



2024「中技社科技獎學金」

2024CTCI Foundation Science and Technology Scholarship

研究獎學金 Research Scholarship

通過電化學生成模板和陽離子取代反應將天然酞菁銅轉化為高負載量單原子電催化劑 Turning natural copper phthalocyanine into high-loading single-atom catalysts using an electrochemically-generated template and cationic substitution

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研究重點

Phthalocyanine (PC) has a unique N_4 coordinated structure that offers an inherent advantage with respect to the accommodation of metal ions. This feature can help overcome the limitations of many single-atom electro-catalysts, i.e. low loading and poor stability. Here, we detail the development of a universal electrochemical template and a cationic substitution synthesis protocol for preparing various single-atom catalysts with high-loading (8.6 wt%) from commercial copper phthalocyanine (CuPC). Commercial CuPC is transformed into Cu NPs and vacant N_4 -sites are created during applied potential cycling. The generated vacant N_4 -sites, with strong negative charges, can take-up Pd^{2+} ions from a precursor solution to create single-atom catalysts with Pd high-loadings. The material's structural transformation and cationic substitution mechanism were investigated by in situ X-ray absorption spectroscopy (XAS). We also demonstrate the viability of extending the proposed electrochemical template synthesis method to the development of other high-loading transition metal single-atom catalysts, e.g., Ni, Co, and Fe.

研究成果

Synthesis

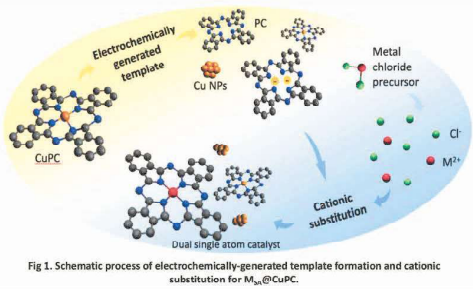


Fig. 1. Schematic process of electrochemically-generated template formation and cationic substitution for $M_n@CuPC$.

Cationic Substitution

Image analysis

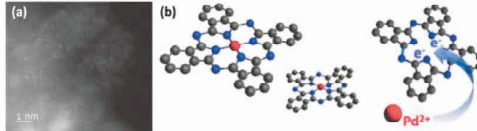


Fig. 5. (a) HAADF-STEM image of Pd single-atoms dispersed on CuPC ($Pd_{0.6}@CuPC$); (b) Schematic diagram of the formation of $Pd-N_4$ sites by the Pd^{2+} cationic substitution process.

Application

CO₂ reduction reaction

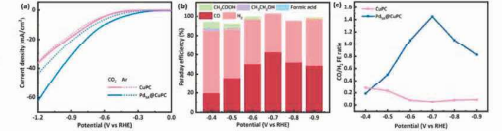


Fig. 8. (a) LSV curve in 0.5 M $KHCO_3$ with CO_2 or Ar atmosphere with a scan rate of 10 mV s^{-1} ; (b) Faradaic efficiency (FE) values of the products generated during the CO_2 RR; (c) Ratio of the FE for CO and H_2 over the same potential range.

Structure characterizations

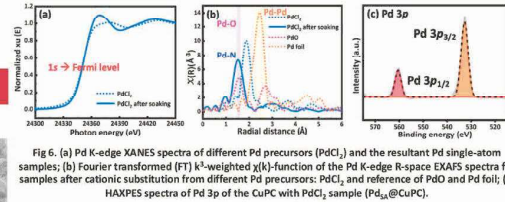


Fig. 6. (a) Pd K-edge XANES spectra of different Pd precursors ($PdCl_2$) and the resultant Pd single-atom samples; (b) Fourier transformed (FT) K' -weighted $X(k)$ -function of the Pd K-edge R-space EXAFS spectra for samples after cationic substitution from different Pd precursors; $PdCl_2$ and reference of PdO and Pd foil; (c) HAXPES spectra of Pd 3p of the CuPC with $PdCl_2$ sample ($Pd_{0.6}@CuPC$).

Electrochemically-Generated Templates

Image analysis

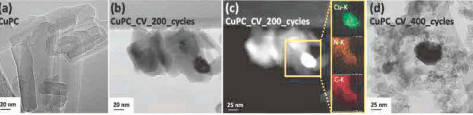


Fig. 2. (a) Transmission electron microscopy (TEM) image of commercial CuPC; (b) bright-field, and (c) dark-field TEM and EDS elemental mapping analysis of the CuPC_CV_200_cycles; (d) TEM image of CuPC_CV_400_cycles.

Structure characterizations

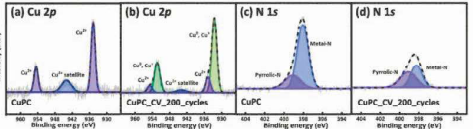


Fig. 3. (a, b) XPS spectra of Cu 2p of the pristine CuPC and CuPC_CV_200_cycles; (c, d) N 1s spectra of the pristine CuPC and CuPC_CV_200_cycles.

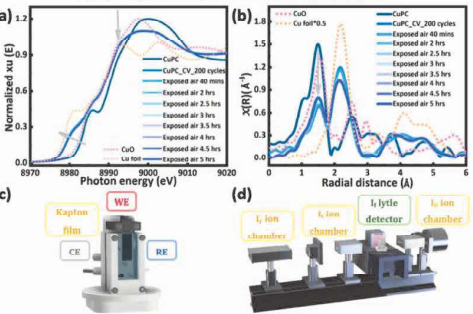


Fig. 4. (a) Cu K-edge XANES spectra for the state between initial and after electrochemical treatment of commercial CuPC; (b) Fourier-transformed EXAFS in R-space of the experimental Cu K-edge EXAFS signals. Schematic diagram of in-situ XAS (c) holder and (d) beamline system.

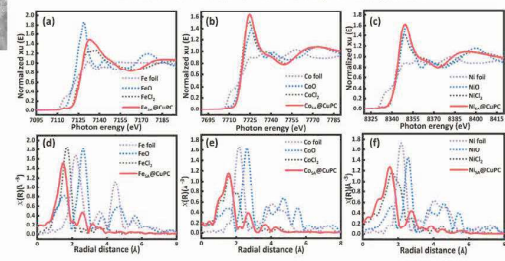


Fig. 7. (a-c) XANES spectra and (d-f) EXAFS FT spectra of $Fe_{0.3}@CuPC$, $Co_{0.3}@CuPC$ and $Ni_{0.3}@CuPC$ compared with precursor (metal chloride), metal oxide and foil.

EGO reaction

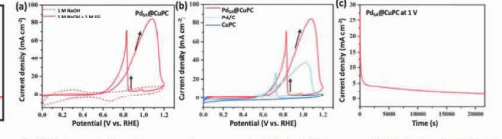


Fig. 9. Electrochemical performance of as-prepared catalysts, (a) CV curves of Pd- N_4 /Cu- N_4 with/without EG in the electrolyte solution, (b) the CV curve of the partial EGO on Pd- N_4 /Cu- N_4 , Pd/C, and CuPC. (c) Chronoamperometric stability applied potential at 3.0 V_{RHE} .

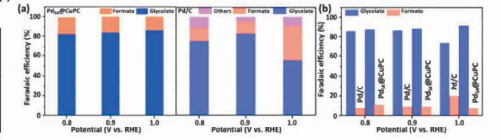


Fig. 10. (a) The faradaic efficiency of the glycolate (blue) and formate (orange) products produced by $Pd_{0.6}@CuPC$ and Pd/C. (b) Selectivity of the EG oxidation products performed at 0.8, 0.9 & 1.0 V_{RHE} on $Pd_{0.6}@CuPC$ and Pd/C.

Table 1. EXAFS best-fitting results of $Pd_{0.6}@CuPC$, $Ni_{0.3}@CuPC$, $Co_{0.3}@CuPC$ and $Fe_{0.3}@CuPC$ materials.

Sample name	Shell	CN	Debye-Waller factor ($\Delta\sigma^2$)	R-factor
$Pd_{0.6}@CuPC$	Pd-N	3.6	2.05	0.0015
$Fe_{0.3}@CuPC$	Fe-N	4.4	2.02	0.0053
$Co_{0.3}@CuPC$	Co-N	4.12	2.05	0.0020
$Ni_{0.3}@CuPC$	Ni-N	4.16	2.10	0.0037

Reference

- [1] C. Y. Chang et al. Turning natural copper phthalocyanine into high-loading single-atom catalysts using an electrochemically-generated template and cationic substitution. *Mater. Today Nano* 25, 100466 (2024). (Q1, Impact factor 8.2)
- [2] B. J. Hwang et al. Sustainable Synthesis of Dual Single-Atom Catalyst of Pd-N₄/Cu-N₄ for Partial Oxidation of Ethylene Glycol. *Adv. Funct. Mater.* 32, 46, 2206887 (2022). (Q1, Impact factor 18.5)

研究生活與獲獎心得

非常榮幸能夠獲得中技社頒發的研究獎學金。這份榮譽對我而言不僅是一種肯定，更是一種激勵，鼓舞我持續追求卓越，深入探索科學研究的未知領域。

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最後，感謝中技社每年為國內博士生提供研究獎學金，支持青年學者的學術發展。我將懷抱更大的熱情，投入更多的努力，精進自我，為科學的進步貢獻綿薄之力。