

Electronic Supplementary Information

A versatile bottom-up interface self-assembly strategy to hairy nanoparticle-based 2D monolayered composite and functional nanosheets

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Experimental Section

Materials. Styrene (St; Aladdin, AR), *tert*-butyl acrylate (*t*BA; Aladdin, 99%) and 4-vinylpyridine (Aladdin, 96%) were purified by passing through a basic alumina column. Copper(I) bromide (Aladdin, AR) was purified by washing sequentially with acetic acid and ethanol, filtration and drying, and was stored under nitrogen before use. Tetraethyl orthosilicate (TEOS; Aladdin, AR), copper(II) bromide (Aladdin, AR), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA; Aladdin, 99%), Tris[2-(dimethylamino)ethyl]amine (Me₆TREN; Aladdin, 98%), 3-aminopropyltriethoxysilane (APTES; Aladdin, AR), 2-bromoisobutryl bromide (BIBB; Aladdin, AR) and other reagents were used as received.

Synthesis of SiO₂-Br nanoparticles. SiO₂ nanoparticles were synthesized according to a previously reported method.¹ First, ethanol (400 mL) and NH₃·H₂O (25 wt % in water, 21 mL) were mixed in a three-necked round-bottom flask and stirred for 10 min at 40 °C. Then 20 mL TEOS was added and stirred for 10 h at 40 °C to obtain SiO₂ nanoparticles with a diameter of 50 nm. 4 mL of APTES was dropped in a three-necked flask for 2 h and then the temperature was raised to 85 °C for 3 h. The solution was centrifuged at 12000 rpm for 10 min, washed with ethanol and dichloromethane twice, respectively, and then dispersed in 180 mL dichloromethane. After purging with N₂ for 30 min, 8.4 mL triethylamine was injected into the solution, and then 7.2 mL BIBB was added at a rate of 14.4 mL h⁻¹ at 0 °C under stirring. The solution was stirred at 0 °C for 3 h and then at 30 °C for 48 h. The SiO₂-Br product was purified by centrifuging at 12000 rpm and washed by tetrahydrofuran (THF) and acetone/water mixture (1:1) for 3 times and dried in a vacuum oven at 40 °C overnight.

Synthesis of Au@SiO₂-Br nanoparticles. Au@SiO₂-Br nanoparticles were synthesized according to a previously reported method.² HAuCl₄ (0.0432 g) and deionized water (475 mL) were heated to boiling with intensive stirring. Then trisodium citrate (0.25 g) was added and heated for 30 min under reflux. After the solution cooled down to room temperature, poly(vinyl pyrrolidone) (PVP, 0.0084 g) was added and the mixed solution was stirred at room temperature for 24 h. The Au nanoparticles were obtained *via* centrifugation at 12000 rpm for 20 min and dispersed in 12 mL deionized water. The resulting Au nanoparticle solution and ethanol (38 mL) were stirred in a three-neck round-bottom flask under ultrasound for 30 min. Next, NH₃·H₂O (1.6 mL, 25 wt%) was added and stirred for another 10 min. TEOS (1.2 mL in 19 mL ethanol) was added to the mixture by a micro-syringe pump in 20 min, followed by stirring for 12 h. The Au@SiO₂ was obtained and redispersed in 30 mL ethanol. APTES (0.15 mL in 20 mL ethanol) was added dropwise to the Au@SiO₂ solution and stirred for 38 h. The Au@SiO₂-NH₂ was obtained *via* washing by ethanol, deionized water, and dichloromethane, respectively. Au@SiO₂-NH₂ was redispersed and kept in 30 mL anhydrous dichloromethane. Triethylamine (1.4 mL) was added into the Au@SiO₂-NH₂ solution under the N₂ atmosphere. BIBB (1 mL in 4 mL anhydrous dichloromethane) was added slowly at 0 °C under stirring. The solution was stirred at 0 °C for 3 h and then at 30 °C for 48 h. The Au@SiO₂-Br product was purified by centrifuging at 12000 rpm and washed by THF and acetone/water mixture (1:1) for 3 times, and finally dried in a vacuum oven at 40 °C overnight.

Synthesis of Ag@SiO₂-Br nanoparticles. Ag@SiO₂-Br nanoparticles were synthesized according to a previously reported method.³ PVP (10 g) and AgNO₃ (400 mg) were dissolved in ethylene glycol (75 mL) at room temperature with continuous stirring. Then, the solution was heated at 120 °C for 1 h. After cooling down to the room temperature, the Ag nanoparticles could be separated from the solution after adding a large amount of acetone, followed by settlement overnight. The precipitate was washed three times with ethanol by centrifugation at 12000 rpm for 60 min and dispersed in 10 mL of ethanol. The Ag nanoparticles were dispersed in 2-propanol (180 mL) and ultra-sonicated for 15 min. After stirring at 40 °C for 5 min, deionized water (18 mL) and NH₃·H₂O (1.6 mL, 25 wt %) were added. Then, 0.8 mL of TEOS in 20 mL of 2-propanol solution was injected dropwise for 1 h. After reacting for 2 h, the as-obtained Ag@SiO₂ nanoparticles were centrifuged at 12000 rpm for 5 min and washed with ethanol for three times. The Ag@SiO₂ nanoparticles were dispersed in ethanol/water solution (v/v=10:1, 110 mL) in a three-necked flask and APTES (1 mL) was added dropwise to solution for 2 h. After reacting for 12 h at room temperature and 2 h at 80 °C, Ag@SiO₂-NH₂ was obtained. Then the product was centrifuged and washed twice with ethanol and twice with dichloromethane. Subsequently, Ag@SiO₂-NH₂ (1 g) was dispersed in anhydrous dichloromethane (30 mL) in a round-bottom flask, and then filled with N₂ for 30 min. After adding 1.4 mL of triethylamine, the reactor was transferred into an ice-water bath, and then 1.2 mL of 2-bromoisobutyryl bromide was added dropwise for 30 min. After stirred for 3 h, the reaction temperature was raised to 25 °C for 48 h. The as-obtained product was washed with THF and acetone/water (v/v=1:1) mixture for three times, respectively, and then

dried in vacuum at 40 °C for 12 h.

Synthesis of SiO₂-g-PS nanoparticles. SiO₂-g-PS was synthesized according to the following recipe: St/SiO₂-Br/CuBr/CuBr₂/PMDETA = 1000/1/4/0.4/4.4 (molar ratio). SiO₂-Br, CuBr₂, PMDETA, and St were stirred in a Schlenk flask under a nitrogen atmosphere for 30 min. CuBr was then added to the mixture and the solution was stirred under a nitrogen atmosphere for 30 min. The reaction was carried out at 90 °C. The polymerization was stopped by opening the flask to expose the catalyst to air after 24 h. The product was precipitated in excess methanol, washed by THF for three times, and then centrifuged and dried in vacuum at 40 °C overnight. The synthesis procedures of the Au@SiO₂-g-PS and Ag@SiO₂-g-PS nanoparticles were the same as those of the SiO₂-g-PS, except Au@SiO₂-Br and Ag@SiO₂-Br were used in the reaction, respectively.

Synthesis of SiO₂-g-PtBA nanoparticles. SiO₂-g-PtBA was synthesized according to the following recipe: tBA/SiO₂-Br/CuBr/CuBr₂/PMDETA = 1000/1/4/0.4/4.4 (molar ratio). SiO₂-Br, CuBr₂, PMDETA, and tBA were stirred in a Schlenk flask under a nitrogen atmosphere for 30 min. CuBr was then added to the mixture and the solution was stirred under a nitrogen atmosphere for 30 min. The reaction was carried out at 60 °C for 24 h. The polymerization was stopped by opening the flask and exposing the catalyst to air. The product was precipitated in excess methanol, centrifuged at 12000 rpm for 10 min, and dried in vacuum at 40 °C overnight.

Synthesis of SiO₂-g-P4VP nanoparticles. SiO₂-Br (0.14 g), Me₆TREN (0.138 mL), isopropanol (1.5 mL) and 4VP (2.5 mL) were stirred in a Schlenk flask under a nitrogen atmosphere for 30 min. CuBr (0.07 g) was then added to the mixture and the solution was stirred under a nitrogen atmosphere for 30 min. The reaction was carried out at 65 °C for 24 h. The polymerization was stopped by opening the flask and exposing the catalyst to air. The product was centrifuged at 12000 rpm for 10 min, washed with ethanol/EDTA mixture (v/v=20:1) for three times, and dried in vacuum at 40 °C overnight.

Synthesis of SiO₂-g-PS-sheet. The SiO₂-g-PS nanoparticles were dispersed in THF (10 mg mL⁻¹) and added onto the surface of saturated aqueous NaCl solution dropwise by a micro-syringe pump (1 mL min⁻¹) until the surface was overspread with the THF solution. After THF evaporated, the nanosheet was formed and collected. The synthesis procedures of Au@SiO₂-g-PS-sheet, Ag@SiO₂-g-PS-sheet, and SiO₂-g-PtBA-sheet were the same as those of the SiO₂-g-PS-sheet, except the corresponding hairy nanoparticles were used, respectively. The SiO₂-g-P4VP-sheet was synthesized by using isopropanol instead of THF as a solvent.

Synthesis of Co-modified porous carbon nanosheet. SiO₂-g-PS-sheet (0.1 g) and H₂SO₄ (98%, 5 mL) were stirred in a round-bottom flask at 40 °C for 16 h. The product was precipitated in excess ethanol, washed by deionized water for three times, and then centrifuged and dried in vacuum at 40 °C overnight to produce SiO₂-g-PSS-sheet. The as-prepared SiO₂-g-PSS-sheet (0.1 g) and

Co(NO₃)₂ aqueous solution (10 mL, 10 mg mL⁻¹) were stirred in a round-bottom flask at room temperature for 24 h and centrifuged at 12000 rpm for 20 min to produce SiO₂-g-PSS-Co-sheet. The Co-modified porous carbon nanosheet was synthesized by carbonization of SiO₂-g-PSS-Co-sheet at 700 °C for 3 h in N₂ atmosphere with a heating rate of 5 °C min⁻¹. For its control sample, the preparation procedures were the same, except carbonization at 800 °C was undergoing.

Synthesis of Au@PSS-sheet. Au@SiO₂-g-PS-sheet (0.1 g) and H₂SO₄ (98%, 5 mL) were stirred in a round-bottom flask at 40 °C for 16 h. The product was precipitated in excess ethanol, washed by deionized water for three times, and then centrifuged and dried in vacuum at 40 °C overnight to produce Au@SiO₂-g-PSS-sheet. The resulting Au@SiO₂-g-PSS-sheet was etched with HF, thus obtaining the target product Au@PSS-sheet.

Characterization: The nanostructures of the samples were investigated by a Hitachi S-4800 scanning electron microscope (SEM) and a FEI Tecnai G2 Spirit transmission electron microscope (TEM). The molecular weight and molecular weight distribution of the polymers were measured on a Waters gel permeation chromatography (GPC). Molecular weights were calibrated based on polystyrene standards. THF was used as an eluent at a flow rate of 1.0 mL min⁻¹. The concentration of nitrobenzene and *p*-nitrophenol was detected by Shimadzu UV-Vis-NIR Spectrophotometer.

Catalytic activity measurement: 2.7 mL nitrobenzene or *p*-nitrophenol aqueous solution (0.1 mM) and 0.5 mL Au@PSS-sheet aqueous dispersion (1 mg mL⁻¹) were mixed in the UV quartz cuvette. Then 0.3 mL sodium borohydride aqueous solution (0.1 M) was added and the concentration of nitrobenzene was tracked by UV-Vis-NIR Spectrophotometer immediately.

Electrocatalytic measurements: The OER activity was evaluated in a three-electrode configuration using a rotating disk electrode with an electrochemical workstation (CHI 760E) at ambient temperature. The glassy carbon electrode (Diameter = 5 mm) was used as the support of the working electrode. The Ag/AgCl electrode was used as the reference electrode and the platinum-carbon electrode was used as the counter electrode. Potentials were referenced to a reversible hydrogen electrode (RHE): $E_{\text{vs RHE}} = 0.197 \text{ V} + 0.059 \times \text{pH} + E_{\text{vs Ag/AgCl}}$, overpotential (η) = $E_{\text{vs RHE}} - 1.23 \text{ V}$. The catalyst suspension was prepared by dispersing 2.0 mg Co-modified porous carbon nanosheet in a mixed solution of 0.3 mL deionized water, 0.26 mL ethanol and 40 μL Nafion solution (5 wt%), followed by ultrasonication for 1 h. 10 μL of the catalyst suspension was added onto the surface of the glassy carbon electrode and then dried at ambient temperature. Linear sweep voltammetry was recorded in 1.0 M KOH at a rotation speed of 1600 rpm to obtain the polarization curves (Scan rate: 10 mV s⁻¹, scan range: 1.2 V-1.8 V vs RHE).

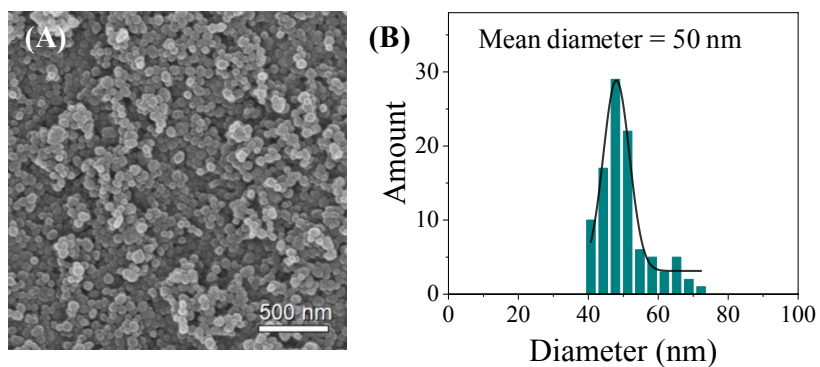


Figure S1. (A) SEM image and (B) particle size distribution curve from SEM image analysis for SiO₂ nanoparticles

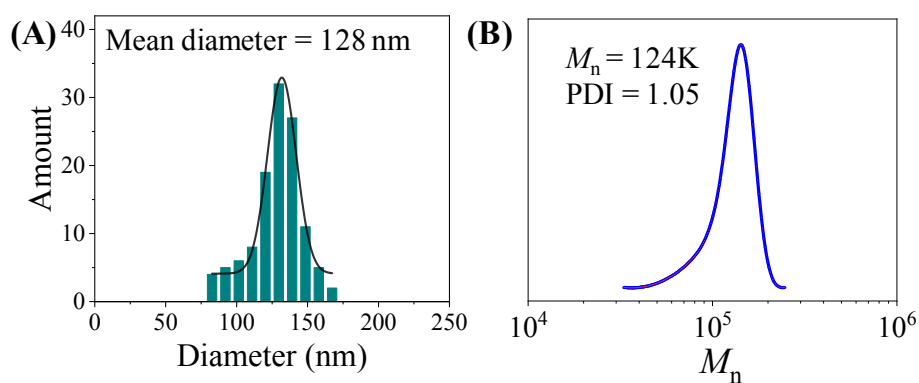


Figure S2. (A) Particle size distribution curve from SEM image analysis for SiO₂-g-PS nanoparticles; (B) GPC trace for cleaved polymers from SiO₂-g-PS nanoparticles

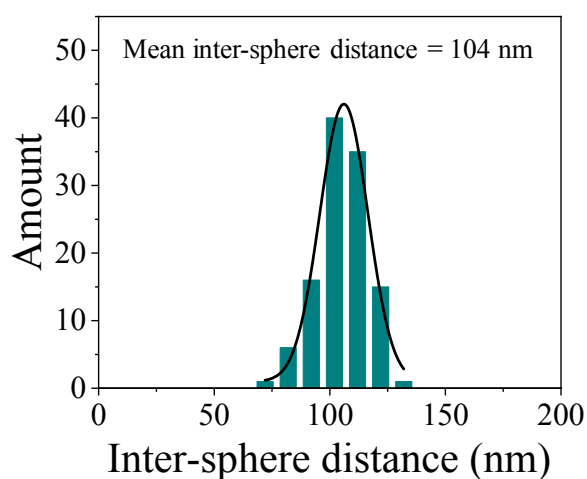


Figure S3. The distribution curve of inter-sphere distance between two adjacent SiO₂ nanoparticles from TEM image analysis for SiO₂-g-PS-sheet

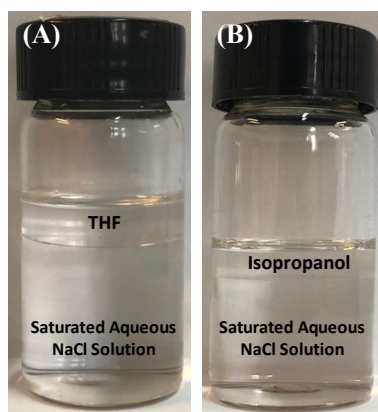


Figure S4. Saturated aqueous NaCl solution is immiscible with (A) THF and (B) isopropanol

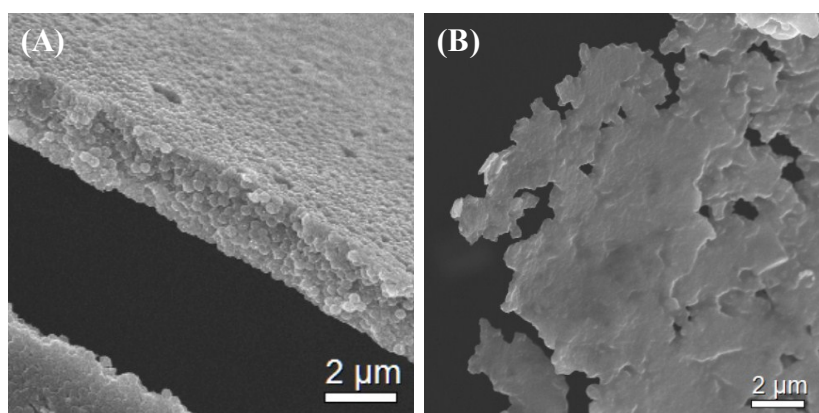


Figure S5. SEM images for (A) the thick multilayered polymer membrane product obtained by using a dropper to add the hairy nanoparticle solution, and (B) the ill-defined 2D polymer nanosheet product obtained by using a very diluted hairy nanoparticle solution.

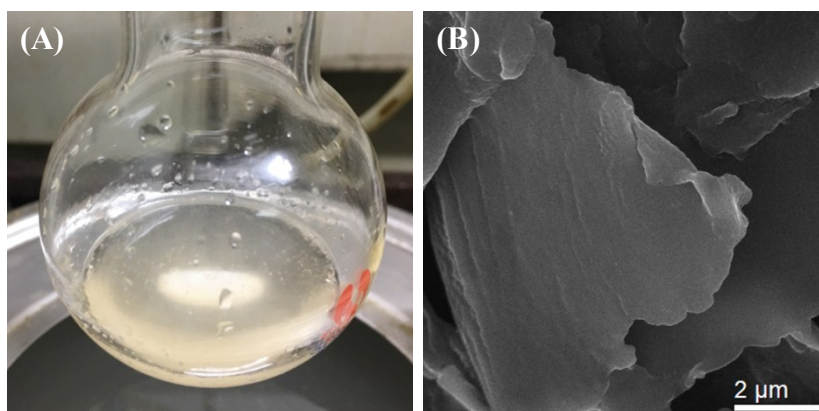


Figure S6. (A) Photograph of SiO₂-g-PSS-sheet in sulfuric acid (98%); (B) SEM image for SiO₂-g-PSS-sheet

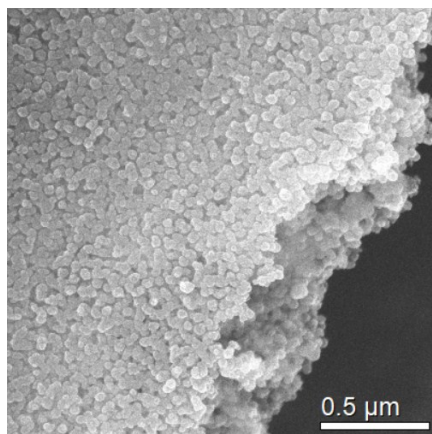


Figure S7. SEM image for the thick multilayered Co-modified porous carbon nanosheet sample obtained with carbonization temperature of 800 °C

Reference

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2. K. Leng, W. Mai, X. Zhang, R. Liu, X. Lin, J. Huang, H. Lou, Y. Xie, R. Fu, D. Wu, *Chem. Commun.* **2018**, *54*, 7159-7162.
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