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Supporting Information

Preparation of the silica templates

Mesoporous silica microspheres of 1 μ m were synthesized under basic pH conditions.¹ In a typical synthesis, 0.46 g of a cationic surfactant (dodecylamine) was dissolved in 125 mL ethanol and water (50:50) under stirring. Afterwards, 5.4 mL of ammonium hydroxide solution and 1.9 g of tetraethyl-orthosilicate (TEOS) were added to the mixture and it was vigorously stirred for 10 min. The reaction mixture was maintained in a closed Teflon vessel at 25 °C for one day. The solid product was filtered, washed with distilled water, dried, and calcined in air at 600 °C. This type of silica, denoted as SS, has a specific surface area of 910 m² g⁻¹, a pore volume of 0.76 cm³ g⁻¹ and a pore size distribution centered at 2.5 nm.

In order to enlarge the pore size of the template, a sample of the silica synthesized at 25 °C was mixed with distilled water (50 mL) and aged for one day at a temperature of 80 °C. The solid product was filtered, washed with distilled water, dried, and calcined in air at 600 °C. This type of silica, denoted

as SSH, has a specific surface area of 680 m² g⁻¹, a pore volume of 0.68 cm³ g⁻¹ and a pore size distribution centered at 3.6 nm.



Figure S1. Nitrogen sorption isotherms and pore size distributions (Insets) of a) SS and b) SSH, and SEM images of c) SS and d) SSH silica templates.



Figure S2. TGA analysis of the N-CS and N-CSH samples in air (heating rate 5 °C min⁻¹).



Figure S3. XPS general spectra of (a) N-CSH and (b) N-CS carbon microspheres.



Figure S4. EDX spectra of (a) N-CSH and (b) N-CS carbon microspheres.



Figure S5. RDE LSV voltammograms (O_2 -saturated) for N-CSH in (a) 0.1 M KOH and (b) 0.5 M H₂SO₄, and for N-CS in (c) 0.1 M KOH and (d) 0.5 M H₂SO₄ at different rotation rates.



Figure S6. (a) Comparison of the Koutecky–Levich plots for N-CSH and N-CS samples with those of an ideal 2-electron and 4- electron processes at 0.67 V in 0.1 M KOH and (b) at 0.48 V in 0.5 M H_2SO_4 .

References

1. A. B. Fuertes and P. Tartaj, *Small*, 2007, **3**, 275-279.