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# **Supporting Information**

# Tailoring Oxygen Evolution Reaction Activity of Metal-Oxide Spinel Nanoparticles via Judiciously Regulating Surface-Capping Polymers

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# **Experimental Section**

#### 1. Materials

Anhydrous N,N-dimethylformamide (DMF, 99.9%), diphenyl ether (DPE), benzyl alcohol (BA, 99%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), propargyl bromide solution (80 wt% in toluene), sodium azide ( $\geq$ 99.5%), methyl ethyl ketone (MEK, 99.9%), poly(ethylene oxide) methyl ether (mPEO, M<sub>n</sub> = 5,000), anhydrous 1-methyl-2-pyrrolidione (NMP, 99.5%), 2-bromoisobutyryl bromide (BIBB, 98%), 2-bromopropionyl bromide, trifluoroacetic acid (TFA, 99.9%), iron(III) 2,4-pentanedionate (Fe(acac)<sub>3</sub>), cobalt(II) acetate tetrahydrate (Co(ac)<sub>2</sub>•4H<sub>2</sub>O, 98%), acetylene black (CB, 99.9%), Nafion® (5%, Beantown Chemical), and triethylamine (TEA). All chemicals listed were used as received. β-cyclodextrin (β-CD, Sigma-Aldrich) was dried in a vacuum oven at 80 °C overnight before use. CuBr (98%, Sigma-Aldrich) was stirred in acetic acid for 24 h, washed with diethyl ether and ethanol, and dried in a vacuum oven at room temperature. Acrylonitrile (AN, Alfa Aesar,  $\geq$ 99%), Styrene (St, Alfa Aesar,  $\geq$ 99%), and *tert*-butyl acrylate (*t*BA, Alfa Aesar, 98%) were distilled over CaH<sub>2</sub> under reduced pressure prior to use. Diphenylmethyl potassium (DPMK) (*c* = 0.52 M) was prepared as reported in previous literature.<sup>1</sup>

#### 2. Synthesis of Brominated β-CD as Macroinitiator

 $\beta$ -CD, possessing 21 –OH groups, was first dissolved in anhydrous NMP under vigorous stirring before adding BIBB at 0 °C, and then maintained at that temperature for 2 h. The reaction was continued with stirring under room temperature for 22 h. After the reaction, the crude solution was diluted with dichloromethane, and then washed sequentially with saturated NaHCO<sub>3</sub> aqueous solution and DI water. The product was then concentrated in a rotary evaporator, crystallized in cold n-hexane, and dried in a vacuum oven at room temperature for 24 h, yielding 21-Br- $\beta$ -CD.<sup>2, 3</sup>

#### 3. Synthesis of 21-arm, Star-like PtBA Homopolymer

After bromination, 21-Br- $\beta$ -CD was utilized as the macroinitiator for growing 21-arm poly(*tert*-butyl acrylate) (PtBA) via atom transfer radical polymerization (ATRP). Typically, 21-Br- $\beta$ -CD, CuBr, PMDETA, tBA, and MEK with a molar ratio of 1:1:2:1000:1000 were mixed in an ampoule, which was then degassed with three freeze-pump-thaw cycles and charged with Ar. The vessel was sealed and submerged in an oil bath at 60 °C. After the desired polymerization time, the reaction was terminated by dipping the vessel into liquid N<sub>2</sub>. The solution was then diluted with THF and passed through a column of neutral alumina to remove the catalyst. Subsequently, the product was precipitated in methanol/water (v/v = 1/1) before being dried in a

vacuum oven at room temperature for 24 h. Further details on this process can be found in our previous work.<sup>2, 3</sup>

#### 4. Synthesis of Amphiphilic 21-Arm, Star-like PAA-b-PS Diblock Copolymer

A mixture of star-like PtBA, CuBr, PMDETA, St and anisole with a molar ratio of 1:1:2:800:800 was placed in an ampoule, which was then degassed with three freeze-pump-thaw cycles and charged with Ar. The vessel was sealed and submerged in an oil bath at 90 °C. After the desired polymerization time, the reaction was terminated by dipping the vessel into liquid N<sub>2</sub>. The solution was then diluted with THF and passed through a column of neutral alumina to remove the catalyst, followed by precipitation of the product in methanol and drying in a vacuum oven for 24 h at room temperature. Subsequently, the resulting star-like PtBA-*b*-PS (0.4 g) was dissolved in dichloromethane (40 mL), followed by the addition of TFA (3 mL). After stirring at room temperature for 24 h, the reaction mixture was dried, re-dissolved in DMF, and precipitated in methanol. The final product star-like PAA-*b*-PS was washed with hexanes and dried under vacuum. Further details on this process can be found in our previous work.<sup>2, 3</sup>

#### 5. Synthesis of 21-Arm, Star-like PAA-b-PEO Diblock Copolymer

To synthesize star-like poly(*tert*-butyl acrylate)-*block*-poly(ethylene oxide) (PtBA-*b*-PEO), 21-arm, star-like PtBA with azide end groups was first prepared. Star-like PtBA (3.6 g) was dissolved in DMF (15 mL), and sodium azide was added to the solution in a molar ratio of 1:10 Br in star-like PtBA:sodium azide. After stirring at room temperature for 24 h, dichloromethane (25 mL) was added to the reaction mixture. The mixture was then washed with distilled water three times. The organic layer was dried with anhydrous MgSO<sub>4</sub>, and the solvent was removed by

vacuum. The final product, 21-arm, star-like PtBA with azide end groups (PtBA-N<sub>3</sub>) was collected and dried under vacuum.

Subsequently, mPEO-OH (5 g) and THF (60 mL) were added to an ampoule, which was then charged with Ar. The DPMK solution was introduced into the system until the solution turned a reddish-brown color. The ampoule was placed in an ice bath and propargyl bromide (5 mmol) was added dropwise over a 2 h period, after which the reaction continued for 24 h at room temperature. The final product, mPEO-alkyne, was obtained by separation of the formed salts and precipitation in diethyl ether twice, and then was dried under vacuum.

Afterwards, 21-arm, star-like PtBA-N<sub>3</sub> and mPEO-alkyne were dissolved in DMF (10 mL); a mixture of mPEO-alkyne, star-like PtBA-N<sub>3</sub>, CuBr, and PMDETA with a molar ratio of 1.5:1:10:10 was placed in an ampoule, which was degassed with three freeze-pump-thaw cycles. The vessel was sealed and submerged in an oil bath at 90 °C. After 24 h, the reaction was terminated by dipping the vessel into liquid N<sub>2</sub>. The solution was then diluted with THF and passed through a column of neutral alumina to remove the catalyst. After removing the solvent, the product, star-like PtBA-*b*-PEO, was precipitated in methanol.

Next, star-like PtBA-b-PEO (0.3 g) was dissolved in dichloromethane (30 mL), followed by the addition of TFA (10 mL). After stirring at room temperature for 24 h, the reaction mixture was gradually precipitated in dichloromethane. The final product, 21-arm, star-like PAA-b-PEO diblock copolymer, was purified, washed with dichloromethane, and dried under vacuum. Further details on this process can be found in our previous work.<sup>2</sup>

## 6. Synthesis of Amphiphilic 8-Arm, Star-like PAA-b-PS Diblock Copolymer

First, to synthesize the star-like macroinitiator 8-Br-4*t*BC8A, 8 hydroxyl groups of 4-*tert*butylcalix [8] arene (4*t*BC8A) were converted to bromine groups via esterification.<sup>4</sup> In a typical bromination process, 4*t*BC8A was first dissolved in anhydrous THF under vigorous stirring, followed by the addition of triethylamine (TEA). The mixture became homogeneous upon continuous stirring. Notably, both THF and TEA were distilled to remove residual water in the solvent before use. BIBB was added dropwise after the solution was cooled to 0 °C. The reaction was continued with stirring under room temperature for 48 h. After the reaction, the crude solution was concentrated via rotary evaporation and precipitated in cold water. The product was then purified using the dissolution-precipitation approach (i.e., dissolved in acetone and precipitated in water) and dried in a vacuum oven to prepare it for further polymerization.

To synthesize amphiphilic 8-arm, star-like PAA-*b*-PS diblock copolymers, a second ATRP step of St monomers and hydrolysis of the P*t*BA block was performed, which is similar to the procedure for preparing 21-arm, star-like PAA-*b*-PS diblock copolymers with the only exception of adding no anisole as solvent for the second ATRP. The reaction solution only contained star-like P*t*BA homopolymer, St, CuBr, and PMDETA, where St served as both monomer and reaction solvent at the same time.

#### 7. Synthesis of Polymer-Ligated CoFe<sub>2</sub>O<sub>4</sub> Nanoparticles

CoFe<sub>2</sub>O<sub>4</sub> (CFO) nanoparticles (NPs) were synthesized by utilizing the as-prepared star-like diblock copolymers as nanoreactors. As a general overview of the process, nanoreactors were dissolved in a mixture of DPE and BA with metal-containing precursors then loaded into the PAA blocks of the nanoreactors under stirring. The CFO NPs, permanently ligated with polymer chains, were finally yielded after thermolysis of precursors.

In a typical procedure (using PS-ligated CFO as an example), 21-arm, star-like PAA-*b*-PS (10 mg) was dissolved in DPE (9 mL) and BA (1 mL) under 50 °C, followed by the addition of

Co(ac)<sub>2</sub> (76 mg) and Fe(acac)<sub>3</sub> (216 mg). The mixture was then stirred overnight under Ar, prior to being heated to refluxing temperature (~258 °C) for 2 h and then gradually cooled to room temperature. The CFO NPs were precipitated and washed with ethanol four times and dried under vacuum overnight.

## 8. Characterization

The MWs and PDIs of hydrophobic polymers were characterized by gel permeation chromatography (GPC) using THF as the mobile phase with a rate of 1.0 ml/min at 35 °C. The MWs and PDIs of amphiphilic and hydrophilic polymers were measured by GPC using DMF (stabilized with LiBr) as the mobile phase with rate of 1.0 ml/min at 35 °C. Both GPCs were calibrated with monodisperse linear PS as the standard. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were measured using a Varian Mercury 400 NMR spectrometer with either CDCl<sub>3</sub> or DMF-d7 as the solvent. Fourier transform infrared (FT-IR) spectra were acquired from a Nicolet 6700 FT-IR spectrometer. The synthesized NPs were examined for size and shape uniformity with transmission electron microscopy (TEM) on a JEOL 100 microscope at 100 kV. TEM samples were prepared by applying a drop of dilute solution onto a carbon-coated copper 300 mesh TEM grid, which was dried under ambient conditions. The crystal structure of the obtained NPs was confirmed by x-ray diffraction (XRD), which was performed on a Panalytical X'Pert PRO X-ray diffractometer using Cu K $\alpha_1$  radiation ( $\lambda$ =1.541 Å) and operating parameters of 40 kV and 40 mA.

#### 9. Electrochemical Measurements

All electrochemical measurements were performed on a Zahner Zennium electrochemical workstation with a Pine Research Modulated Speed Rotator (MSR). During testing, a standard

three-electrode setup was employed; a rotating disk electrode (RDE) with a 5 mm diameter glassy carbon (GC) tip, purchased from Pine Research, was used as the working electrode, a graphite rod as the counter electrode, and either a Ag/AgCl or saturated calomel electrode (SCE) as the reference electrode. O<sub>2</sub>-saturated 1 M KOH was used as the electrolyte for all experiments. All potentials were converted to the reversible hydrogen electrode (RHE) potential using  $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.0592pH$  or  $E_{RHE} = E_{SCE} + 0.241 + 0.0592pH$ .

Catalyst inks were prepared by combining the as-synthesized CFO NPs, acetylene black, 5% Nafion®, DI water, and ethanol into a vial, followed by sonication for 3 h to ensure homogeneity. The obtained ink was dropcast onto the RDE GC tip and dried at room temperature, yielding a mass loading of ~0.25 mg/cm<sup>2</sup>, with a 4:1 mass ratio of CFO:acetylene black.

Prior to collecting measurements, O<sub>2</sub> was bubbled into the electrolyte for 30 minutes and then continuously during testing. Upon immersion of the working electrode in the electrolyte, the catalyst film surface was activated through 20 cyclic voltammetry (CV) scan cycles at a scan rate of 100 mV/s. Linear sweep voltammetry (LSV) curves were collected at a scan rate of 10 mV/s. To test the stability of the ligated CFO NPs, the accelerated degradation CV cycling method was used. Samples were cycled from 1.13 V to 1.83 V vs RHE at a scan rate of 100 mV/s for 500 cycles. LSV curves were collected after 100, 300 and 500 CV cycles. Electrochemical impedance spectroscopy (EIS) was performed at 1.57 V vs RHE with a 5 mV amplitude in a frequency range of 100 kHz to 0.1 Hz for most samples. In order to collect enough data points to obtain a representative portion of the Nyquist curve, EIS was performed over a frequency range of 100 kHz to 0.01 Hz for CFO NPs ligated with 21 PS chains. All measurements were obtained under rotation at 1600 RPM. Impedance spectra were fit to equivalent circuits using "ZView" software from Scribner. Ohmic losses were corrected for by subtracting 95% of the ohmic voltage drop from the

measured potentials (**Figures S1-S2**), using the electrolyte resistance determined at high frequency during EIS.

The electrochemical double-layer capacitance ( $C_{dl}$ ) of the electrocatalysts was measured to gauge differences in electrochemically active surface area (ECSA). This was achieved by performing CV scans in a non-Faradaic potential range at varying scan rates. To more accurately measure the  $C_{dl}$  of the active material, all ECSA tests were run on electrocatalysts prepared without acetylene black.

For all linear sweep voltammetry LSV measurements, the resulting data was corrected, as is typical, for uncompensated resistance within the electrochemical system. This was accomplished by measuring the solution resistance ( $R_s$ ) of the cell through electrochemical impedance spectroscopy EIS. The measured potentials were then corrected for 95% of this uncompensated resistance, which is common practice to prevent overcorrection, using **Eq. S1**.

$$E_{corrected} = E_{measured} - (IR_s * 0.95)$$
(S1)

where *E* is the potential, and *I* is the measured current.



Figure S1: LSV data comparing 21PS-ligated CFO NPs and 8PS-ligated CFO NPs before and after iR correction



**Figure S2:** LSV data comparing 21PS-ligated CFO NPs and 21PEO-ligated CFO NPs before and after iR correction.



**Figure S3:** <sup>1</sup>H-NMR spectrum of star-like macroinitiator heptakis[2,3,6-tri-O-(2-bromo-2-methylpropionyl]-β-cyclodextrin (denoted 21-Br-β-CD).



Figure S4: GPC traces of as-prepared 21-arm, star-like PtBA and PtBA-b-PS.



**Figure S5:** FT-IR spectra of 21-arm, star-like PtBA, PtBA-N<sub>3</sub>, and PtBA-*b*-PEO. The arrow highlights the newly appeared peak present at  $\sim$ 2100 cm<sup>-1</sup>, which is characteristic of the stretching mode of azide groups.



Figure S6: GPC traces of as-prepared 21-arm, star-like PtBA and PtBA-b-PEO.



**Figure S7:** <sup>1</sup>H-NMR spectrum of brominated star-like macroinitiator 4-tert-butylcalix [8] arene (8-Br-4tBC8A).



Figure S8: GPC traces of as-prepared 8-arm, star-like PtBA and PtBA-b-PS.

**Table S1:** Summary of molecular weight (MW) and polydispersity index (PDI) of star-like block copolymers as nanoreactors, and the corresponding dimensions of the polymer-ligated CFO NPs.

Samples	M <sub>n,PAA</sub> a (g/mol)	$M_{n,PS}^{b}$ (g/mol)	<i>M<sub>n,PEO</sub><sup>c</sup></i> (g/mol)	<i>PDI</i> <sup>d</sup>	Diameter of CFO NPs <sup>e</sup> (nm)
21-arm PAA- <i>b</i> -PS	5,600	6,200	-	1.07	5.1±1.2
8-arm PAA- <i>b</i> -PS	5,900	6,600	-	1.25	5.1±1.1
21-arm PAA- <i>b</i> -PEO	6,300	-	5,000	1.08	5.9±1.0

 ${}^{a}M_{n, PAA}$  is the MW of single-arm PAA calculated based on <sup>1</sup>H NMR data from the MW difference between single-arm PtBA (before hydrolysis) and PAA (after hydrolysis).  ${}^{b}M_{n, PS}$  is the MW of single-arm PS calculated based on <sup>1</sup>H NMR data.  ${}^{c}M_{n, PEO}$  is the MW of single-arm PEO obtained from DMF GPC prior to "click" reaction.  ${}^{d}PDI$  of the polymer was recorded by DMF GPC. <sup>f</sup>The dimensions of the resulting CFO NPs were determined by performing image analysis on TEM images.



**Figure S9:** LSV curves of 21PS-ligated CFO, performed at a scan rate of 10 mV/s, after 0, 100, 300 and 500 accelerated degradation CV cycles, performed at a scan rate of 100 mV/s, which demonstrate the stability of the synthesized polymer-ligated CFO NPs under harsh OER conditions.



Figure S10: CV scans performed within a non-faradaic potential range at various scan rates to determine the double-layer capacity ( $C_{dl}$ ) of (a) 8PS-ligated CFO and (b) 21PS-ligated CFO.



**Figure S11:** Nyquist plots for 21PS-ligated CFO and 8PS-ligated CFO obtained from EIS performed at a potential of 1.57 V vs RHE, an amplitude of 5 mV, and a frequency range of 100 kHz to 0.1 Hz for 8PS-ligated CFO and 100 kHz to 0.01 Hz for 21PS-ligated CFO.



**Figure S12:** Nyquist plots for 21PS-ligated CFO and 21PEO-ligated CFO obtained from EIS performed at a potential of 1.57 V vs RHE, an amplitude of 5 mV, and a frequency range of 100 kHz to 0.1 Hz for 21PEO-ligated CFO and 100 kHz to 0.01 Hz for 21PS-ligated CFO.

	21PS-ligated CFO	8PS-ligated CFO	21PEO-ligated CFO
$R_{Total}(\Omega)$	577	276	158
<b>Rs</b> (Ω)	5.997	5.549	5.979
<b>Rp</b> (Ω)	0.8	0.0	1.9
$R_{ct}(\Omega)$	220	190	130
CPE <sub>1</sub> -T	0.4E-4	1.3E-4	0.7E-4
CPE <sub>1</sub> -P	0.78	0.83	0.89
$R_W(\Omega)$	350	80	20
Tw	2.80	0.012	0.23
Pw	0.5	0.5	0.5
CPE <sub>2</sub> -T	4.4E-3	0.12E-3	3.1E-3
CPE <sub>2</sub> -P	0.67	1.00	1.00

**Table S2:** Equivalent circuit fit values calculated for 21PS-ligated CFO, 8PS-ligated CFO, and 21PEO-ligated CFO.

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