Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

One-Step Synthesis of Silica@Resorcinol-Formaldehyde Spheres and their Application for the Fabrication of Polymer and Carbon Capsules

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Experimental Section

Synthesis of the Materials. In a typical synthesis of the silica@RF spheres (diameter ~ 220 nm), 1.25 mL (20.4 mmol) of ammonia aqueous solution (32 wt %) was added to 40 mL ethanol/water mixture (ethanol/water volume ratio = 2) and then stirred for 30 minutes at 30 ºC. Subsequently the following compounds were added under vigorous stirring: a) tetraethyl orthosilicate (1.4 mL, 6.4 mmol), b) ten minutes later resorcinol (0.2 g, 1.8 mmol) and c) ten minutes after that formaldehyde solution (0.28 mL, 3.6 mmol). The reaction mixture was stirred for 24 h at 30 ºC and subsequently at 100 ºC for 24 h (static conditions). The solid product was collected by centrifugation, washed with water and ethanol, and air-dried at 100 ºC for several hours. The polymer RF capsules were obtained by dissolving the silica core with HF (15 wt %). For the fabrication of hollow carbon spheres, firstly, the silica@RF particles were heated under N_2 up to 750 ºC (5 K/min) for 1 hour. Subsequently, the carbonized product (silica@carbon spheres) was treated with hydrofluoric acid (15 wt %) in order to dissolve the silica core.

Materials Characterization. The morphology of the powders was examined by scanning (SEM, Quanta FEG650 FEI) and transmission (TEM, JEOL-2000 FXII) electron microscopy. Nitrogen adsorption and desorption isotherms were performed at -196 °C in a Micromeritics ASAP 2020 volumetric adsorption system. The BET surface area was deduced from an analysis of the isotherm in the relative pressure range of 0.04-0.20. The total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore volume was obtained by means of a t-plot analysis. The pore size distributions were determined by means of the Quenched Solid State Functional Theory (QSDFT) method using nitrogen adsorption data and assuming

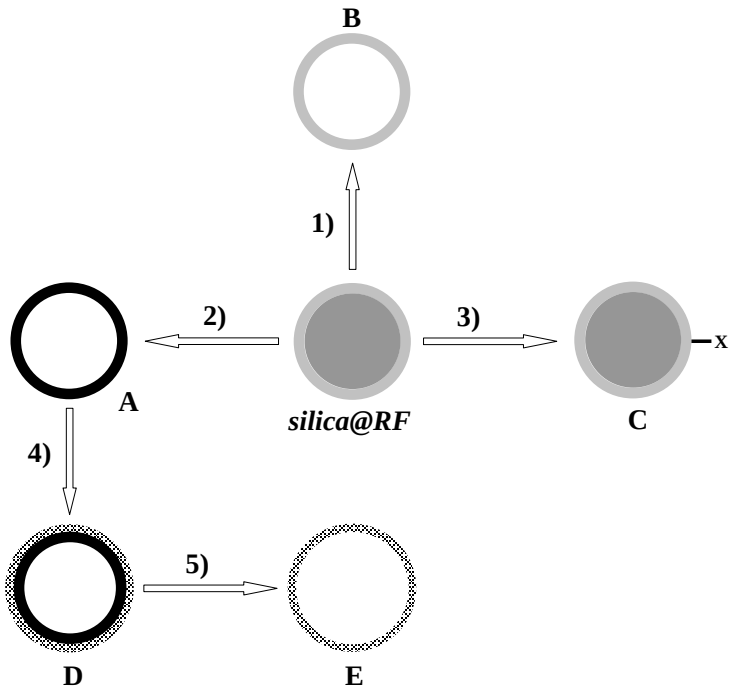
a slit pore model. Diffuse reflectance Fourier-Transform Infrared (FT-IR) spectra were recorded on a Nicolet Magna-IR 560 spectrometer fitted with a diffuse reflection attachment. X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 instrument operating at 40 kV and 20 mA and using CuK*a* radiation (λ=0.15406 nm). The thermogravimetric analyses (i. e. carbonization and calcinations) of the products were performed on a CI Electronics system.

Table S1. Typical synthesis parameters for Silica@RF, Silica Stöber and Resorcinol-Formaldehyde spheres (Reaction temperature: 30ºC)

Spheres	Concentration, $mol \cdot L^{-1}$				(E/W), v/v	Reaction time, h	Diameter of spheres, nm	Reference
	TEOS	NH_3	Resorcinol	Formaldehyde				
Silica@RF	0.06-0.36	0.5	0.045	0.09	2-7	48	150-500	This work
Silica Stöber	0.16	0.6	-	-	7	1	200	Büchel et al. [a]
RF	-	0.05	0.065	0.13	0.4	48	520	Liu et al. [b]

[a] G. Büchel, K. K. Unger, A. Matsumoto, K. Tsutsumi, *Adv. Mater*. 1998, **10**, 1036.

[b] J. Liu, S. Z. Qiao, H. Liu, J. Chen, A. Orpe, D. Y Zhao, G. Q. (Max) Lu, *Angew. Chem. Int. Ed*. 2011, **50**, 5947.



Scheme S1. Illustration of the procedures used to synthesize a variety of materials derived from silica@RF spheres: (A) carbon capsules, (B) polymer capsules, (C) functionalized silica@RF spheres, (D) carbon capsules coated with an inorganic phase, (E) inorganic capsules. The basic synthesis procedures used were: (1) silica etching, (2) carbonization and silica etching, (3) incorporation of functional groups, (4) coating the carbon capsule with an inorganic phase (e. g. metallic oxides) and (5) calcination.

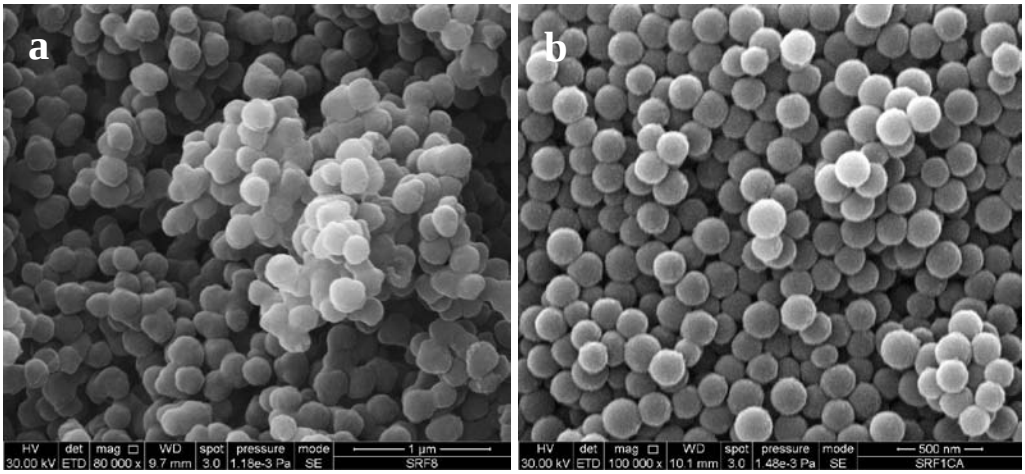


Figure S1. SEM images of: (a) Silica-RF composite produced by using high resorcinol and formaldehyde concentrations of 0.09 M and 0.18 M respectively, and (b) silica cores produced by the calcination of silica@RF spheres.

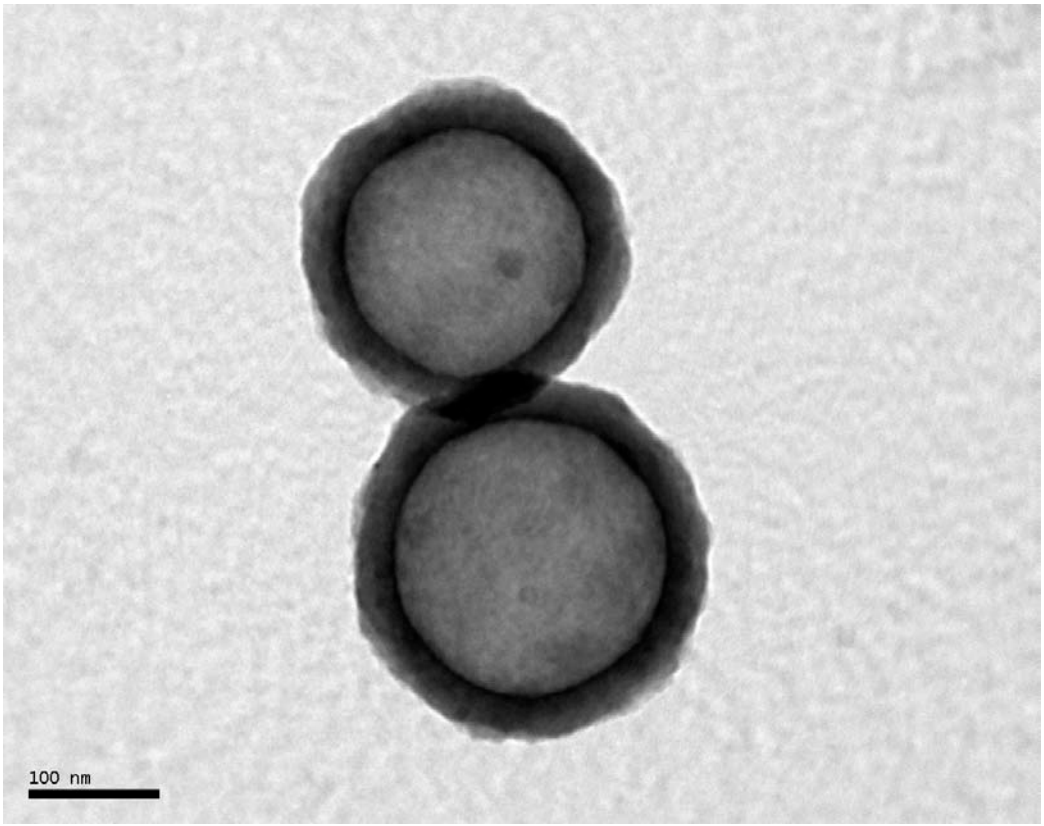
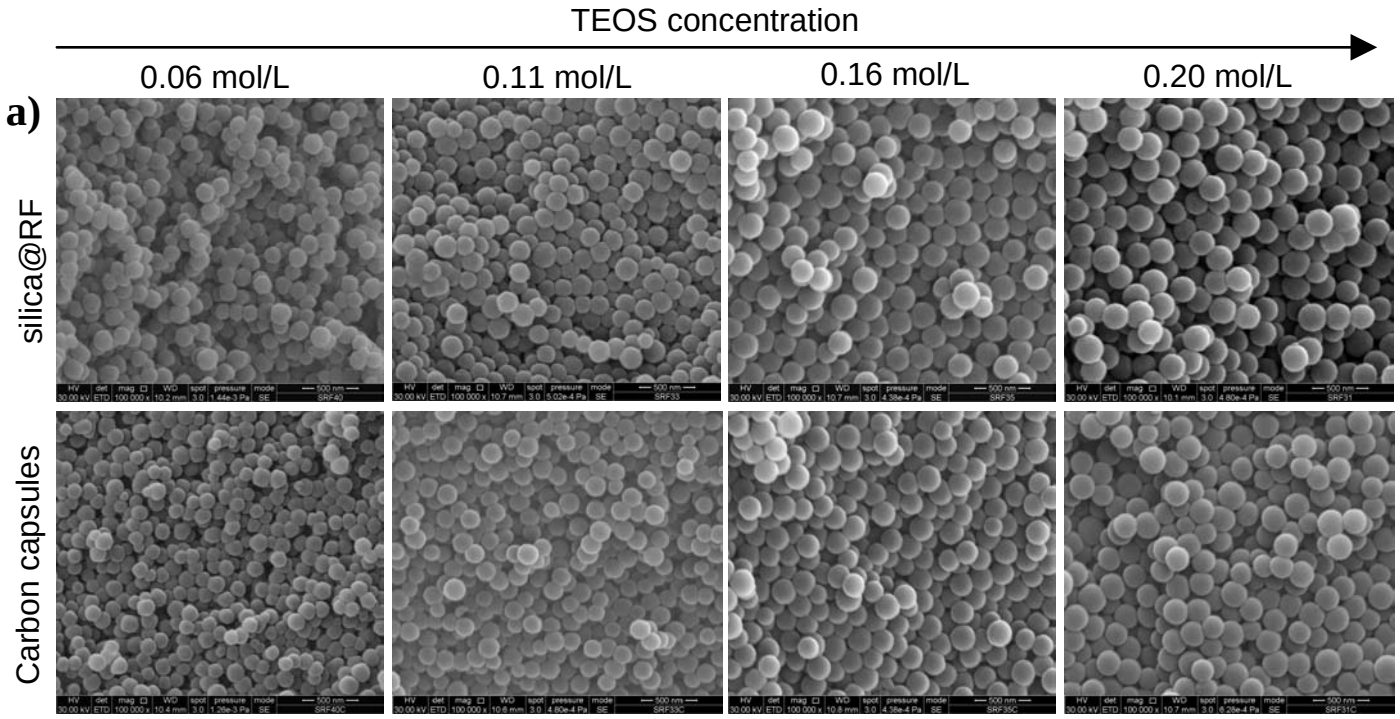


Figure S2. High-magnification TEM image of the resorcinol-formaldehyde capsules. (E/W=2, C_{TEOS}=0.16 mol·L^{-1})



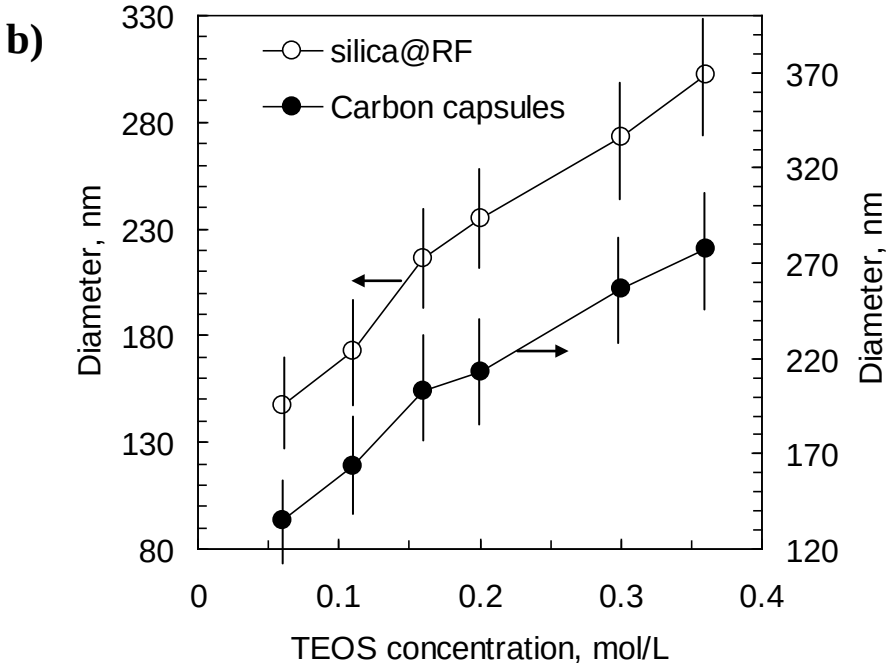


Figure S3. (a) SEM images of silica@RF spheres and carbon capsules of different particle sizes synthesised using different TEOS concentrations and (b) particle diameter of silica@RF spheres and carbon capsules as a function of the TEOS concentration. The mean particle diameters and standard deviations were estimated from a large number of particles (>100). (E/W=2).

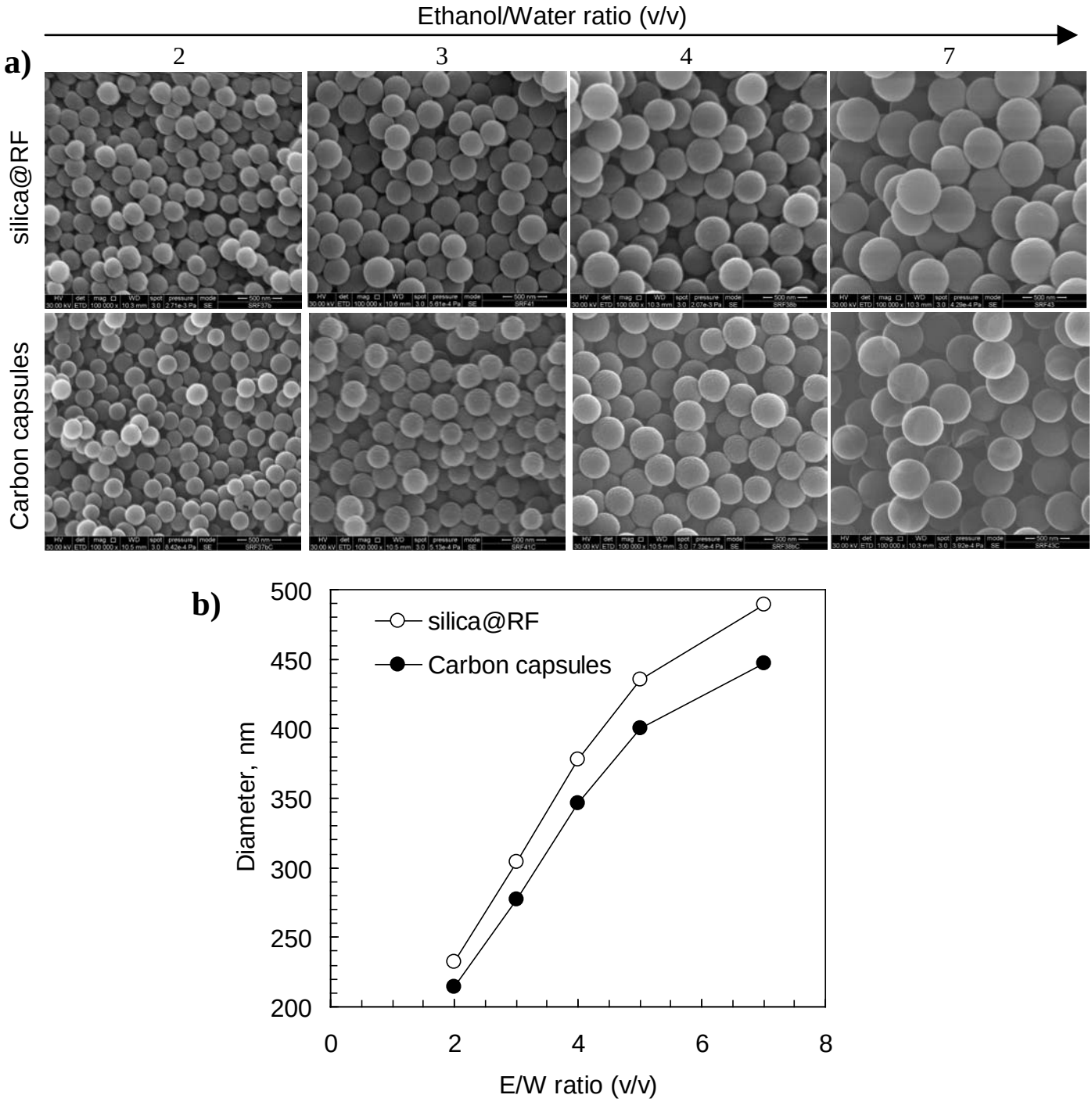


Figure S4. (a) SEM images of silica@RF spheres and carbon capsules of different particle sizes synthesised using different (E/W) ratio values and (b) particle diameter of silica@RF spheres and carbon capsules as a function of the (E/W) ratio. (C_{TEOS}= 0.20 mol·L^{-1}).

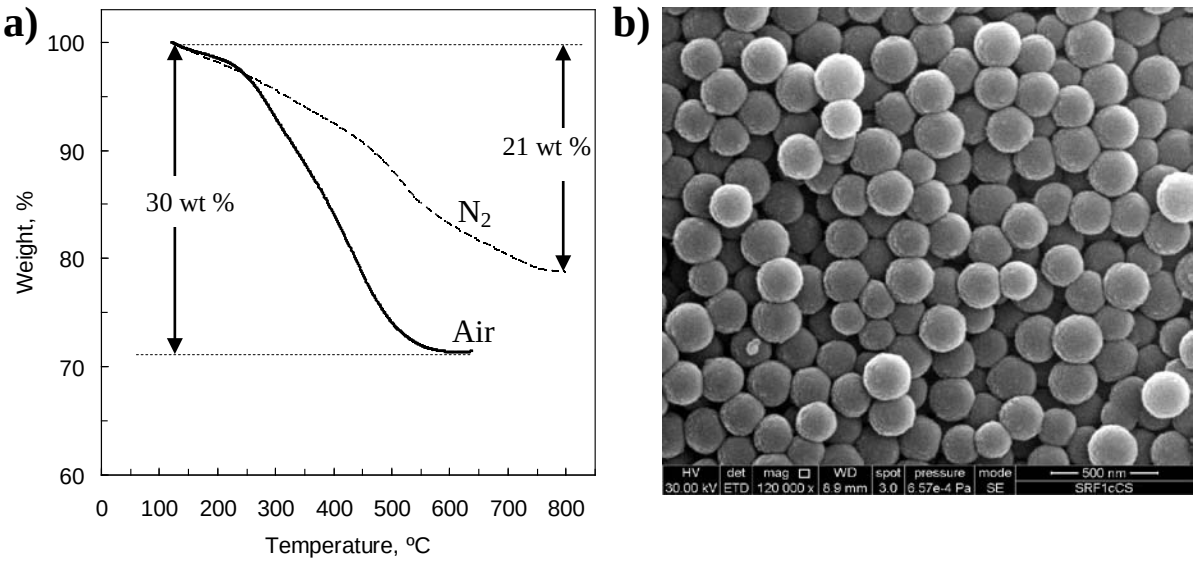


Figure S5. (a) TGA of silica@RF spheres in air (continuous line) and N_2 (dotted line) (Heating rate: 5 K/min). RF content of around 30 wt %. Weight loss in N_2 ~21 wt %. Carbon content in the silica@carbon composite was ~10 wt %. (b) SEM images of silica@carbon spheres. (E/W=2, C_{TEOS}=0.16 mol·L^{-1}).

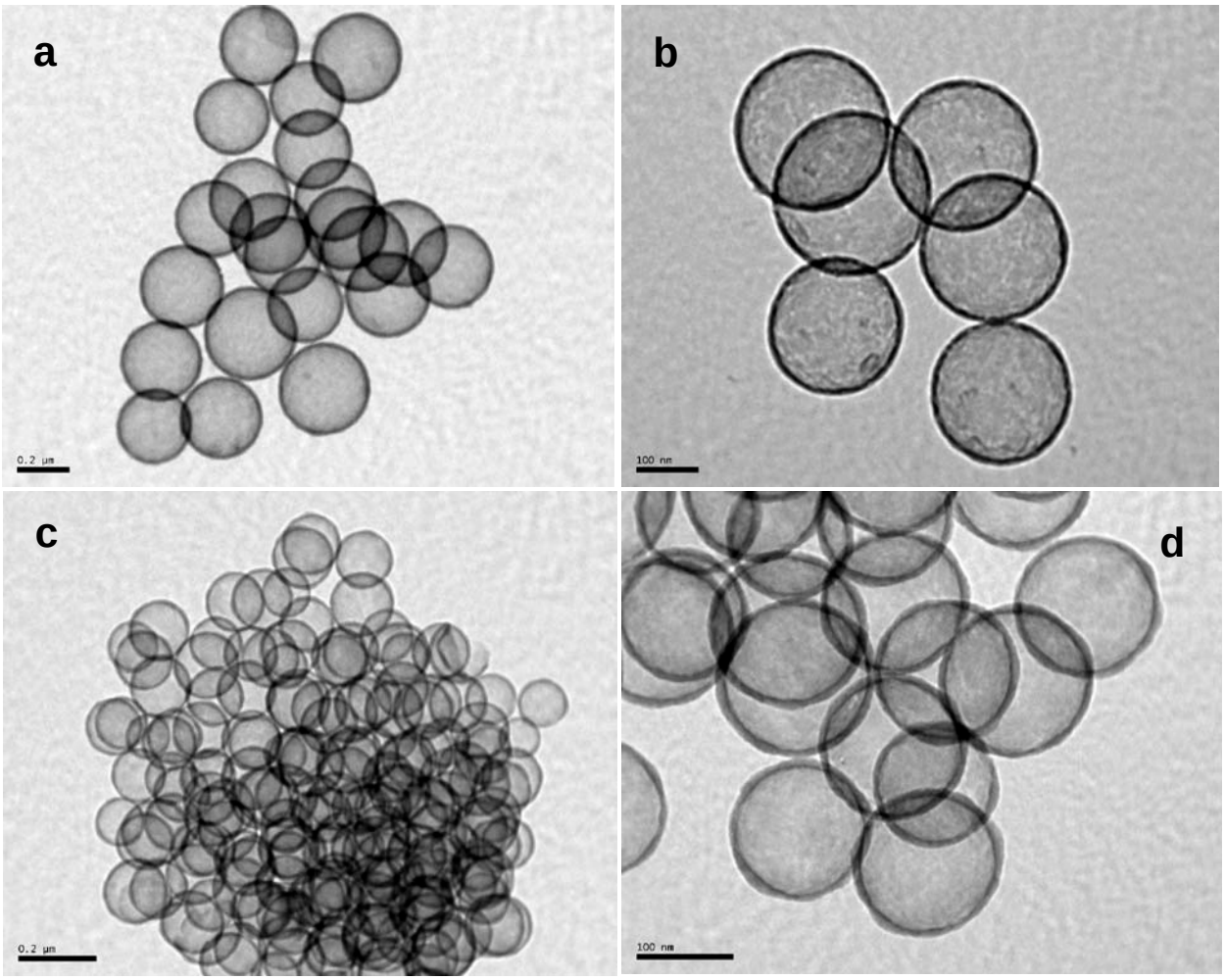


Figure S6. TEM images of carbon capsules obtained from silica@RF spheres synthesised by using TEOS concentrations of: (a) 0.36 mol/L, (b) 0.30 mol/L and (c, d) 0.11 mol/L. (E/W=2)

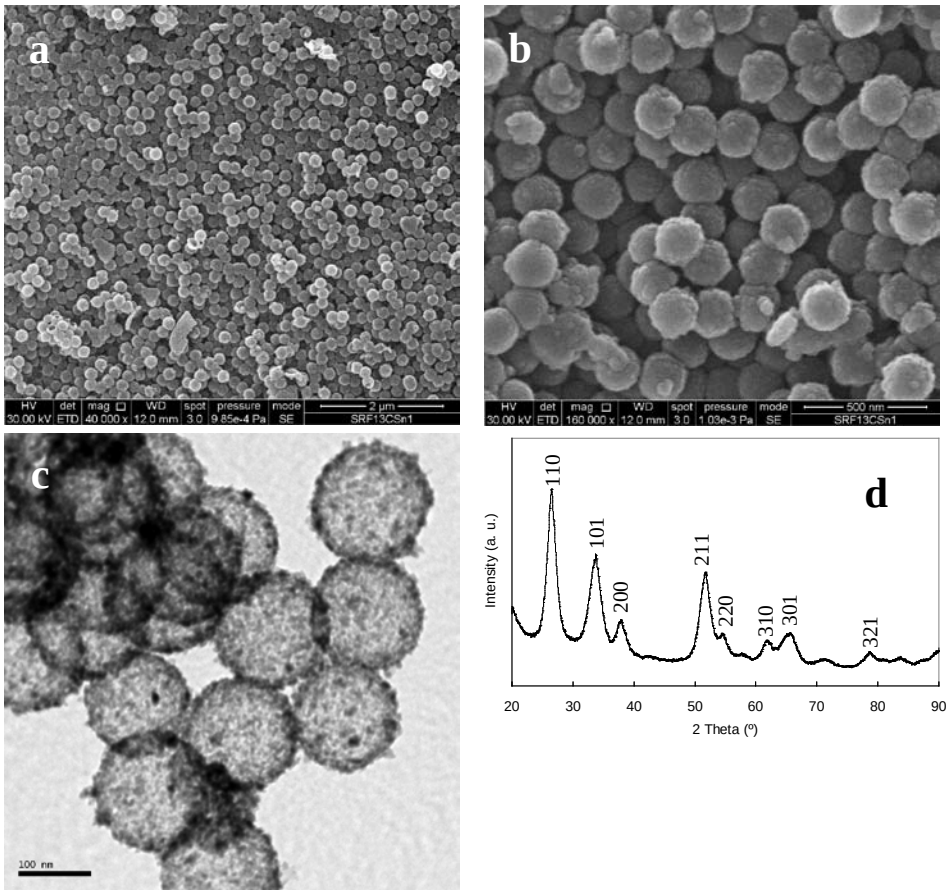


Figure S7. SEM (a, b) and TEM (c) images of carbon capsules coated with SnO_2 nanoparticles, and (d) XRD pattern of the deposited SnO_2 phase (JCPDS 41-1445, SnO_2 crystallyte size of ~ 5 nm). The deposition of SnO_2 nanoparticles upon the outer surface of hollow carbon spheres was carried out by using the procedure reported by Cao et al. [Y. Cao, J. Cao, J. Liu, M. Zheng, K. Shen, *Chem. Lett*. 2007, **36**, 254]

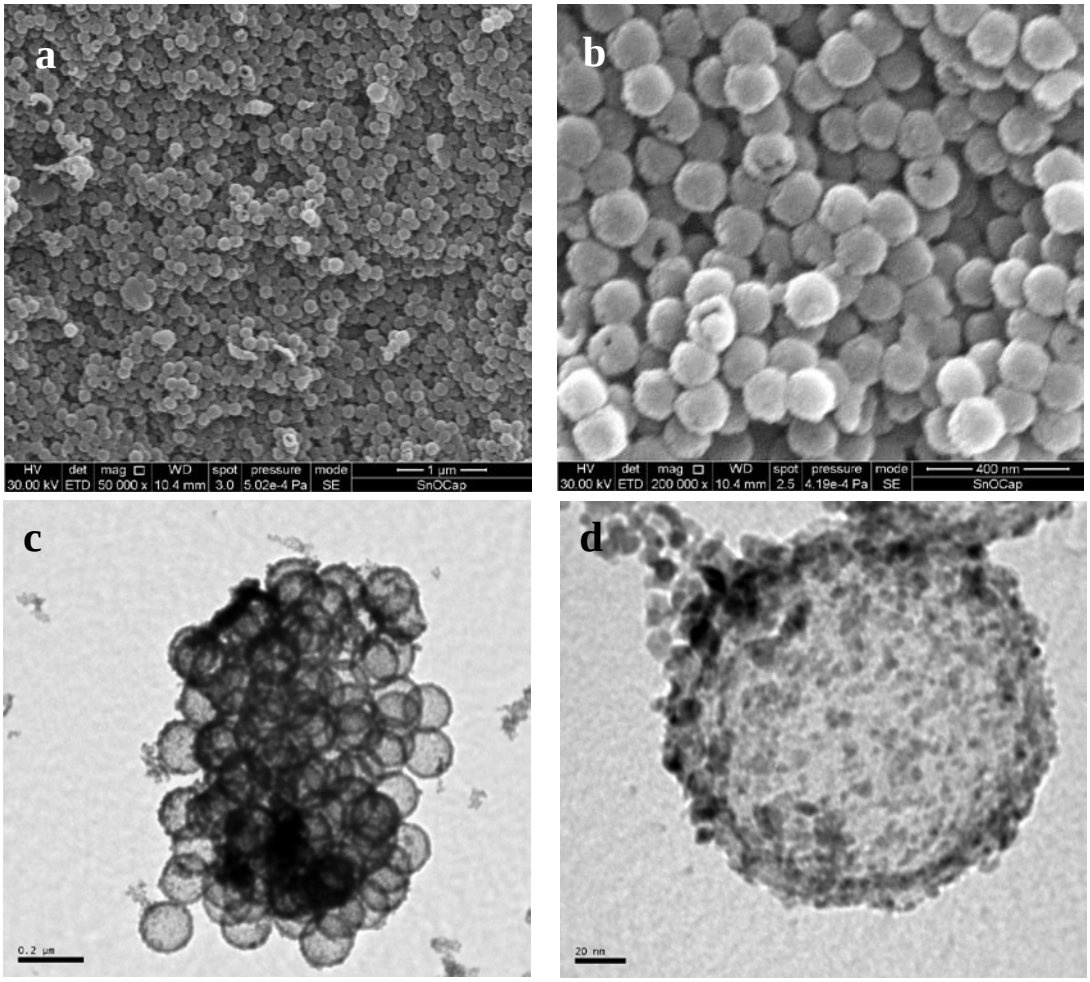


Figure S8. SEM (a, b) and TEM (c, d) images of SnO_2 capsules produced by calcining SnO_2-C hybrid hollow spheres (in air up to 500ºC).