Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Mind the Gap! Tailoring Sol-gel Ceramic Mesoporous Coatings on Labile Metal-organic Frameworks through Kinetic Control.

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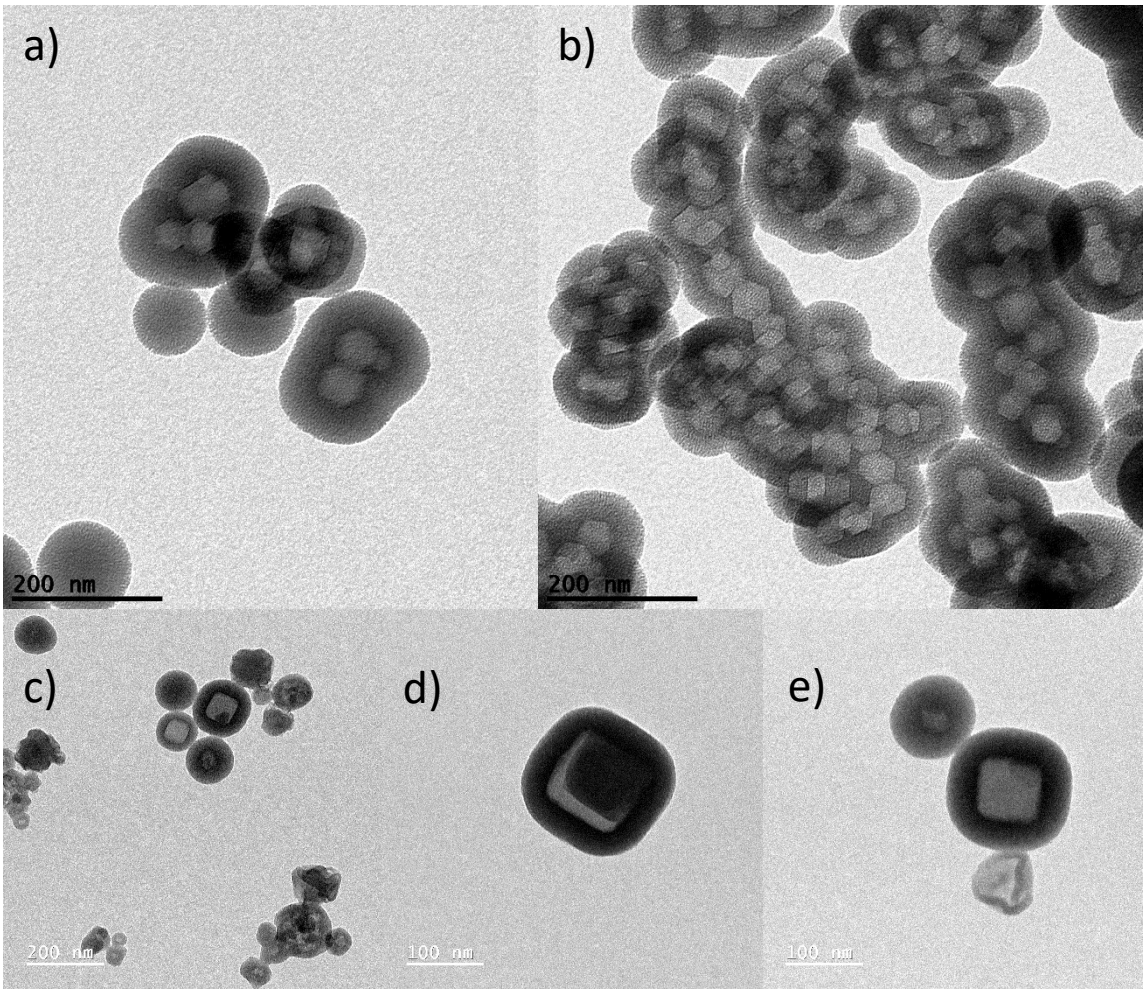
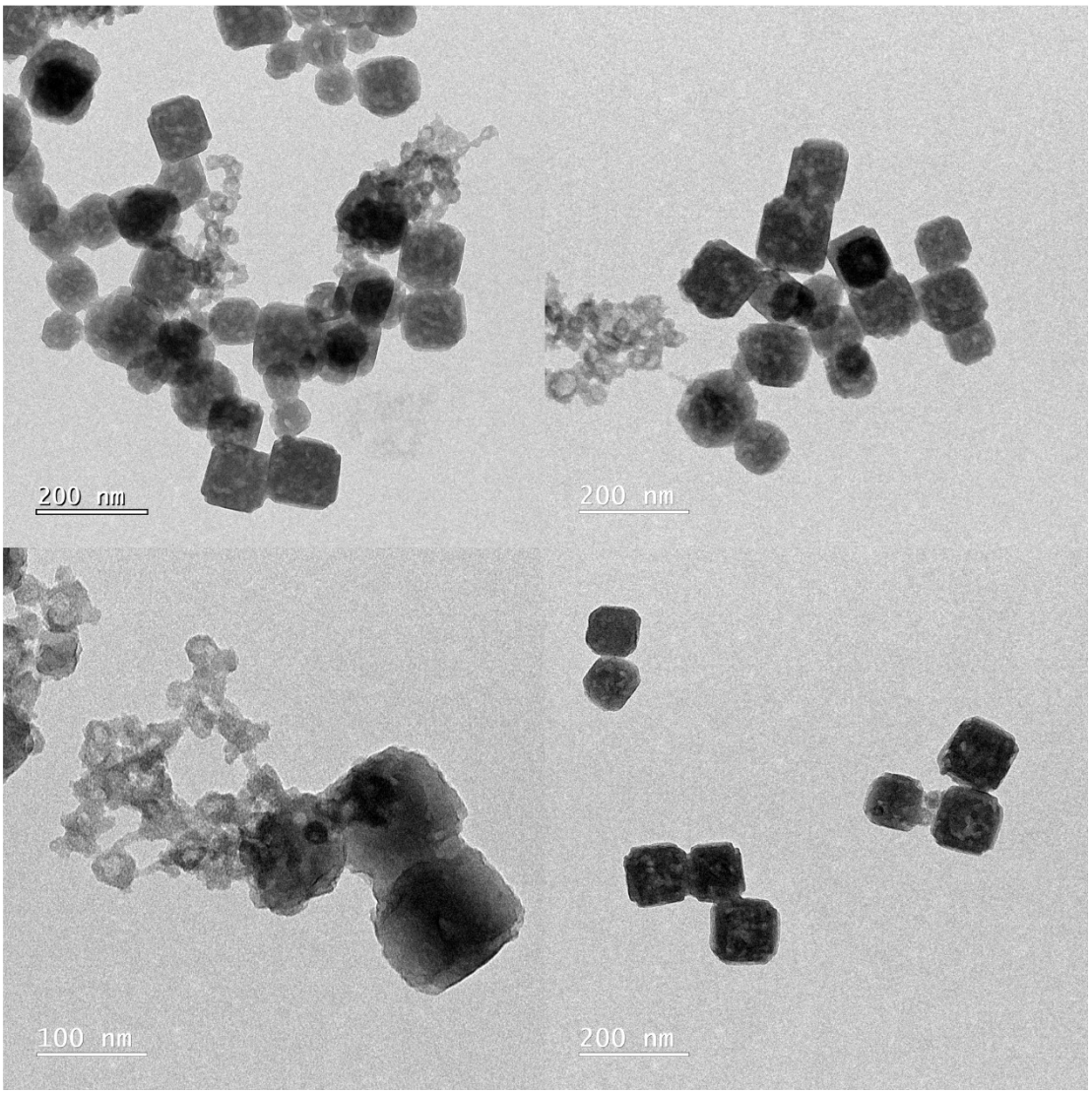
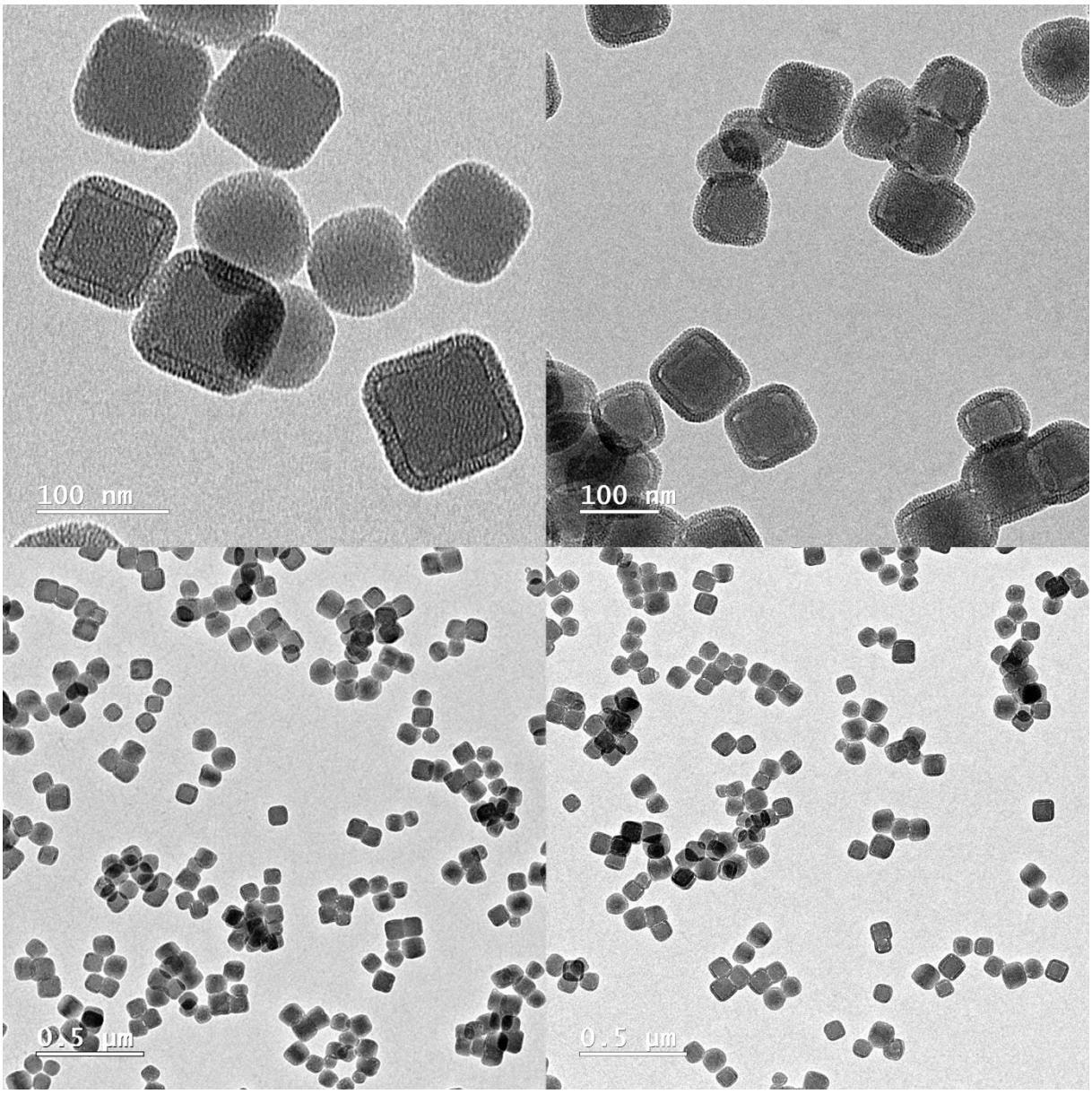


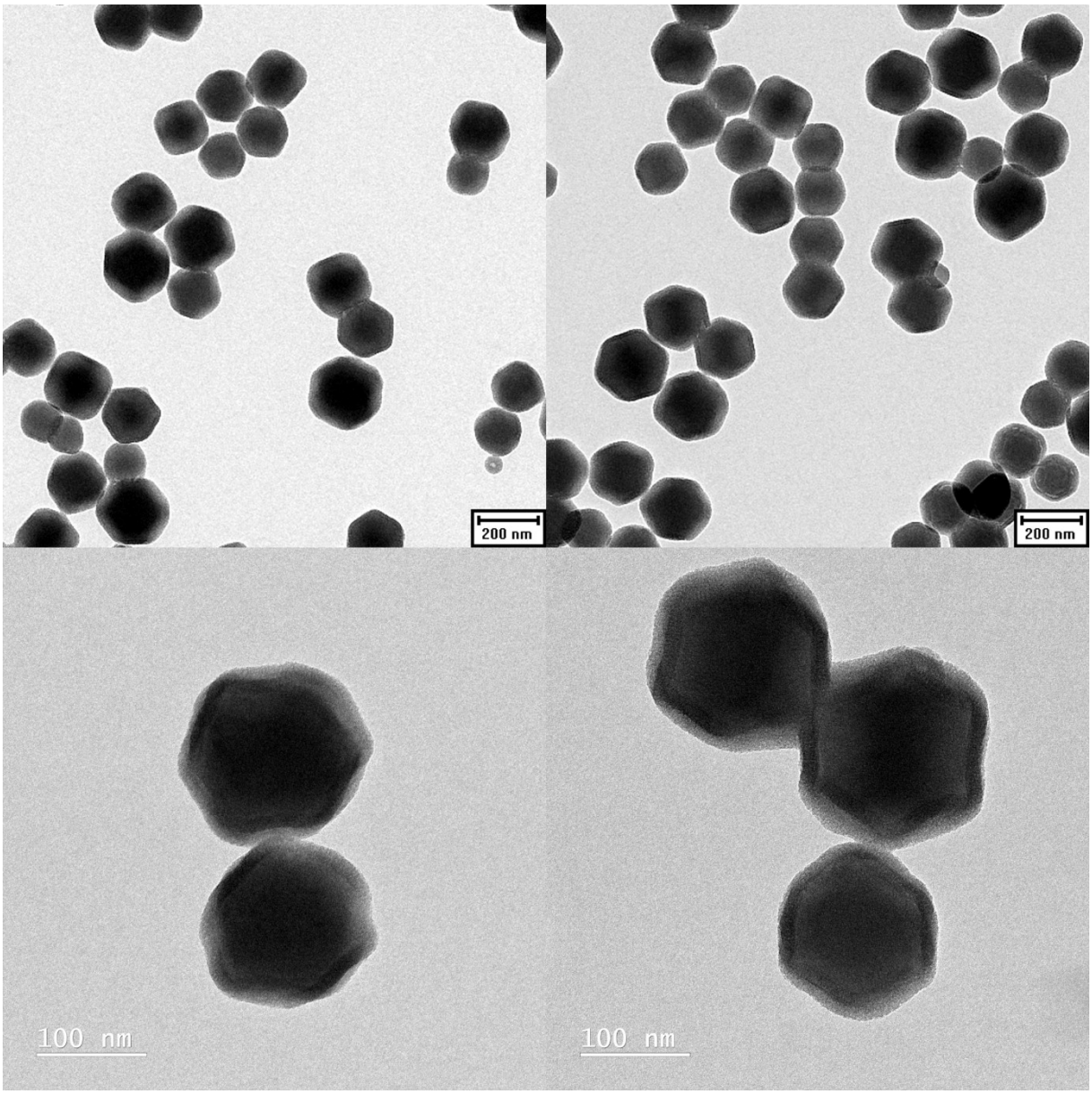
S1: ZIF-8@SiO2 NPs synthesized with a high TEOS/Zn ratio:. ***a-b)*** *r>55* ***c-e)*** *r=55. We can observe dissolution of the ZIF seed and aggregation proportional to TEOS amount. In* ***a-b)*** *the ZIF is completely dissolved while in* ***d)*** *we can observe a yolk-shell structure, even if the majority of NPs obtained in this condition (r=55) are hollow.*



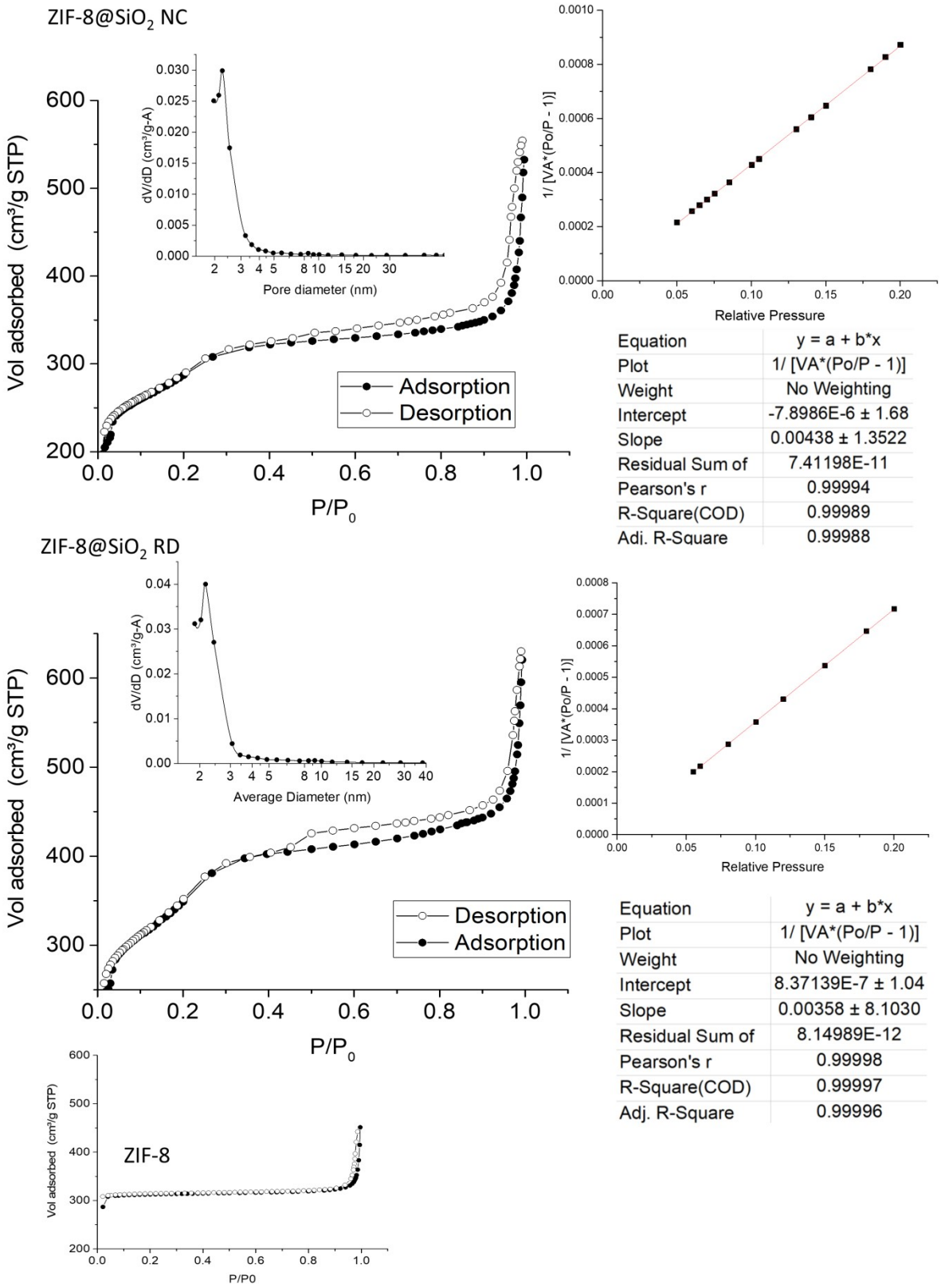
S2: TEM images of ZIF-8@SiO_2 NC particles, synthesized with a TEOS/Zn ratio r=27 and a reaction time of 1h.



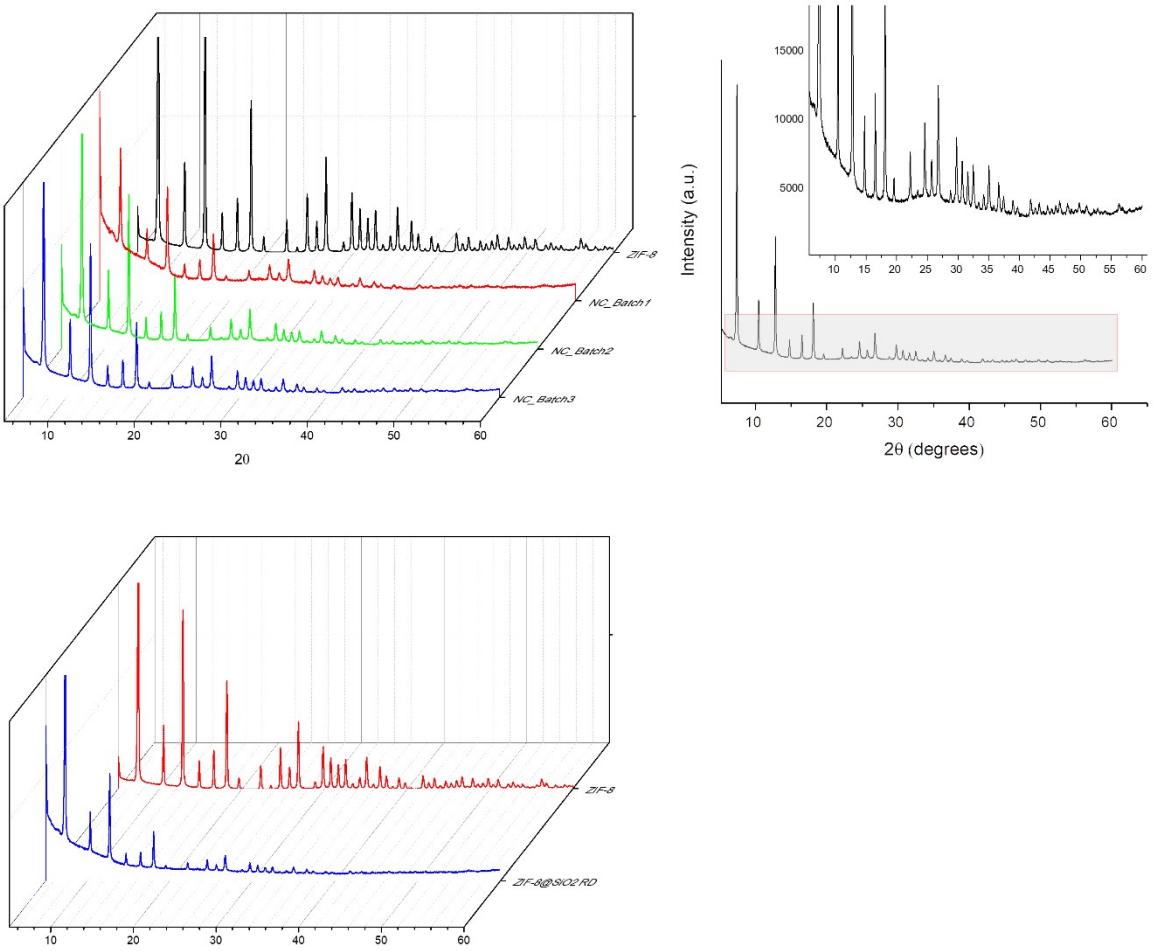
S3: TEM images of ZIF-8@SiO_2 NC particles, synthesized with a TEOS/Zn ratio r=15 and a reaction time of 3h.



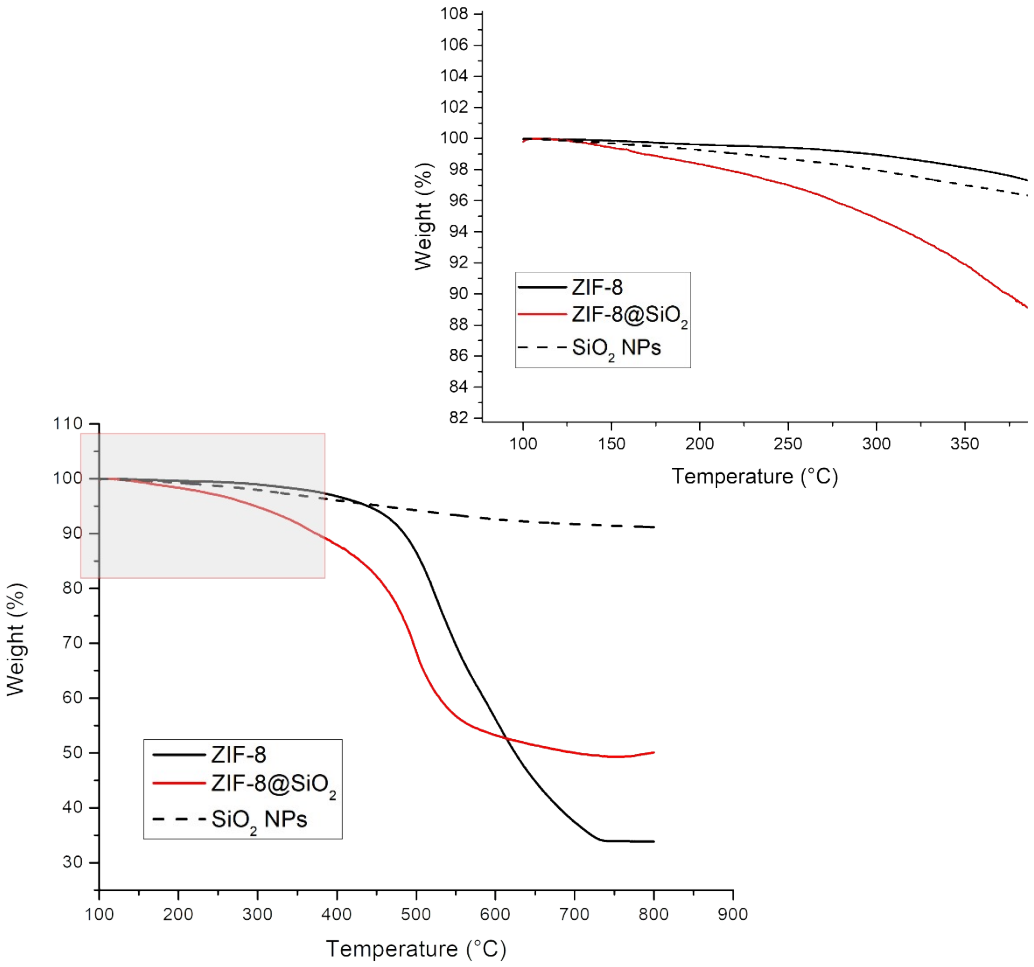
S4: TEM images of ZIF-8@SiO_2 RD particles, synthesized with a TEOS/Zn ratio r=15 and a reaction time of 3h.



S5: Adsorption/Desorption isotherms of N_2 for ZIF-8@SiO_2 NPs and the corresponding pore size distribution, calculated from the Adsorption branch. Samples have been degassed overnight at 250°C prior to the measurement. On the left, points used to calculate BET surface area are reported. On the bottom is reported the adsorption/desorption isotherm of model ZIF-8 nanocrystals, as basis for comparison.



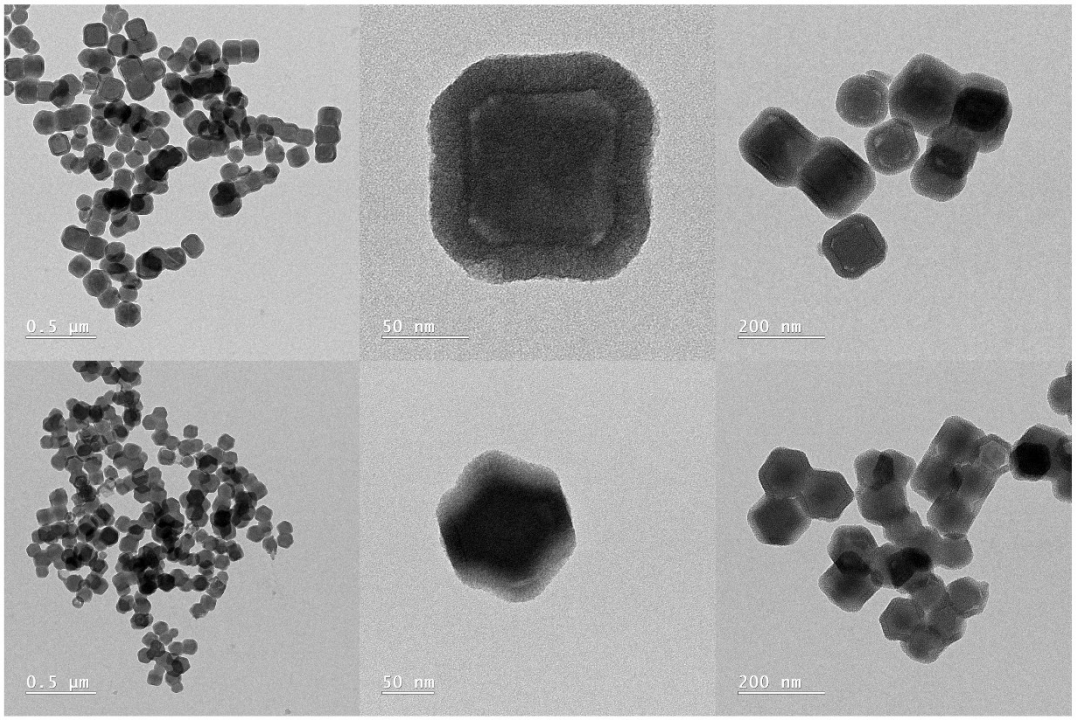
S6: XRD analysis of ZIF-8@SiO_2 NC (top) and RD (bottom). The broad peak of amorphous silica is visible at 25 degrees (zoom on NC_Batch1 sample, top right). The ZIF-8 pattern is found in every batch analyzed, confirming the presence of a ZIF-8 core in the core-shell NPs obtained.



S7: TGA curves of ZIF-8 NPs (black line), ZIF-8@SiO_2 NP (red line) and SiO_2 NPs (dashed line). On the top right is reported a zoom of the graph corresponding to the grey rectangle. Analysis has been done under a N_2 flow with a temperature ramp of 10°C /min and a starting equilibration step of 20 min at 100°C. ZIF-8@SiO_2 NP lose more water than ZIF-8 or SiO_2 NPs in the water removal phase (<300°C), suggesting a possible contribute of a thin layer of hydrate zinc silicate between ZIF-8 and silica.

NC

RD



S8: TEM images of ZIF-8@SiO_2 NC (top) and RD (bottom) nanoparticles after calcination at 250°C for 4h in N_2 atmosphere.