

Electronic Supplementary Information

Facile one-step synthesis of mesoporous Pt-based alloy nanospheres for ethanol electrooxidation†

Experimental section

1.1 Materials

Potassium hexachloroplatinate (IV) (K_2PtCl_6 , 98%), hexadecyl trimethyl ammonium bromide (CTAB, 99%), ascorbic acid (AA, 99.99% metals basis), iron (III) chloride ($FeCl_3$, 98%), copper chloride ($CuCl_2$, 98%), cobalt (II) acetate tetrahydrate ($C_4H_6Co \cdot 4H_2O$, ACS) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 98%) were all purchased from Shanghai Aladdin Biochemical Technology Co. Ltd., China. Pluronic F127 was obtained from Sigma-Aldrich Co. Ltd., China. Ethanol, hydrochloric acid (HCl, 36~38 wt%) and sulfuric acid (H_2SO_4 , 95~98 wt%) were obtained from Yunnan Jingrui Technology Co. Ltd., China. The commercial Pt/C (40%) and Nafion PFSA polymer dispersion D520 (5%) were obtained from Suzhou Sinero Technology Co. Ltd., China. Deionized water (Milli-Q, 18.2 $M\Omega \cdot cm$) was used in all experiments. All chemicals and solvents were used as received without further purification.

1.2 Synthesis of mesoporous Pt nanospheres

In a typical synthesis, 2.1 g of CTAB and 0.4 g of F127 were completely dissolved in 80 ml H_2O by using ultrasound. Then, 20 ml of K_2PtCl_6 solution (0.02 M) was added to above solution and stayed at 85 °C for 15 min. After addition of 20 ml freshly prepared AA aqueous solution (1 M), the obtained mixed was aged at 85 °C for 4 h.

Finally, the product was separated by centrifugation at 8000 rpm for 5 min, washed by ethanol and deionized water. To extract the surfactant, the product was ultrasonically dispersed in ethanol solution containing HCl (36~38 wt%) and vigorously stirred at 80 °C for 4 h. The above steps were repeated for three times.

1.3 Synthesis of mesoporous Pt based alloy nanospheres

The procedure of mesoporous Pt based alloy nanospheres was similar with mesoporous Pt nanospheres, except adding 10 ml of other metal precursor solution (0.02 M) and 10 ml of K_2PtCl_6 solution. The other steps were the same.

1.4 Electrochemical measurement

The electrochemical measurement was performed in a conventional three-electrode cell, including an Ag/AgCl (containing 3.0 M KCl solution) electrode as a reference electrode, a platinum wire as a counter electrode, and a modified glassy carbon electrode (GCE, 3 mm in diameter) as a working electrode. The working electrode was prepared by polishing the GCE, 5.0 μ l of Nafion alcohol solution (0.05 wt% of Nafion) was coated on the surface of the modified GCE with 5.0 μ g of sample material and dried before electrochemical experiments. Prior to electrochemical experiments, the GCE modified with the samples were activated electrochemically by cycling the electrode potential between -0.2 V and +1.0 V (vs. Ag/AgCl) in 0.5 M H_2SO_4 until cyclic voltammetry (CV) curves that were characteristic for a clean Pt electrode were obtained. Ethanol electrooxidation measurements were performed in a solution of 0.5 M H_2SO_4 containing 0.5 M ethanol at a scan rate of 50 mV/s. The CV measurements were performed at scan rates of 10, 20, 50, 100 and 200 mV/s and the EIS measurements of the amplitude was 10 mV in the frequency range from 0.1 Hz to 1000 kHz. The chronoamperometric measurement was carried out at a constant potential of 0.6 V for 3600 s

1.5 Characterization

Scanning electron microscopy (SEM) was carried out using a Hitachi Regulus 8100 microscope operated at 5.0 kV (Hitachi High-Tech Corporation, Japan). Transmission electron microscopy (TEM), energy dispersive X-ray (EDX) maps and high-angle annular dark-field scanning TEM (HAADF-STEM) observations were performed using

a JEM-F200 operated at 200 kV equipped and JEM-1400Flash operated at 120 kV accelerating voltage (JEOL Ltd., Japan). A statistical analysis of the average size of the mesoporous Pt and Pt-based alloy particles was estimated by counting the diameter of 50 random particles from the TEM images. N₂ adsorption-desorption isotherms were acquired on Belsorp Max (Microtracbel Japan, Inc.) at 77 K. Brunauer-Emmett-Teller (BET) surface areas and pore size distribution was estimated from the N₂ adsorption-desorption isotherms via the BJH method. X-ray diffractometer (XRD, D2 PHASER, Bruker, Germany) was employed to record the diffraction signal of varies composition of samples with Cu K radiation ($\lambda=1.542 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were on Thermo Scientific K-Alpha (Thermo Fisher Ltd., USA). The composition of the mesoporous PtCu was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES) via Agilent 5110 ICP-OES (Agilent Ltd., USA). Electrochemical measurements were conducted a RST5210F electrochemical workstation (Zhengzhou Shiruisi Technology Co. Ltd., China).

1.6 Electrochemical surface area (ECSA) calculations

ECSA was calculated according to the reported method¹⁻³, CV was recorded in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹ to measure the ECSA of m-Pt, m-PtM and Pt/C. Here, the calculation method is simply introduced with Pt/C as an example. The ECSA of Pt/C in the working electrode is calculated using Equation 1 from the hydrogen desorption charge (Q_H) in the positive-going potential scan (-0.13 ~ 0.15 V) in CV profile in Figure S8 after correction for double-layer charging (by subtracting the current at 0.15 V from total current). The minimum potential is selected just above the potential of the H₂ desorption peak, as shown in Figure S8a. The charge of full coverage for clean polycrystalline Pt is Q_H = 210 $\mu\text{C cm}^{-2}$, which is used as the conversion factor. m (mg) is the Pt mass in the electrode.

$$\text{ECSA} = 10^5 \times Q_{\text{H-desorption}} / 210m \text{ (m}^2/\text{g)} \quad (1)$$

1.7 DFT calculations

DFT calculations were performed with the first principle calculations. Electronic structures were calculated using the generalized gradient approximation with the

Perdew-Burke-Ernzerh (GGA-PBE) functional. The projector-augmented-wave (PAW) pseudopotentials were used to describe electron-ion interactions. The kinetic energy cutoff for the plane-wave expansion was 450 eV. The geometry optimization was considered convergent when the force change was smaller than 0.05 eV/Å. The Brillouin zone was sampled with a gamma-centered grid $3 \times 3 \times 1$ through all the computational process. Periodic boundary conditions were used in all directions and a vacuum layer of 15 Å was used in the z-direction to eliminate the slab interaction in the z direction. The adsorption energy (E_{ads}) of adsorbate molecule was defined as:

$$E_{\text{ads}} = E_{\text{mol/surf}} - E_{\text{surf}} - E_{\text{mol}}$$

where $E_{\text{mol/surf}}$, E_{surf} and E_{mol} are the total electronic energy of adsorbate molecule adsorbed on the surface, the energy of clean surface, and the energy of free adsorbates respectively.

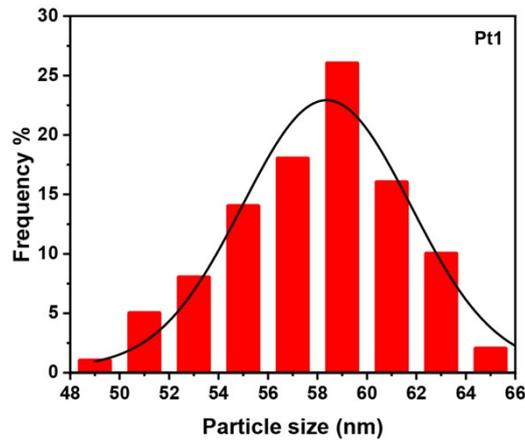


Figure S1 The particle size distribution of m-Pt1.

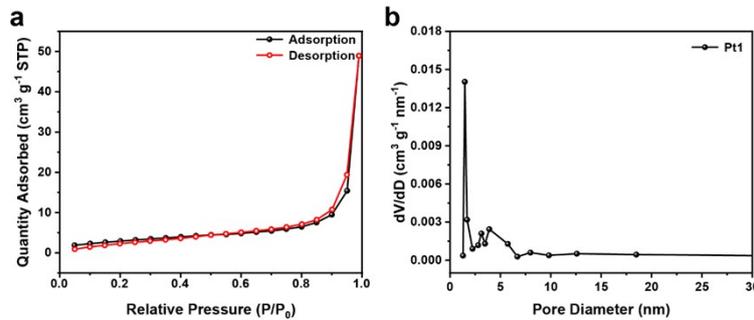


Figure S2 (a) N_2 adsorption/desorption isotherms of m-Pt1 and (b) the pore-size distribution curve obtained from BJH method.

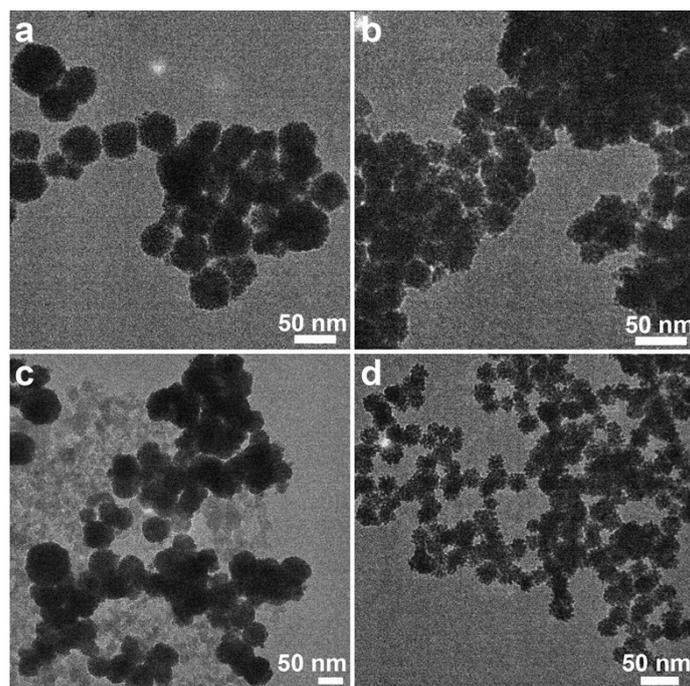


Figure S3 TEM images of mesoporous Pt nanospheres with different mass ratios of CTAB/F127: (a) 1/0, (b) 1/1, (c) 1/5 and (d) 0/1.

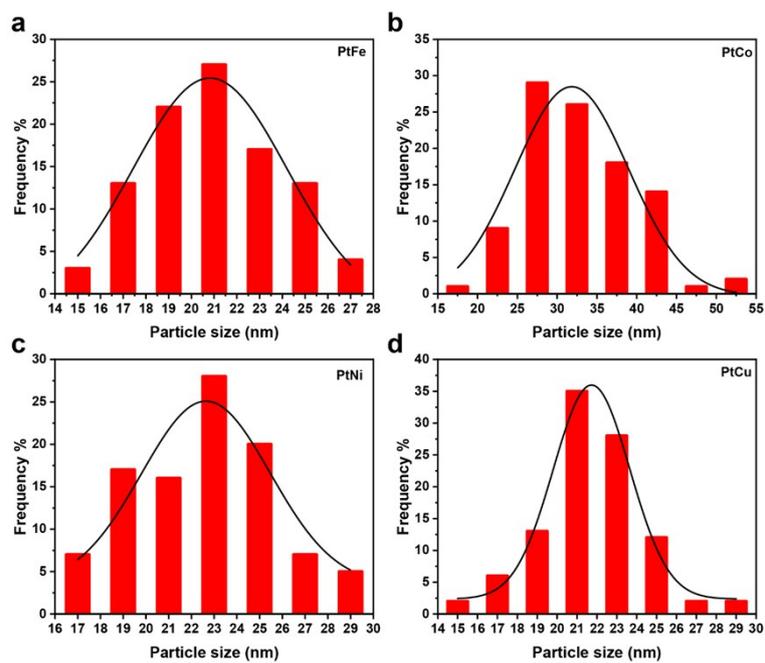


Figure S4 The particle size distribution of m-PtM alloys.

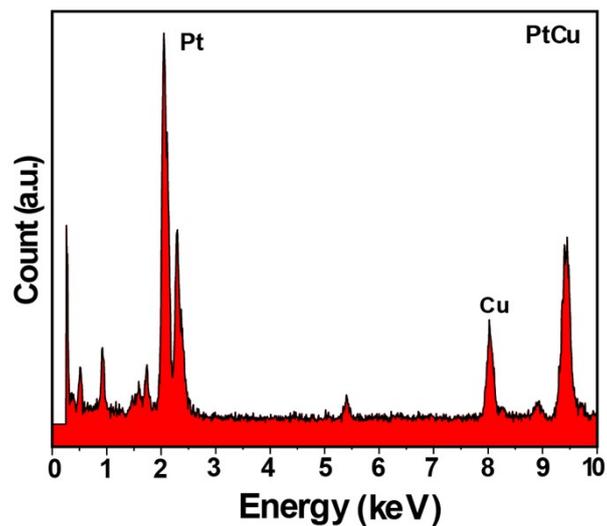


Figure S5 EDX elemental spectrum corresponding to PtCu alloy.



Figure S6 Photographs of colloidal suspensions taken at 85 °C with different reaction times: (a) 0.02 M CuCl_2 ; (b) 0.02 M K_2PtCl_6 and (c) the volume ratio of $\text{K}_2\text{PtCl}_6/\text{CuCl}_2=1/1$.

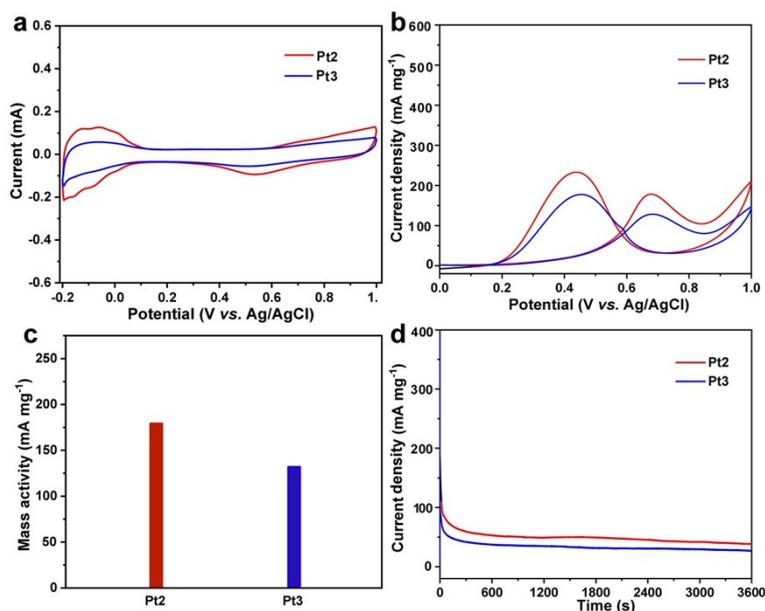


Figure S7 Electrocatalytic properties of m-Pt2 and m-Pt3: CV curves recorded in (a) 0.5 M H₂SO₄ and (b) 0.5 M H₂SO₄+0.5 M ethanol at a scan rate of 50 mV s⁻¹, (c) mass activity and (d) CA curves (recorded at 0.6 V vs. RHE for 3600 s) for EOR in 0.5 M H₂SO₄ + 0.5 M ethanol.

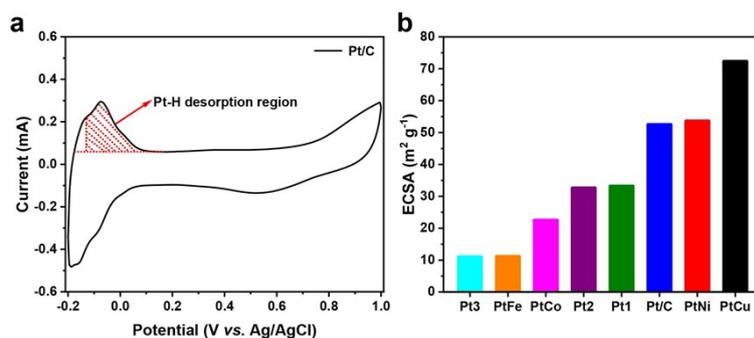


Figure S8 (a) CV curves of the Pt/C recorded in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹, the shaded region showed the area integrated for hydrogen desorption; (b) the ECSA corresponding to each sample.

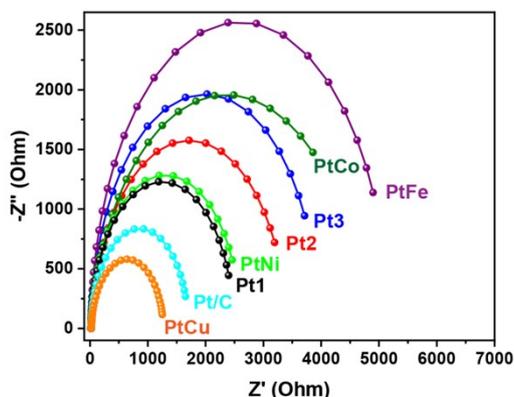


Figure S9 EIS curves of m-Pt and m-PtM alloys compared with commercial Pt/C.

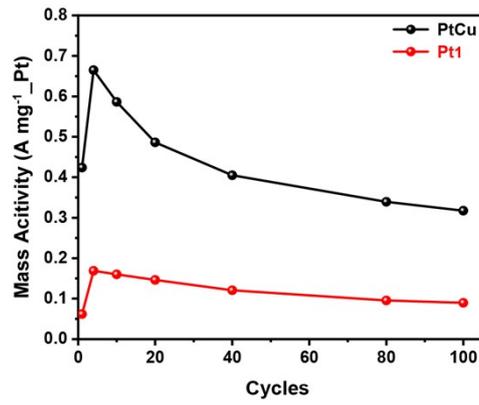


Figure S10 Cycling stability curves of m-Pt1 and m-PtCu for EOR.

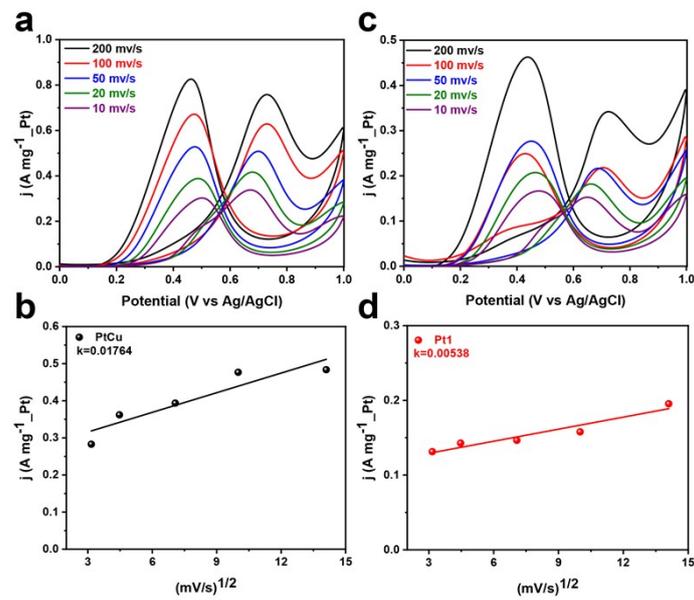


Figure S11 CV curves of (a) m-PtCu and (c) m-Pt1 with different scan rates, the relationship of forward oxidation peak current density vs. scan rate for (b) m-PtCu and (d) m-Pt1.

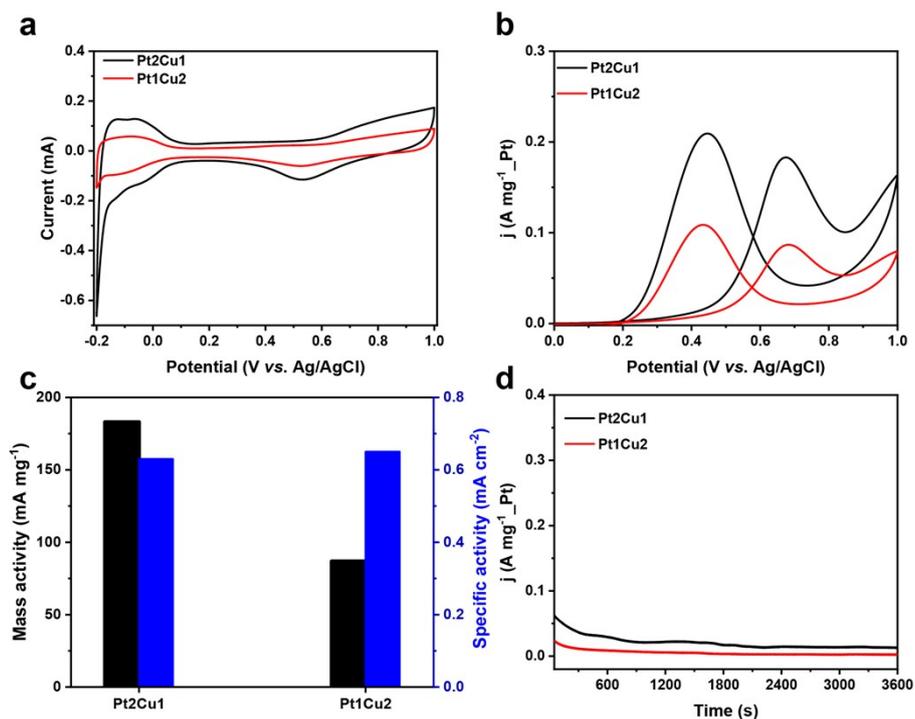


Figure S12 Electrocatalytic properties of m-Pt₂Cu₁ and m-Pt₁Cu₂: CV curves recorded in (a) 0.5 M H₂SO₄ and (b) 0.5 M H₂SO₄+0.5 M ethanol at a scan rate of 50 mV s⁻¹, (c) mass and specific activities, (d) CA curves (recorded at 0.6 V vs. RHE for 3600 s) for EOR in 0.5 M H₂SO₄ + 0.5 M ethanol.

The ESCA values of m-Pt₂Cu₁ and m-Pt₁Cu₂ were determined to be 29.2 m² g⁻¹ and 13.4 m² g⁻¹, respectively. The CV measurements and mass activities of m-Pt₂Cu₁ and m-Pt₁Cu₂ for the EOR are shown in Fig. S12b and c. The mass activities of m-Pt₂Cu₁ and m-Pt₁Cu₂ were measured to be 183.1 and 86.6 mA mg⁻¹, respectively.

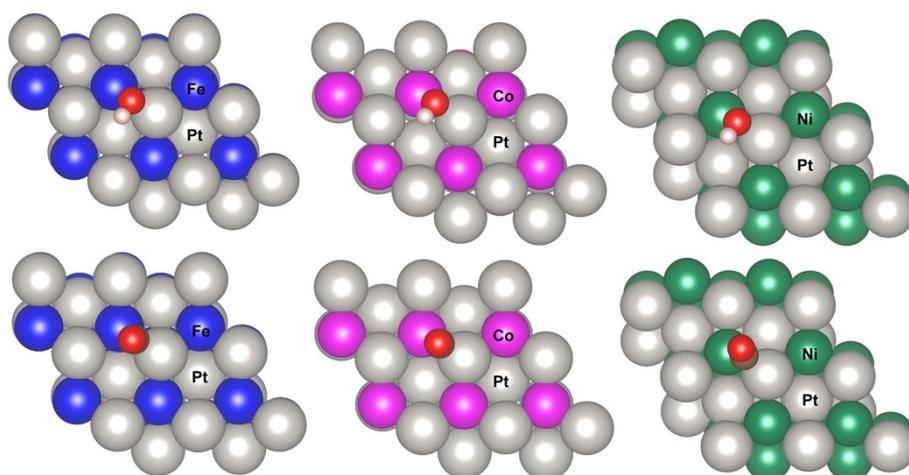


Figure S13 Adsorption configurations of OH and CO on the (111) surface of PtFe, PtCo, and PtNi alloys.

Ruyi Wang: conceptualization, conducting experiments, visualization, draft preparation. Shichun Gu: methodology. Dexiang Li: conceptualization. Chaoman Wang: collecting and analyzing data. Chongyuan Zhai: visualization. Yu Sun: DFT calculation and analysis. Xue Wang: conceptualization, supervision, review and editing. Hui Huang: funding acquisition and resources. Zhongcheng Guo: provision of research materials, instruments and analysis tools. Yapeng He: conceptualization, supervision, review and revision of the draft.

References

1. C. Han, Y. Lyu, S. Wang, B. Liu, Y. Zhang, J. Lu and H. Du, *Carbon Energy*, 2023, **5**, e339.
2. X. Fu, C. Wan, A. Zhang, Z. Zhao, H. Huyan, X. Pan, S. Du, X. Duan and Y. Huang, *Nano Res.*, 2020, **13**, 1472-1478.
3. T. H. T. Vu, T. T. Nguyen, T. H. Nguyen, M. D. Nguyen and Q. M. Nguyen, *Electrochim. Acta*, 2021, **380**, 138258.