

Supplementary Information for

**“Epoxide Assisted Metal Oxide Replication (EAMOR): a new technique of patterning
metal oxide structures”**

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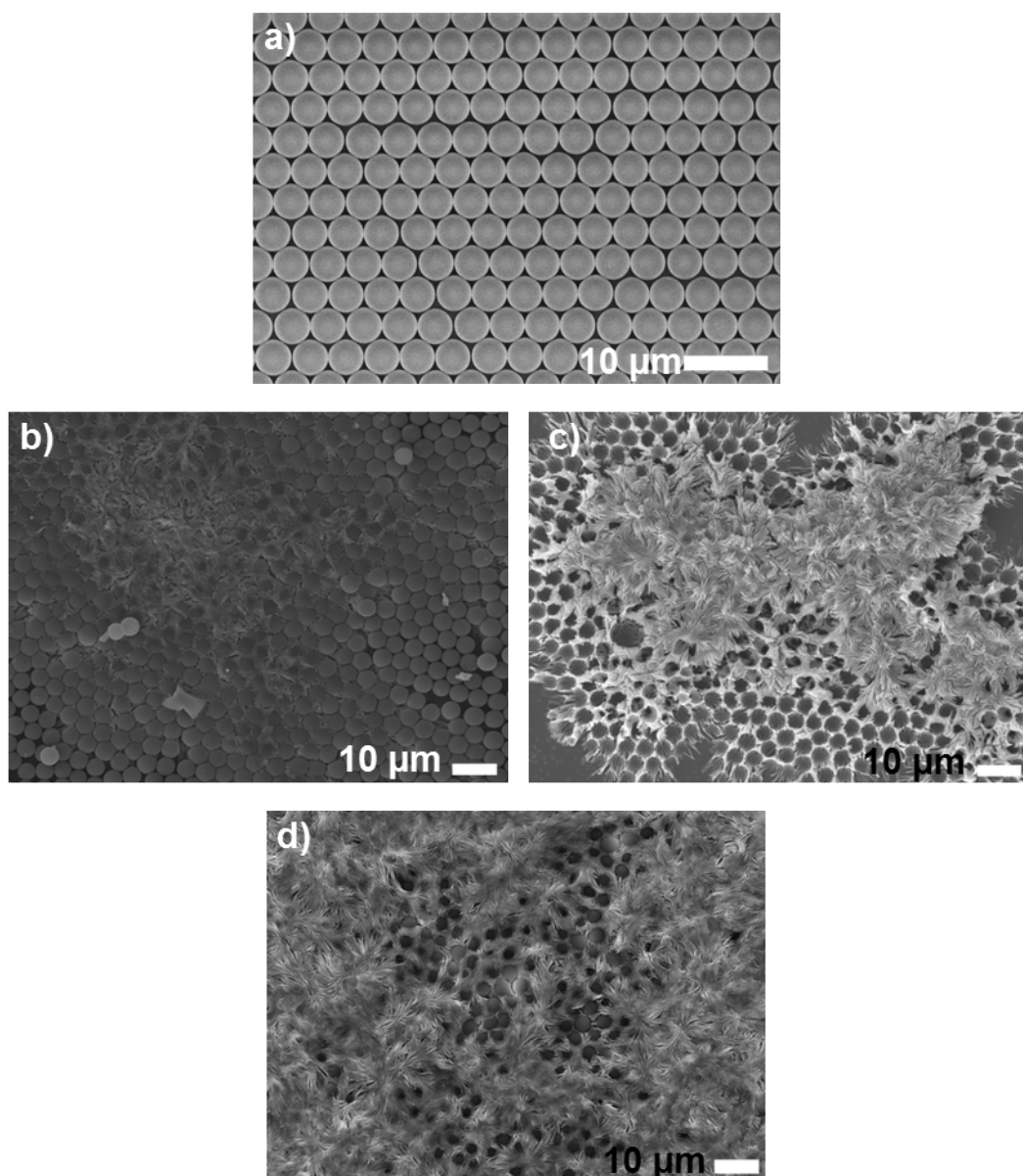


Figure 1. a) Top view SEM image of self assembled monolayer of PS microspheres obtained by Langmuir-Schaeffer deposition. b, c, d) SEM images of overgrown structures of ZnO before and after annealing, obtained at: b,c) 1M, and d) 3M precursor concentrations with 12 coating cycles.

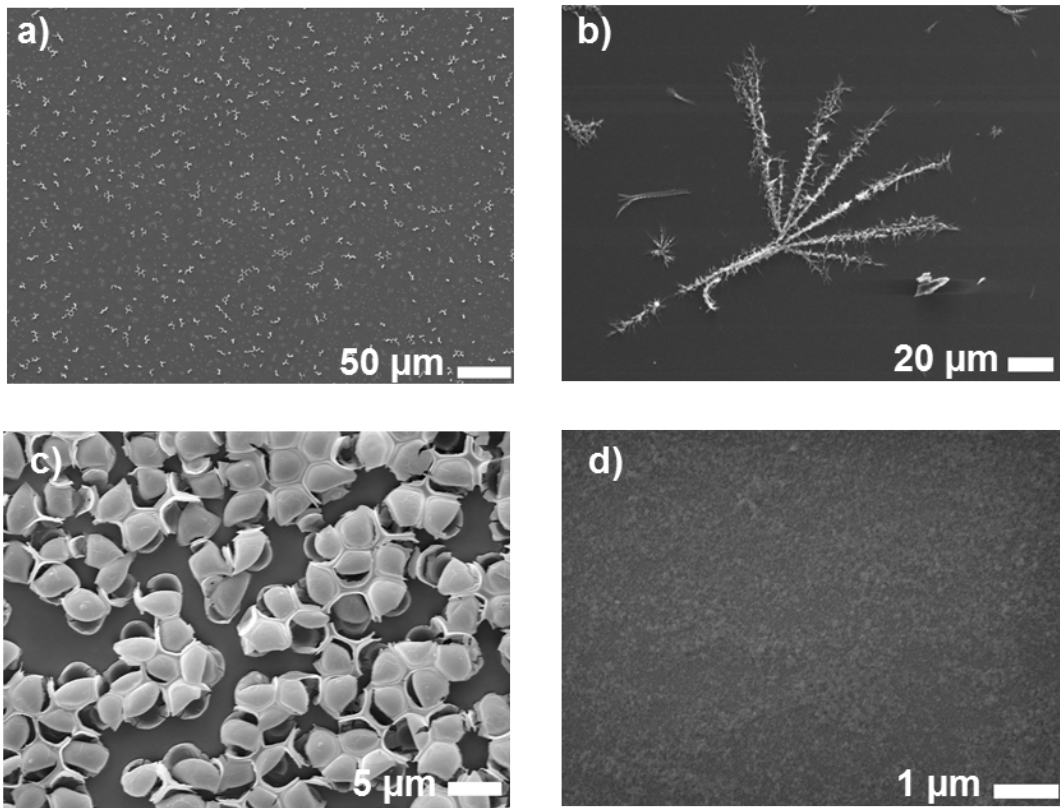


Figure 2. SEM images (top view) of Control Experiments: a, b) ZnO, 0.3M precursor concentration and 12 coating cycles, where - a) no propylene oxide is used, and b) no PS template is used, c, d) SnO₂, 0.03M precursor concentration and 12 coating cycles, where - c) no propylene oxide is used, and d) no PS template is used.

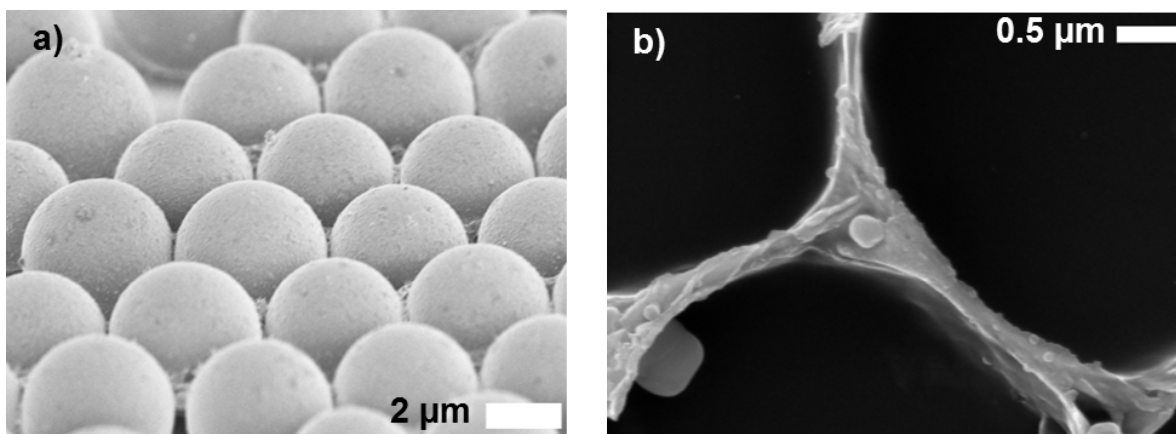


Figure 3. a) Side view SEM image of ZnO clearly illustrating the deposition within the voids of PS template, b) Top view SEM image of ZnO obtained at the interface of three PS spheres with 0.3M precursor concentration and 6 coating cycles.

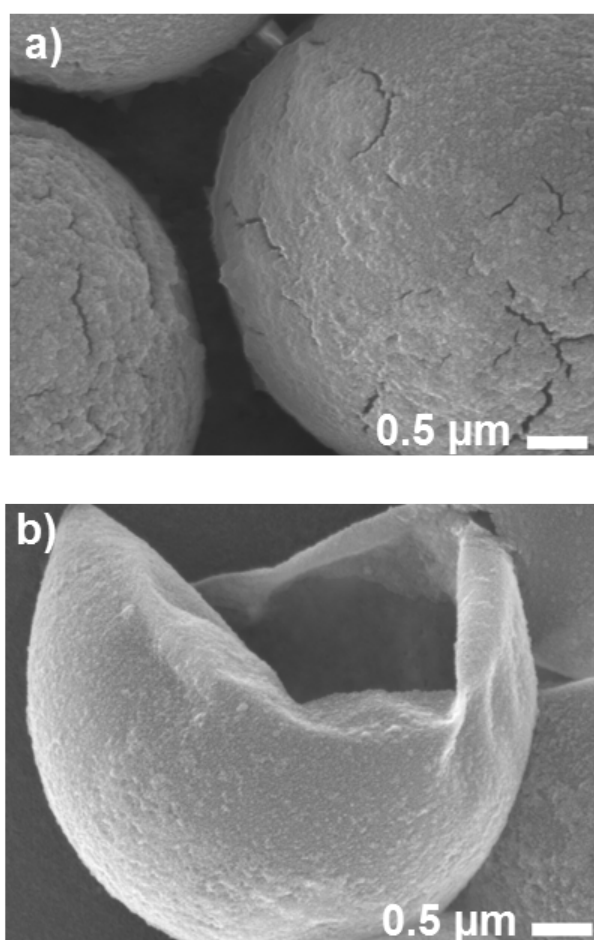


Figure 4. SEM images of tin oxide hollow spheres obtained at 0.3M tin tetrachloride precursor and 12 coating cycles, a) before annealing, and b) after annealing

EAMOR chemistry and postulates:

In a way, EAMOR must be thought of as the adaptation of epoxide assisted sol-gel chemistry to a microreactor format. The solution phase chemical processes are well-known and understood. Metal salts in aqueous systems exist as mixed anion/aqua complexes. Bound water ligands are considerably more acidic than molecular water, due to the electron accepting properties of the central metal ion which weakens the O-H bond. Thus, a water ligand is more readily deprotonated and can pass on a proton to the epoxide. Said proton is then trapped by nucleophilic attack of the corresponding metal salt anion (NO_3^- or Cl^-) and irreversible ring opening of the epoxide. This reaction is thermodynamically driven by the high strain energy of the three-membered epoxide ring. The deprotonated aqua ligands left behind as hydroxide species can then undergo polycondensation reactions which yield polymeric or cluster-like metal-polyolates or poly-oxolates. Temporal and structural evolution of these clusters leads to colloidal metal oxide nanoparticles (volume templating) or the growth of a conformal oxide coating (surface templating). The rate of the proton scavenging reaction strongly depends on the type of epoxide used but also on the central metal ion type and oxidation state which determines the acidity of the solvated aqua ions.

Postulates:

Combining the results of control experiments and the non-templated surface ZnO deposition, we would like to postulate the following reaction mechanism for the EAMOR process:

- Microstructured surfaces (template, lines, grooves, rough surfaces) are necessary to create well defined “microreactors”. Without these, random nucleation occurs.
- In a first filling or adsorption step, interparticle voids are filled with a rather well-defined amount of metal precursor solution. A part of the metal precursor is adsorbed on polar (e.g. carboxylate terminated PS sphere) surfaces depending on the specific metal ion – surface interactions, whereas the rest remains in solution, trapped inside the microreactor voids.

- In a second step, the propylene oxide fixating agent is added which mixes with the metal precursor salt and drives the formation of metal-oxygen-metal bonds which leads to oxide formation. This causes precipitation in the microreactor volumes (volume templating) or surface specific growth of metal oxide layer on the template surface (surface templating)
- Drying of the sample leads to partial compacting of the deposited oxide which still contains a significant porosity. With each cycle, pores are filled more and more, leading to a gradual increase in the grown oxide layer thicknesses.
- Annealing leads to partial collapse of the grown oxide structures (e.g. by evaporation of pore fluids, water elimination from hydroxides etc.)