tyndall effect of BP



Figure S2. SEM images at different magnifications of (a, b) (PEI/PAA)₁₅-CoNPs; (c, d) [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs before calcination



Figure S3. EDS of (PEI/PAA)₁₅-CoNPs-Cal



Figure S4. EDS of [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs-Cal



Figure S5. SEM images of a) bare CC and b) (PEI/PAA)₁₅-Cal modified CC



Figure S6. XRD pattern of (PEI/PAA)₁₅-CoNPs and [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs before calcination



Figure S7. TGA curves of (PEI/PAA)₁₅, (PEI/PAA)₁₅-CoNPs, and [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs in N₂ atmosphere Thermogravimetric analysis (TGA) in N₂ atmosphere at the temperature range 25 to 1000 °C was conducted, aming at investigating the carbonization process(Figure S7). It is clear that there are two decomposition steps. At the temperature of around 140 °C, an endothermic peak occurs and the weigh loss is about 5.4%, corresponding to the removal of absorbed water in the environment. There is a large weight loss of 16.1% between 310 °C and 810 °C, which indicates the partial carbonization of polymer PEI and PAA. **B**ased on the results of TGA, the [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs annealed at 550 °C for 2 h experienced carbonization.



Figure S9. XPS a) C 1s and b) O 1s spectra of [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs before calcination



Figure S10. XPS a) C 1s and b) O 1s spectra of [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs-Cal



Figure S11. The k³-weighted EXAFS of (PEI/PAA)₁₅-CoNPs-Cal, [(PEI/PAA)-(PEI/BP/PAA)₂]₅-CoNPs-Cal and Co references in k-space **Table S1** Local structure parameters around Co estimated by EXAFS analysis

Sample	Path	N	R	σ²	Eo
Co foil	Co-Co	12.0	2.493	0.0062	-6.0
(PEI/PAA) ₁₅ -CoNPs-Cal	Co-Co	9.4	2.491	0.0062	-5.7
[(PEI/PAA)-(PEI/BP/PAA) ₂] ₅ -CoNPs-Cal	Co-Co	9.5	2.490	0.0061	-6.7

The coordinated number of 1st shell is shown in Supplementary Table S1. The reduction of the coordination number N of $(PEI/PAA)_{15}$ -CoNPs-Cal and $[(PEI/PAA)-(PEI/BP/PAA)_2]_5$ -CoNPs-Cal comparing to Co foil indicates the decreases of adjacent Co atoms to the central atom Co, indicating Co vacancy is formed, probably due to the large fraction of surface Co atoms in the nanoscopic particles. δ^2 (Debey-Waller factor, disorder factor) is the result of thermal disorder and structural disorder. The δ^2 of $(PEI/PAA)_{15}$ -CoNPs-Cal and $[(PEI/PAA)-(PEI/BP/PAA)_2]_5$ -CoNPs-Cal are very close to Co foil, indicating they are very similar in structural.



Figure S12 Top views of geometric configuration unit of N-graphene with a) zero P dopint, b) low P doping, c) medium P doping, and d) high P doping



Figure S13 Top views of geometric configuration unit of N-graphene-CoNPs with a) zero P dopint, b) low P doping, c) medium P doping, and d) high P doping

References

- 1.
- M. Liu and J. Li, *Acs Appl Mater Interfaces*, 2016, **8**, 2158-2165. Z. Yan, G. Ning, D. Wang, Y. Cao, C. Meng, T. Li and Y. Chen, *Angewandte Chemie*, 2016, **127**, 14936-14940. 2.
- Y. Shi and B. Zhang, *Chemical Society Reviews*, 2016, **45**, 1781-1781. 3.
- Q. Zhou, Z. Shen, C. Zhu, J. Li, Z. Ding, P. Wang, F. Pan, Z. Zhang, H. Ma and S. Wang, Advanced Materials, 2018, 1800140-1800147. 4.
- F. Wang, Y. Li, T. A. Shifa, K. Liu, F. Wang, Z. Wang, P. Xu, Q. Wang and J. He, Angewandte Chemie, 2016, 55, 6919-6924. 5.
- 6. Y. Yin, J. Han, Y. Zhang, X. Zhang, P. Xu, Q. Yuan, L. Samad, X. Wang, Y. Wang and Z. Zhang, Journal of the American Chemical Society, 2016, 138, 7965-7972.
- 7. Momma, K.; Izumi, F. Journal of Applied Crystallography 2011, 44, 1272-1276.