Electronic Supplementary Information

Molybdenum-doped Mesoporous Carbon/ Graphene Composites as an Efficient Electrocatalyst for Oxygen Reduction Reaction

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1、Experiment Section

Synthesis of graphene oxide (GO): GO was prepared following the modified Hummers' method.[1] Graphite powder (2 g, 325 mesh) was put into a mixture of 12 mL of concentrated H_2SO_4, 3.0 g of $K_2S_2O_8$, and 3.0 g of P_2O_5. The solution was heated to 80 °C using an oil bath and stirred for 5 h. Next, the mixture was cooled to room temperature overnight and diluted with deionized water (500 mL). Then, the product was obtained by filtering using 0.2 μm Nylon film and dried naturally. Pretreated graphite powder was put into 0 °C concentrated H_2SO_4 (150 mL), and 25 g of $KMnO_4$ was added gradually under stirring while the temperature of the mixture was kept around 5 °C by using an ice bath. Successively, the mixture was stirred at 35 °C for 4 h and then diluted with 250 mL of deionized water by keeping the temperature under 50 °C. One liter of water was then injected into the mixture followed by adding 30 mL of 30% H_2O_2 drop by drop. The mixture was filtered and washed with 1:10 HCl aqueous solution (1 L) to remove metal ions followed by 1 L of deionized water to remove the acid. It was purified by dialysis for 1 week to remove the remaining metal species. Finally, brown GO powder was obtained by filtrating the product and drying in vacuum.

Resol prepolymer: Resol prepolymer was prepared in an alkaline solution according to a previously reported method.[2] 1.0 g phenol and 3.5 mL formaldehyde aqueous solution (37 wt%) were dissolved in 30 mL 0.1 M NaOH aqueous solution, and the mixture was heated at 70 °C for 1 h to obtain the low-molecular weight resol prepolymer. A solution of triblock copolymer Pluronic F127 (1.1 g, Mw =12600, $PEO_{106}PPO_{70}PEO_{106}$, Aldrich) dissolved in 110 mL deionized water was added. The mixture was stirred at 65 °C for 18 h to obtain the resol prepolymer that contained Pluronic F127.

Mo-doped MCG composites: 0.5 g ammonium molybdate and 30 mg GO powder were dispersed in 20 mL deionized water, and the exfoliation of GO was achieved by ultrasonication. Then 14 mL as-prepared resol prepolymer solution was added into the above solution. Following ultrasonic mixing, the obtained solution was transferred into an autoclave and heated at 150 °C for 20 h. The precipitated powders were filtered, washed thoroughly with water and ethanol, dried at 60 °C. Mo-doped MCG composites were obtained after the precursor was carbonized at 700 °C in an argon atmosphere for 3 h and the triblcok copolymer templates were removed during this process. For comparison, molybdenum-doped mesoporous carbon (Mo-doped MC) composites was synthesized under the same conditions without GO. Mesoporous carbon/graphene (MCG) composites was synthesized under the same conditions without ammonium molybdate. Mesoporous carbon (MC) was synthesized under the same conditions without GO and ammonium molybdate.

2. Characterizations

XRD patterns were obtained via a D8 Advance (Bruker) X-ray diffractometer with CuK a radiation (l=1.5418). SEM images were obtained by means of a JSM 7401F, 3 KV. TEM images

were obtained with a Hitachi model H-800 transmission electron microscope operating at an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera Scanning X-ray Microprobe using a monochromic Al-Kα (λ = 1486.7 eV) (Binding energy is calibrated with C1s - 284.8 eV). Nitrogen adsorption-desorption isotherms were performed by using a Micromeritics TriStar II apparatus. The samples were outgassed for 10 h at 200 °C under vacuum before the measurements.

3. Electrochemical measurement

All experiments were performed at room temperature. Before every measurement, the glassy carbon electrode (GCE) surface was polished using 50 nm Al_2O_3 slurry and washed with ethanol and deionized water in ultrasonic bath. The electrochemical cell was assembled with a conventional three-electrode system: a glassy carbon working electrode, an Ag|AgCl/KCl (saturated) reference electrode, and a Pt wire counter electrode. The homogeneous ink was prepared by dispersing 1 mg catalyst 1 mL in Nafion solution (0.5 wt%, aq) with at least 30 min sonication. Then 6 and 20 mL of the catalyst inks were coated onto a clean GCE of 3 and 5 mm in diameter for CV and RDE measurements. Electrochemical measurements were performed using a CHI 830 electrochemical analyzer coupled with a RDE system (Princeton Applied Research, Model 616).

1 W. Hummers, R. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.
2 Y. Fang, D. Gu, Y. Zou, Z. Wu, F. Li, R. Che, Y. Deng, B. Tu, D. Zhao, *Angew. Chem. Int. Ed.*, 2010, **49**, 7987.

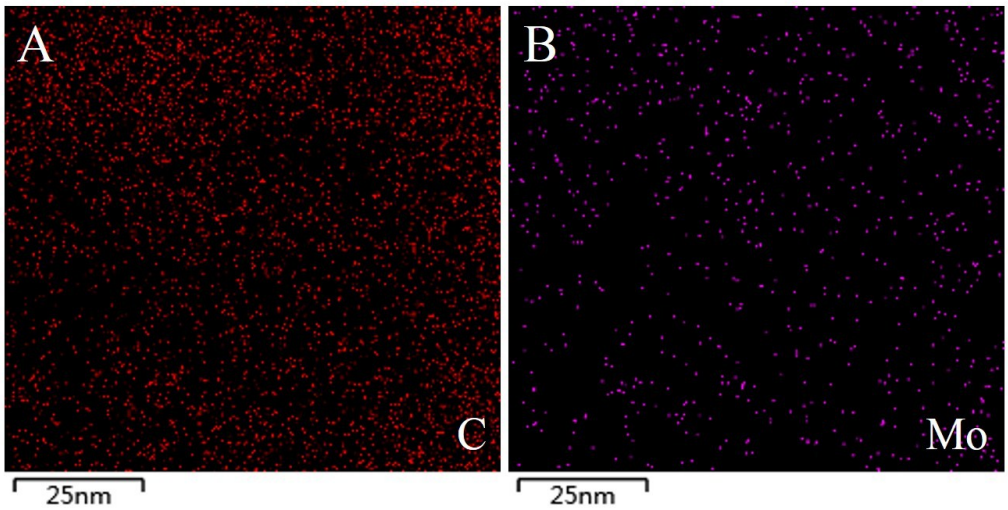

Figure S1. Elemental mapping of A) C and B) Mo.

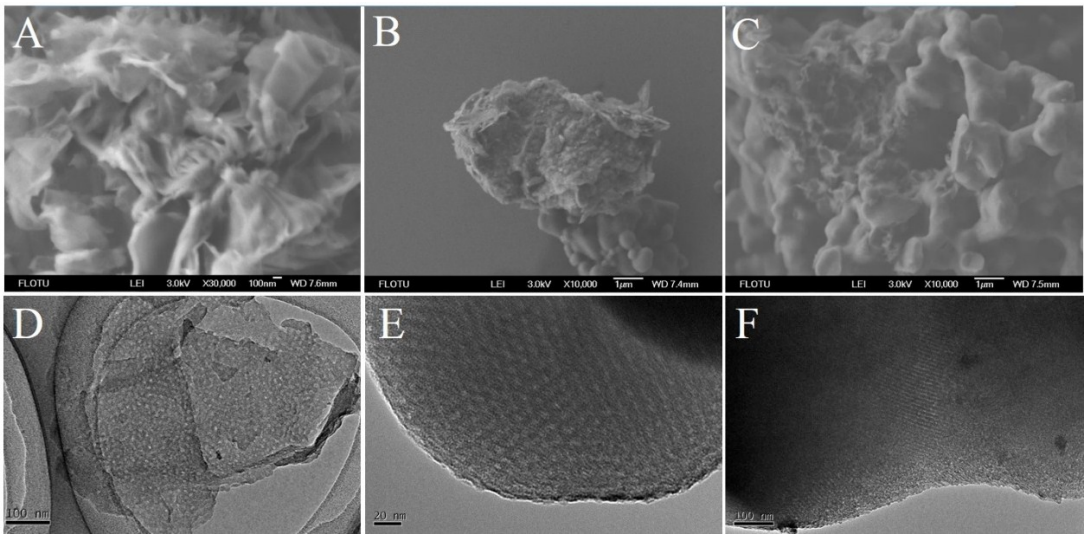

Figure S2. (A, D) SEM and TEM images of MCG (mesoporous carbon/graphene composites), (B, E) SEM and TEM images of MC (mesoporous carbon), (C, F) SEM and TEM images of Mo-doped MC (molybdenum-doped mesoporous carbonomposites).

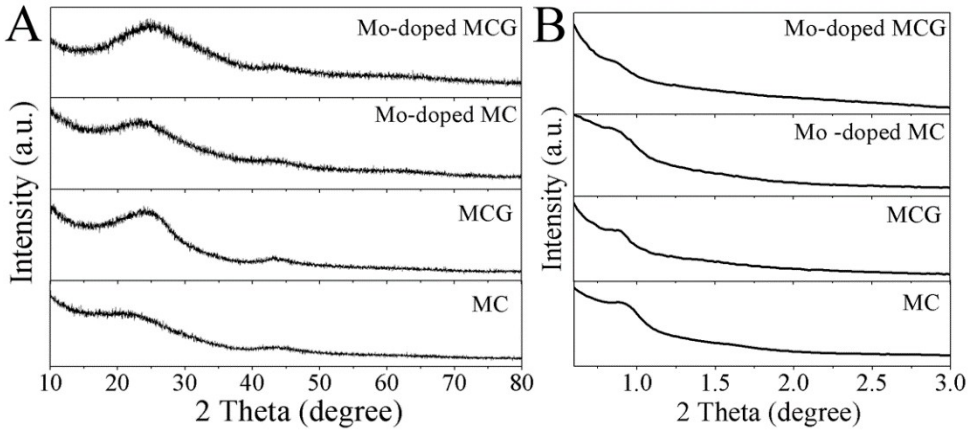

Figure S3. (A) Wide-angel XRD and (B) low-angel XRD patterns of MC (mesoporous carbon), Mo-doped MC (molybdenum-doped mesoporous carbon composites), MCG (mesoporous carbon/graphene composites) and Mo-doped MCG (molybdenum-doped mesoporous carbon/graphene composites).

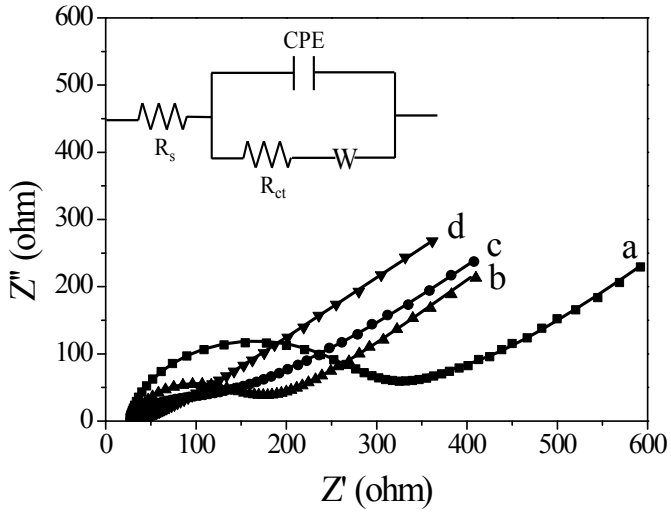

Figure S4. Electrochemical Impedance Spectra of of (a) MC (mesoporous carbon), (b) Mo-doped MC (molybdenum-doped mesoporous carbon composites), (c) MCG (mesoporous carbon/graphene composites) and (d) Mo-doped MCG (molybdenum-doped mesoporous carbon/graphene composites) in 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.5 M KCl from 0.5 Hz to 100 kHz with a signal amplitude of 10 mV. Inset is the equivalent circuit used to fit the impedance spectra. In the equivalent circuit, R_s, R_{ct}, and CPE are the electrolyte resistance, the electron-transfer resistance, and the chemical capacitance, respectively.

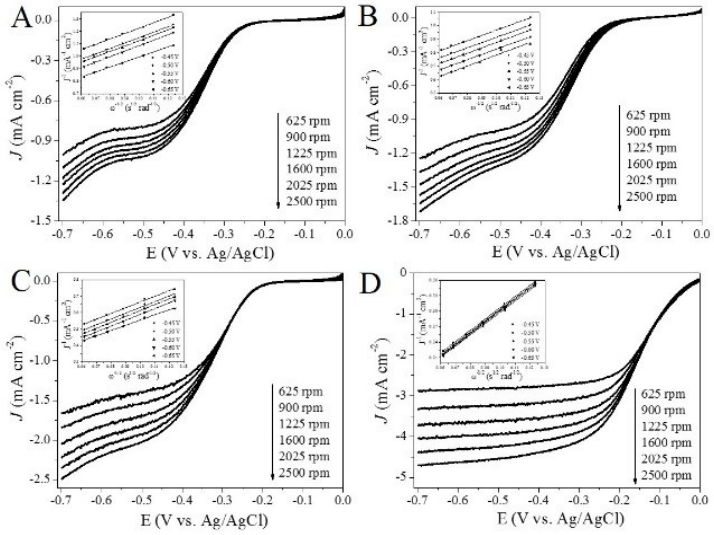

Figure S5. Rotating disk electrode voltammograms of (A) MC (mesoporous carbon), (B) Mo-doped MC (molybdenum-doped mesoporous carbon composites), (C) MCG (mesoporous carbon/ graphene composites) and (D) commerial Pt/C in O_2-saturated 0.1 M KOH solutions at different rotation rates. Sweep rate: 5 mV s^{-1}. Insets are the corresponding Koutecky-Levich plots at different potentials.

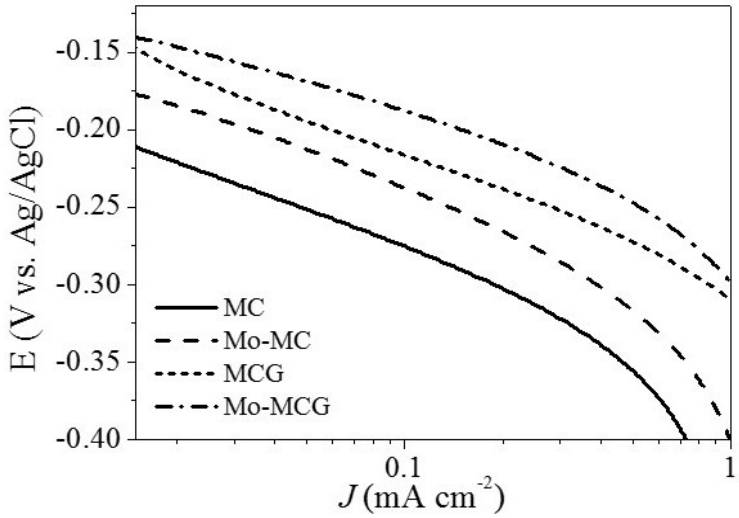

Figure S6. The Tafel curves of MC, Mo-MC, MCG and Mo-MCG.

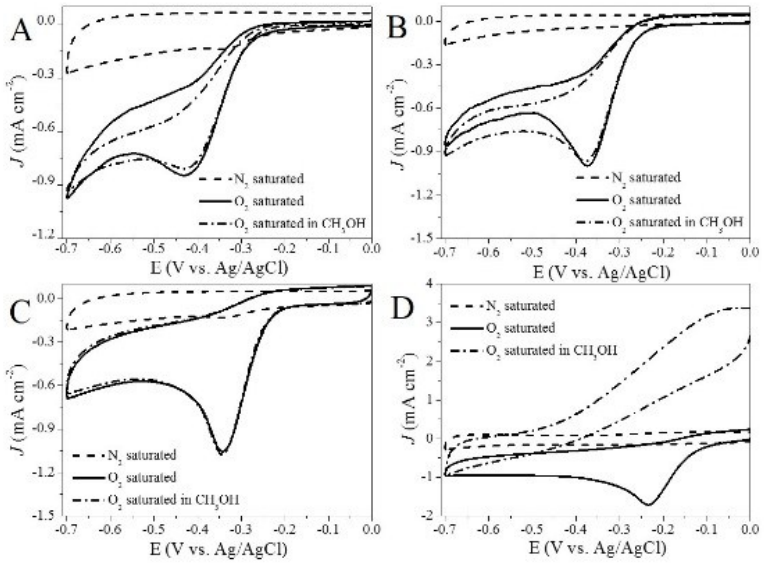

Figure S7. Cyclic voltammograms of (A) MC (mesoporous carbon), (B) Mo-doped MC (molybdenum-doped mesoporous carbon composites), (C) MCG (mesoporous carbon/graphene composites) and (D) commerial Pt/C in N_2- and O_2-saturated 0.1 M KOH solutions as well as O_2-saturated 0.1 M KOH solution with 3 M methanol. Scan rate: 50 mV s^{-1}.