

Experimental section:

The SiO₂@ZrO₂ core-shell binary exotemplates were prepared according a method described elsewhere (see ref. 5) and used without further treatment. The synthesis of the composites is briefed as follows: The shell mesopores of the SiO₂@ZrO₂ core-shell template were selectively filled with an organic monomer, in the presence of a polymerization catalyst, by the incipient wetness method at room temperature. The monomers were subsequently converted in a polymer by thermal treatment. Specifically for carbons, furfuryl alcohol (FA) was chosen as the organic monomer, with oxalic acid as a catalyst (FA/H₂C₂O₄ molar ratio ~ 30), in an ethanol/ether mixture. Initial loadings of FA were varied from 100 to 200% relative to the pore volume of the binary template used (typically 0.065 cc/g). The samples were then subjected to freeze-vacuum-thaw cycles using liquid N₂ in order to remove air, facilitating diffusion of FA in the pore system. After 1 hour at 35°C under vacuum, FA was polymerized overnight at 90°C under air. Finally, the polymerized alcohol was converted to carbon at 800°C under vacuum. In the case of vinyl-based polymer core-shell composites, the preparation is derived from the procedure published recently for polymer-silica mesoporous composites (see ref. 13), with incipient wetness impregnation of a vinyl monomer, a cross-linking monomer (ethylene glycol dimethacrylate, for example) and a radical initiator, together in diethyl ether. A typical polymer loading employed corresponds to 5 wt %. After impregnation, the materials were dried at 40 °C during 3 h. The samples were subsequently heated under reduced pressure for polymerization. To remove components of the core-shell binary template, the particles are either treated with a 1 N solution of NaOH at 50 °C, or specific amounts of diluted HF to remove only the ZrO₂ from the shell and an excess to completely remove the template.

Nitrogen physisorption measurements were performed at 77 K using a Micromeritics ASAP 2010 adsorption unit. SEM pictures were taken with a Hitachi S3500N scanning electron microscope at 25 kV. Elemental analyses were performed with an Oxford INCA EDX-system. TEM pictures were obtained with a Hitachi H-7500 microscope operated at 100 kV.

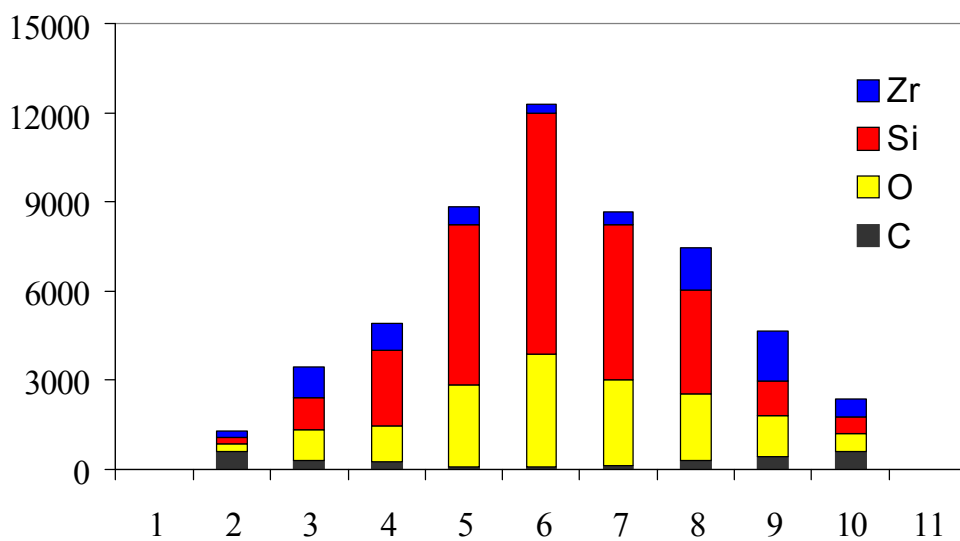
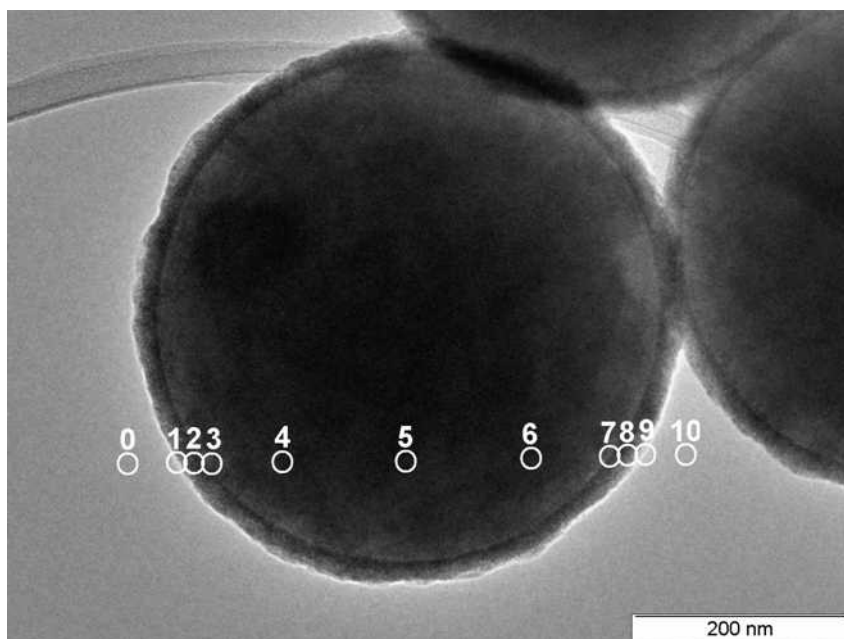


Figure S1. TEM-image of one SiO₂@ZrO₂,C sphere (top) and EDX-line-scan in total counts at different positions (bottom).

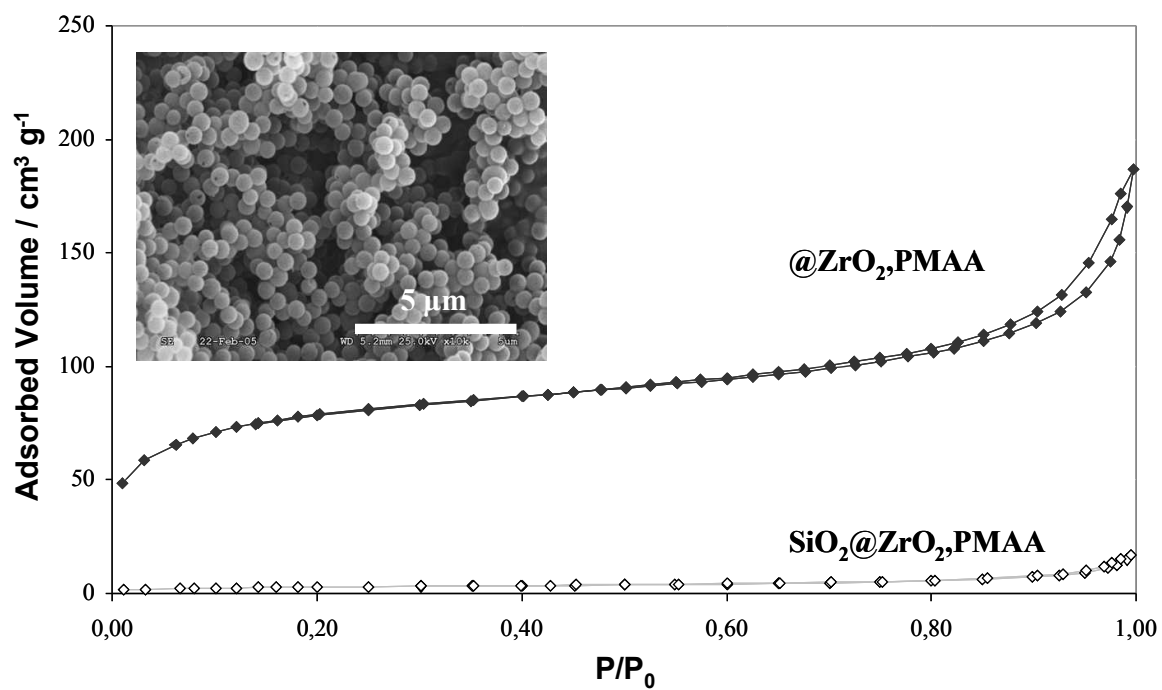


Figure S2. Sorption isotherms of $\text{SiO}_2@ZrO_2, \text{PMAA}$ before (bottom) and after (top) the removal of the siliceous core. Inset: SEM-image of $@ZrO_2, \text{PMAA}$.

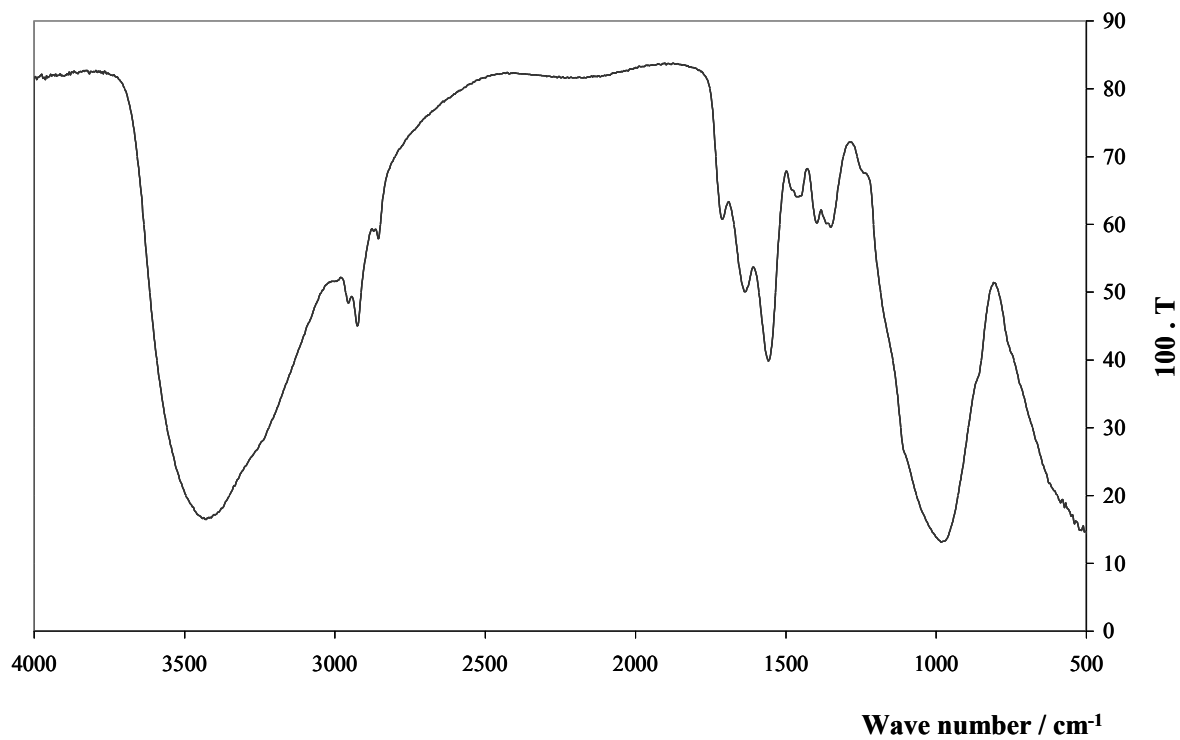


Figure S3. FT-IR spectrum of @ZrO₂, PMAA: ν_{\max} /cm⁻¹ 2855, 2925 and 2955 (aliphatic backbone), 1711 (CO), and 1633 (H₂O).