Electronic Supplementary Information

Periodic mesoporous organosilica from zwitterionic precursors

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General details

Nitrogen sorption experiments

Nitrogen sorption isotherms were obtained at 77K with a Micromeritics ASAP 2020 apparatus. Prior to measurement, the samples were degassed for 18 hours at 100°C. The surface areas (S_{BET}) were determined from BET treatment in appropriate p/p_0 ranges and assuming a surface coverage of nitrogen molecule estimated to 13.5 Å^2. Pore size distributions were calculated from the adsorption branch of the isotherms using the BJH method. The pore width was estimated at the maximum of the pore size distribution.

X-ray diffraction experiments

XRD experiments were carried out with a Xpert-Pro (PanAnalytical) diffractometer equipped with a fast X'celerator detector using Cu-Kα radiation.

Solid state NMR measurements

Solid state ^{13}C and ^{29}Si CP MAS NMR experiments were recorded on a Varian VNMRS 400 MHz solid spectrometer using a two channel probe with 7.5 or 3.2 mm ZrO2 rotors. The ^{29}Si solid state NMR spectra were recorded using both Cross Polarization (CP) MAS and One Pulse (OP) sequences with samples spinning at 5 kHz. CP MAS was used to get high signal to noise ratio with 5 ms contact time and 5 s recycling delay. For OP experiments, p/6 pulse and 60 s recycling delay were used to obtain quantitative information on the silane–silanol condensation degree. The ^{13}C CP MAS spectra were obtained using 5 ms contact time, 5 s recycling delay and 5 kHz spinning rate. The number of scans was in the range 1000–3000 for ^{29}Si OP MAS spectra and of 2000–4000 for ^{13}C CP MAS spectra.

Precursor syntheses:

3-(Tris(3-(triethoxysilyl)propyl)ammonio)propane-1-sulfonate (2)
A solution of 1,3-propane sultone (3g, 2.8mmol) and the trisilylated precursor *tris*(3-(triethoxysilyl)propyl)amine (**1**) (1.63g, 2.6mmol) in anhydrous acetonitrile (5ml) was stirred under argon at 90 °C for 72 h. After cooling, the solvent was eliminated under vacuum. The title compound was obtained as a highly viscous orange-yellow product. Yield: 1.75g (90%)
^{1}H NMR ($CDCl_3$) δ 0.58 (m, 6H), 1.16 (t, 27H, J = 7.0Hz), 1.76 (m, 6H), 2.11 (m, 2H), 2.86 (m, 2H), 3.11 (m, 6H), 3.61 (m, 2H), 3.75 (q, 18H, J = 7.0Hz); ^{13}C NMR ($CDCl_3$): δ 6.0, 14.9, 17.3, 17.7, 46.1, 57.5, 57.6, 59.5; FT-IR (neat) ν_{max}/cm^{-1} 2974, 2935, 2889, 1651, 1471, 1346, 1170, 1095, 1073, 960; HRMS [ESI+] calcd. for $C_{30}H_{70}N_1O_{12}S_1Si_3$ $(M+H)^+$ 752.3927, found 752.3910.
3-(Tris(3-(triethoxysilyl)propyl)ammonio)butane-1-sulfonate (3)
Tris(3-(triethoxysilyl)propyl)amine (**1**) (2.52g, 4mmol) and 1,4-butane sultone (0.81g, 6mmol) were mixed with 1.5ml of toluene and stirred for 72h under argon at 115°C. After cooling to room temperature, the solvent was eliminated under vacuum, and the title compound was obtained as a highly viscous yellow oil. Yield: 2.75g (90%).
^{1}H NMR ($CDCl_3$) δ 0.59 (m, 6H), 1.16 (t, 27H, J = 7.0Hz), 1.71 (m, 6H), 1.86 (m, 4H), 2.81 (m, 2H), 3.11 (m, 6H), 3.33 (m, 2H), 3.75 (q, 18H, J = 7.0Hz); ^{13}C NMR ($CDCl_3$): δ 7.0, 16.0, 18.3, 20.8, 22.6, 50.1, 58.6, 59.1, 60.6; FT-IR (neat) ν_{max}/cm^{-1} 2975, 2934, 2890, 1391, 1352, 1169, 1093, 1076, 958, 783; BRMS [ESI+] calcd. for $C_{13}H_{36}N_1O_{12}S_1Si_3$ $(M+H)^+$ 514.1, found 514.2 (fully hydrolyzed precursor).

Propyl-(tris(3-triethoxysilyl)propyl)ammonium iodide (4)
At room temperature and under argon, 1-iodopropane (10mmol, 1.7g) was added to of tris(3-triethoxysilylpropyl amine (1.5mmol, 0.94g) in 5ml of acetone. The reaction mixture was heated to 70°C for 48h. After cooling to room temperature, the title compound was obtained as a yellow oil after repeated washing with anhydrous diethyl ether and drying under vacuum at 50 °C. Yield: 1.02g (85%).
^{1}H NMR ($CDCl_3$) δ 0.64 (m, 6H), 0.99 (‘t’, 3H, J = 7.4Hz), 1.16 (t, 27H, J = 7.2Hz), 1.76 (m, 8H), 3.21 (m, 2H), 3.28 (m, 6H), 3.76 (q, 18H, J = 7.2Hz); ^{13}C NMR ($CDCl_3$): δ 5.96, 9.92, 14.93, 15.38, 17.34, 57.69, 59.88 (*two signals*); FT-IR (neat) ν_{max}/cm^{-1} 2972, 2926, 2886, 1443, 1390, 1365, 1164, 1098, 1067, 954, 770; HRMS [ESI+] calcd. for $C_{30}H_{70}N_1O_9Si_3$ (cation) 672.4358, found 672.4350.

Materials’ syntheses

Materials A, D, G, synthesized in the presence of the cationic surfactant CTAB
A solution of the precursor (0.8mmol) in ethanol (0.5ml) was added to a solution of hexadecyltrimethylammonium bromide (0.58mmol, 209mg) in a mixture of distilled water and NH_3 (0.6mL of a 25wt.-% solution in water) at 35°C. A white precipitate formed after approx. 15 seconds. The formed suspension was vigorously stirred for further 10 min. The mixture was heated at 80 °C under static condition for 72h. The resulting white precipitate was filtered and dried under air at 70 °C for 15h. The surfactant was removed by washing 0.3g of the solid in 60 ml ethanol/3ml conc. hydrochloric acid to give the zwitterionic silica hybrid material.

Materials B, E, H, synthesized in the presence of the non-ionic surfactant P123

P123 (0.25g) was dissolved in 1.9M hydrochloric acid (8mL). The resulting solution was stirred at 40°C during 3h. The precursor (0.5mmol) was added to this solution. The resulting suspension was vigorously stirred at the same temperature during 16h and was then allowed to stand at 80 °C during 48h. The material was isolated and washed in the same way as previously described.

Materials C, F, I, synthesized in the presence of the anionic surfactant sodium cetyl stearyl sulfate (SHS)

Sodium cetyl stearyl sulphate (a mixture consisting of 60% of sodium cetyl sulfate and 40% of sodium stearyl sulfate, 0.732g, 0.5mmol) was dissolved in a solution of distilled water (11.5ml) and 1M hydrochloric acid (2ml) under stirring at 60°C. Then, the precursor (0.6mmol) dissolved in 0.25mL of ethanol was added to the surfactant solution at the same temperature. After stirring for 10 min, the mixture was heated to 70°C under static condition for 72h. After this time, the reaction mixture was cooled to room temperature. The resulting solid products were recovered by filtration and dried under air at 70 °C for 15h. The surfactant was removed by washing 0.5g of the solid in 100 ml ethanol/5ml conc. hydrochloric acid.

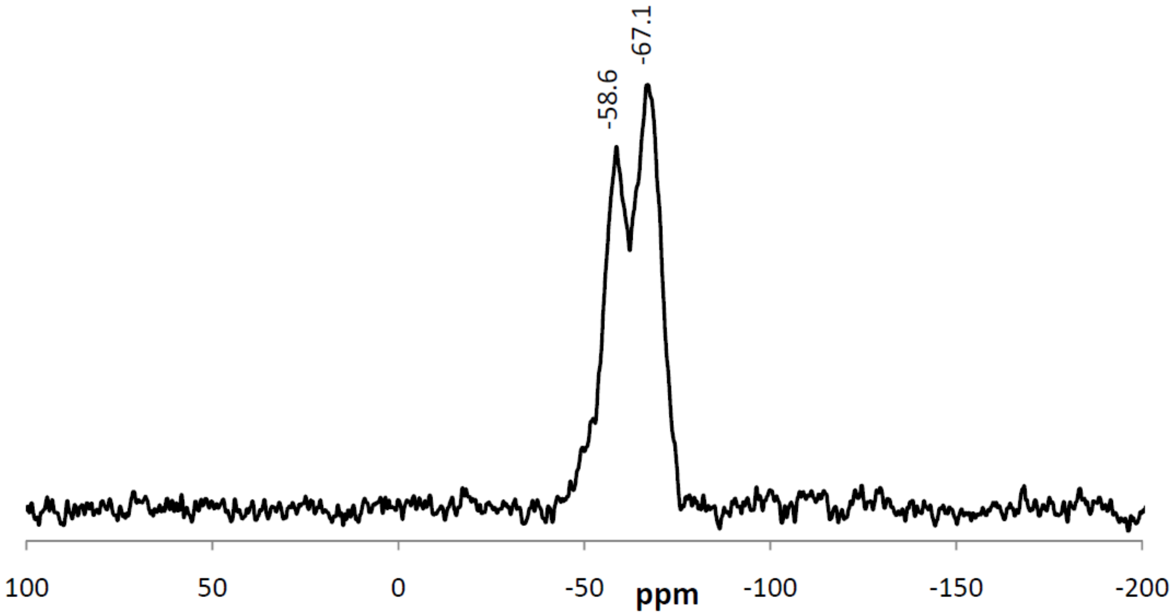

Figure 1 ^{29}Si OP-MAS solid state NMR spectrum of material **D**

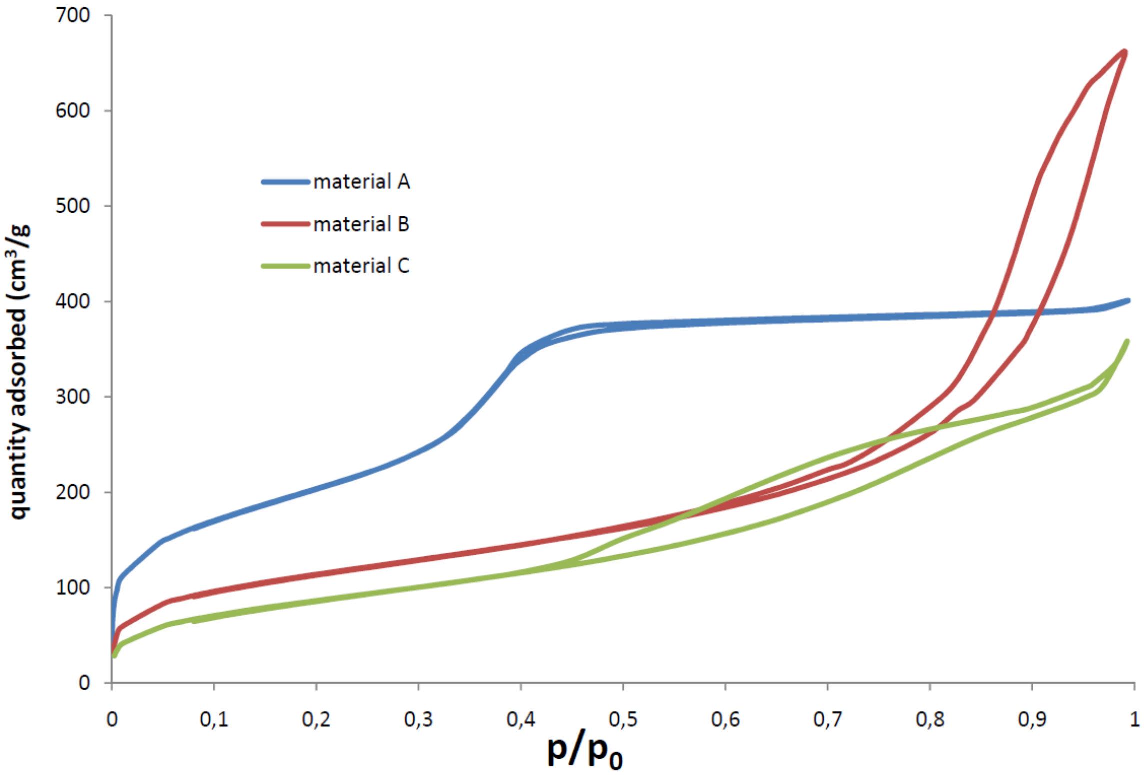

Figure 2 Nitrogen adsorption-desorption isotherms of materials **A**, **B** and **C**

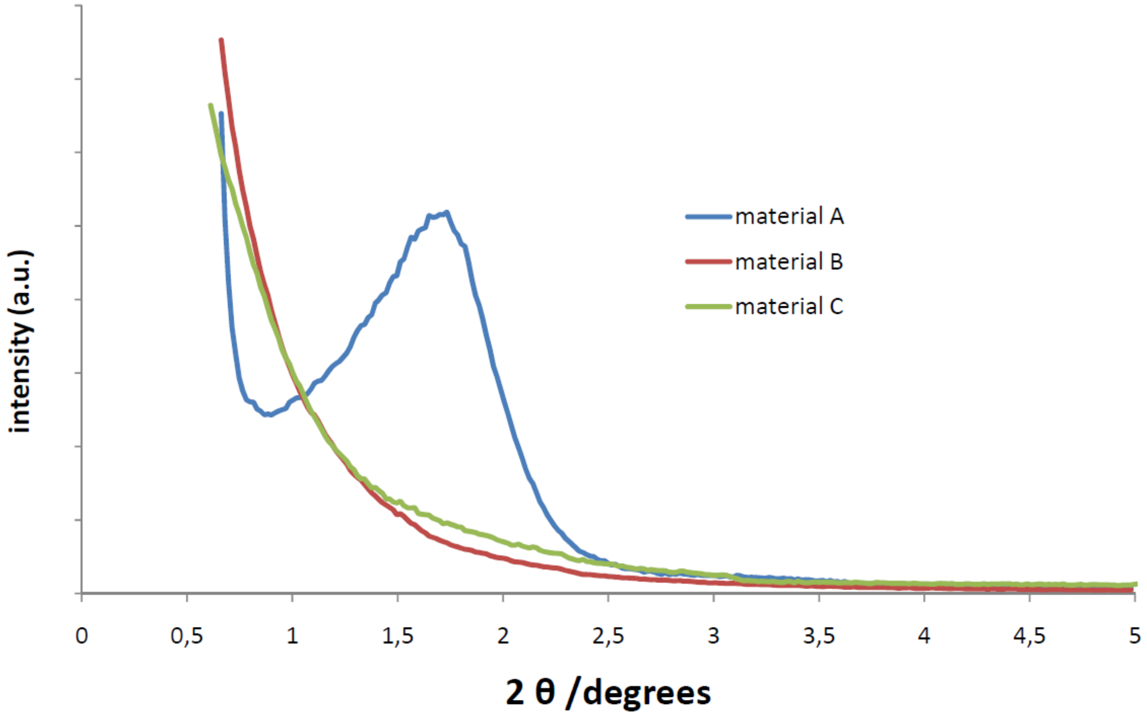

Figure 3 X-ray diffractograms of materials **A**, **B** and **C**

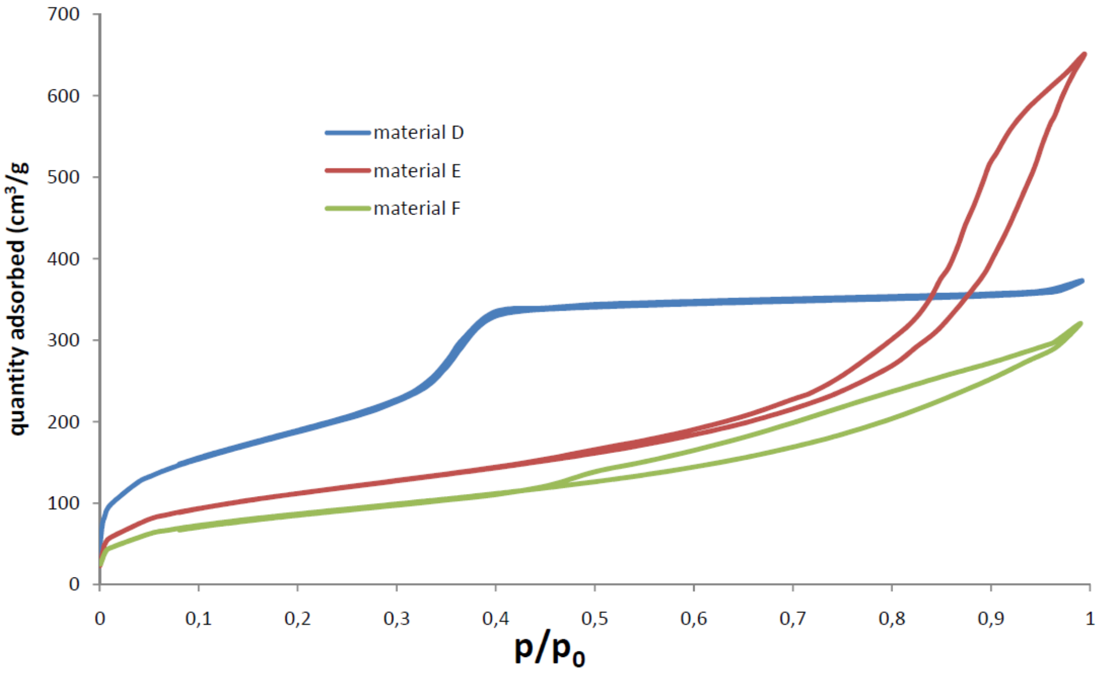

Figure 4 Nitrogen adsorption-desorption isotherms of materials **D**, **E** and **F**

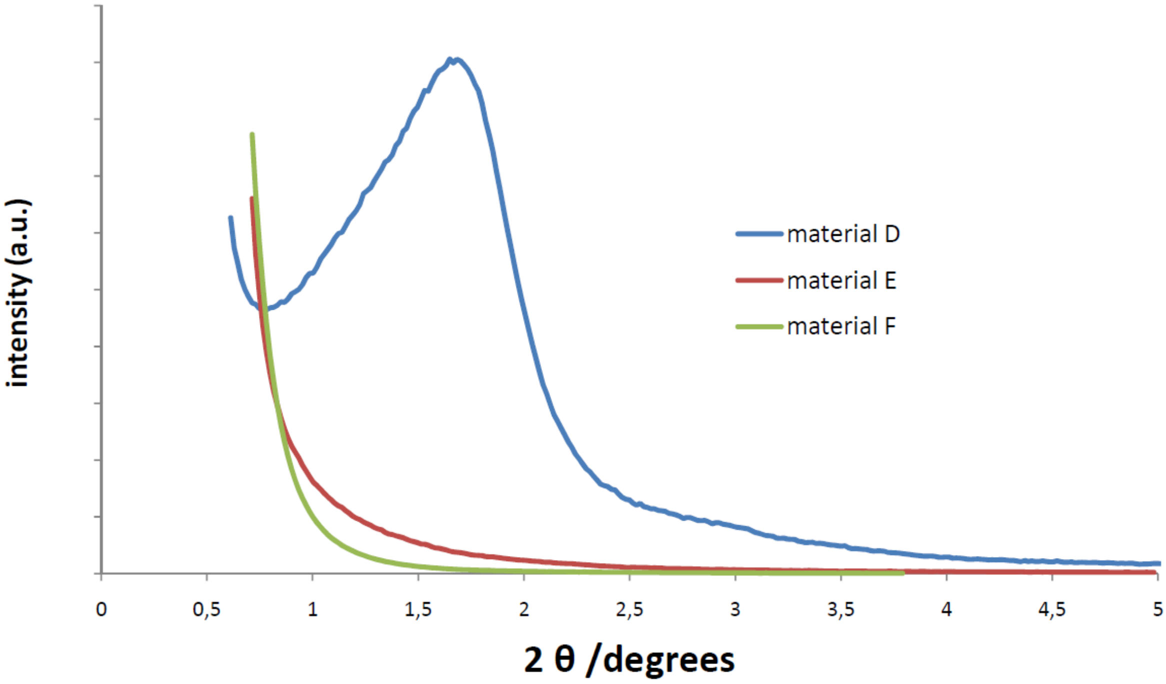

Figure 5 X-ray diffractograms of materials **D**, **E** and **F**

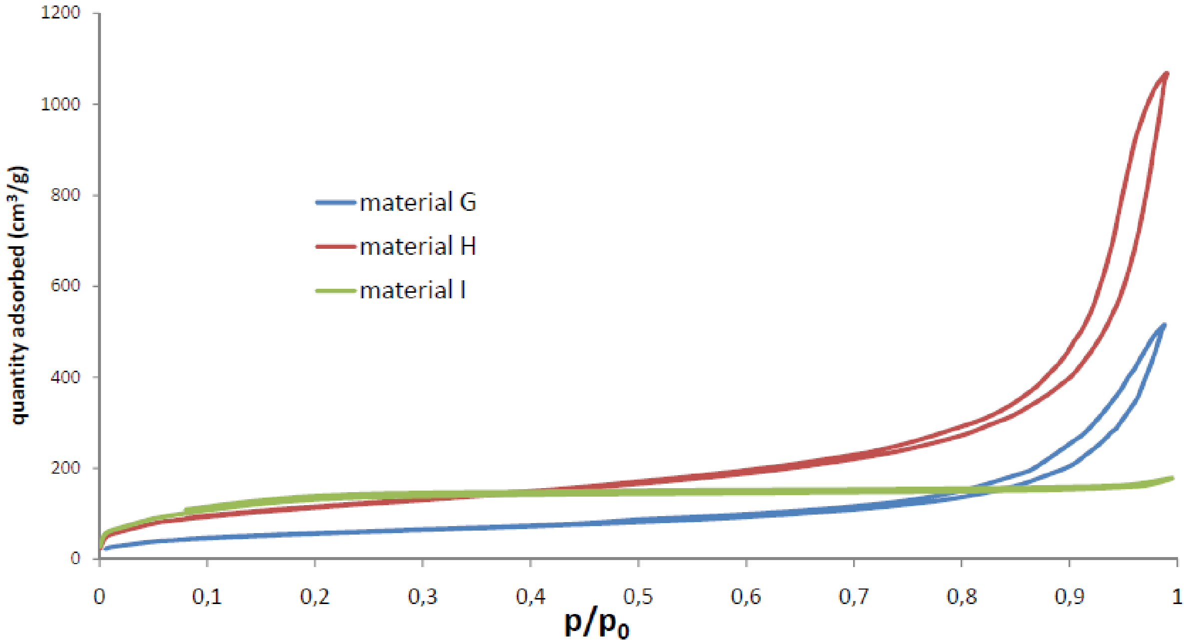

Figure 6 Nitrogen adsorption-desorption isotherms of materials **G**, **H** and **I**

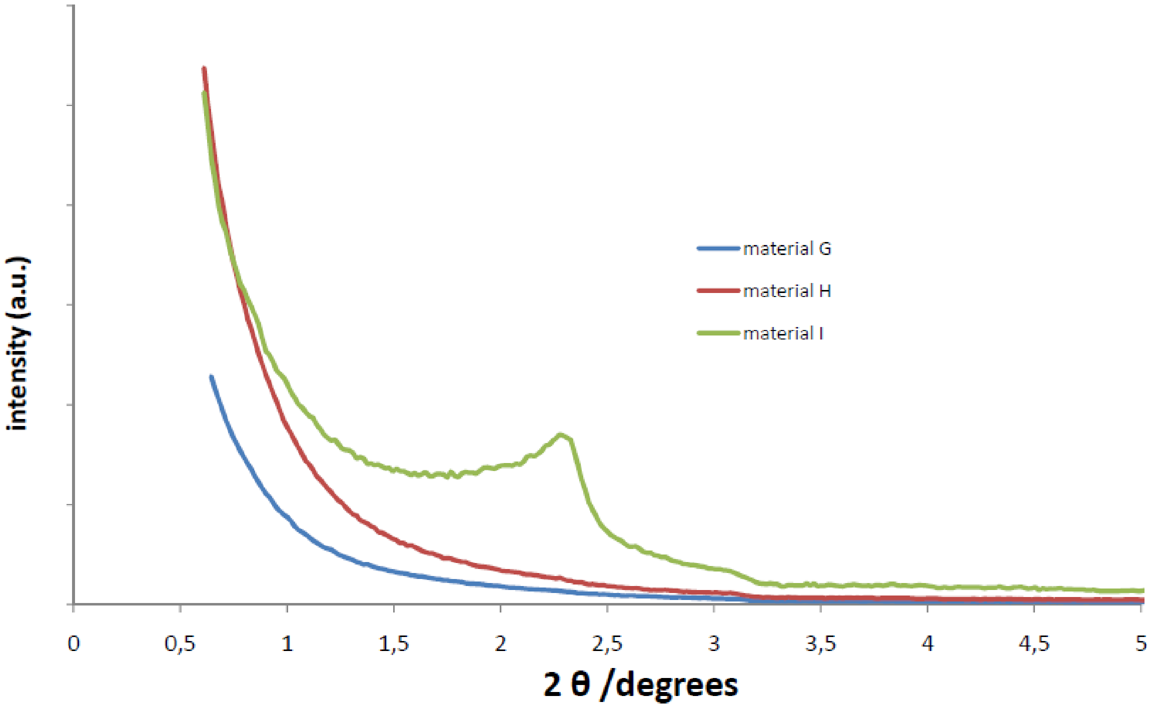

Figure 7 X-ray diffractograms of materials **G**, **H** and **I**

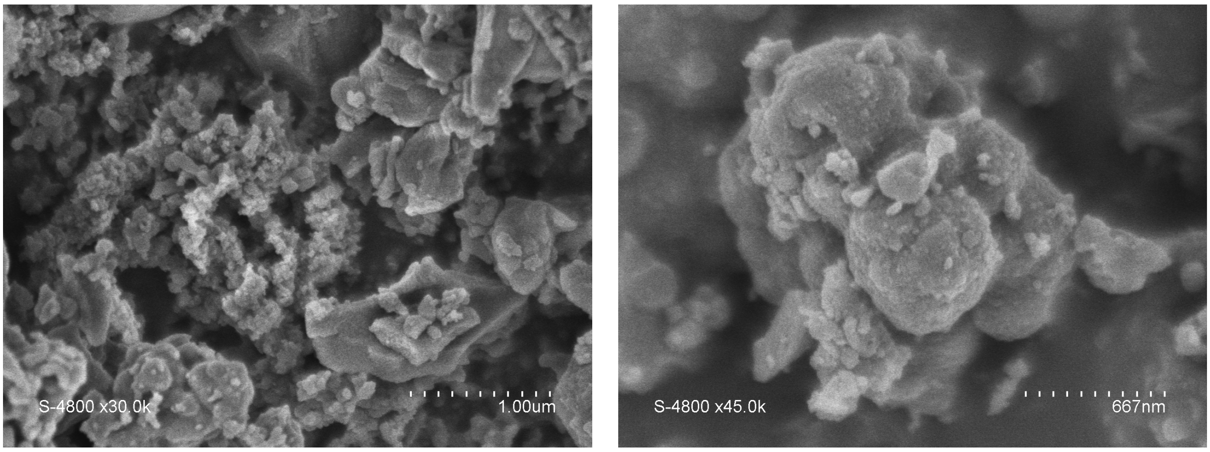

Photo 1-2 SEM pictures of material **A**

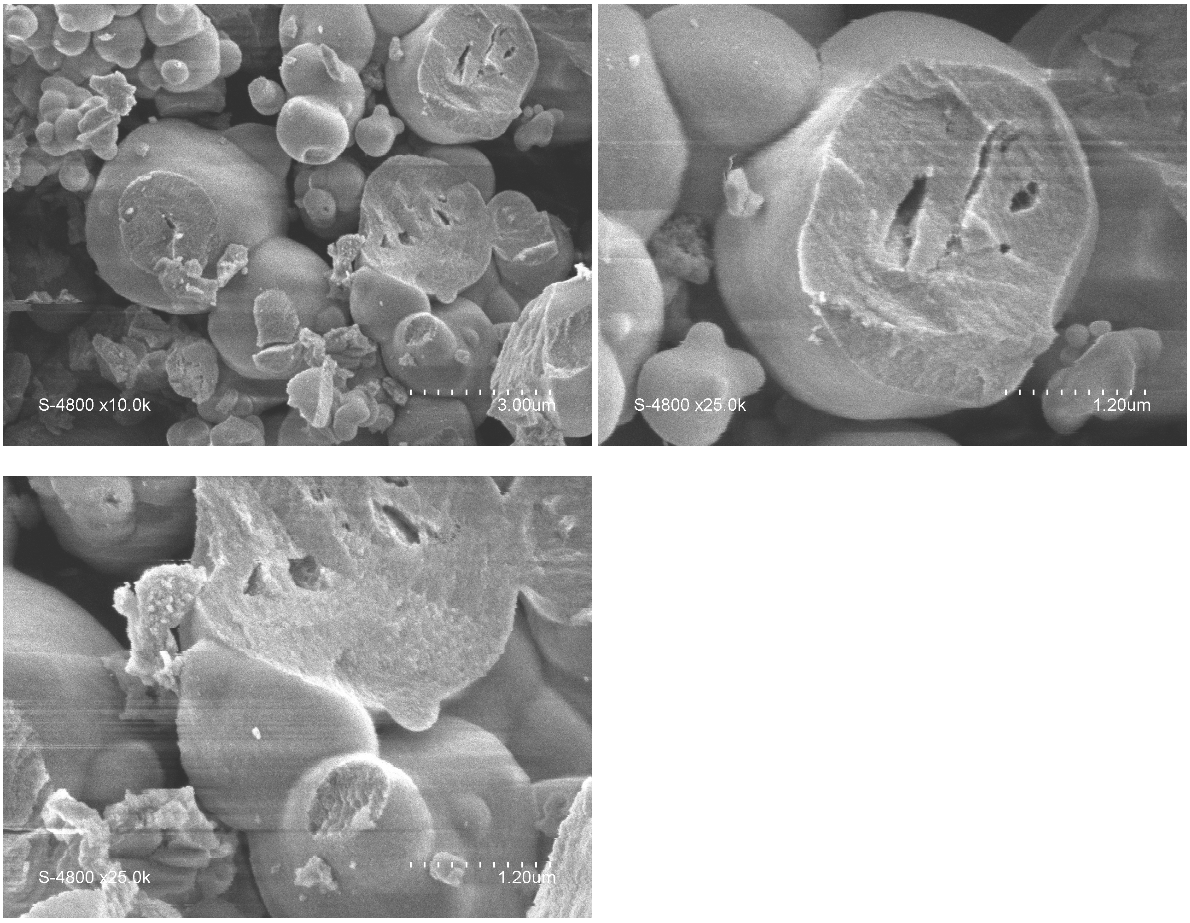

Photo 3-5 SEM pictures of material **D**

Biginelli reaction, general procedure:

The zwitterionic hybrid material **D** was treated overnight in an ethanolic solution of sulfuric acid (2M). After filtration and washing with ethanol, the protonated material **D(H$^+$)** was dried under vacuum at 50ºC during 4 hours.

The Biginelli reactions were carried out in the following way: to a mixture of p-anisaldehyde (2.2 mmol), ethyl acetoacetate (2.2 mmol), urea (3.3 mmol) was added the hybrid material **D(H$^+$)** (98.4mg corresponding to 10 mol-% of ammonium sulfonate species as obtained from TGA analysis) and acetonitrile (5mL). The reaction mixture was stirred under reflux during 4h under inert atmosphere. After cooling, the solution was filtered and an aliquote of the filtrate was analyzed by ^{1}H-NMR after removing the solvent under vacuum. After each run, the catalyst was washed with ethanol, dried at room temperature, and treated with an ethanolic solution of 2M sulfuric acid.