Supporting Information

Optimizing ZIF-8 Membrane Growth on Top of Semiconductive Ga-Doped ZnO Sensitive Layers

Kevin Dedecker^{1*}, Benjamin Paret², Lionel Presmanes^{2*}, Benjamin Duployer², Antoine Barnabé², Philippe Menini³, David Farrusseng⁴, Mikhael Bechelany^{1,5}, Martin Drobek^{1*}, and Anne Julbe¹

1. Institut Européen des Membranes (IEM-UMR 5635) CNRS, ENSCM, Univ Montpellier, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

2. Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT-UMR 5085), Université Toulouse 3 Paul Sabatier, Toulouse INP, CNRS, Université de Toulouse, 118 Route de Narbonne, Cedex 9, 31062 Toulouse, France

3. Laboratoire d'Analyse et d'Architecture des Systèmes (LAAS-UPR 8001), Université de Toulouse, CNRS, UPS, 7 Avenue du Colonel Roche, Cedex 4, 31031 Toulouse, France

4. Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON-UMR 5256), Université de Lyon, CNRS, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

5. Functional Materials Group, Gulf University for Science and Technology, Mubarak Al-Abdullah, 32093, Kuwait

I. Scanning Electron Microscopy Analysis



Figure S1. SEM observations (surface view) of a) a bare substrate covered by SiO_2 and b) a ZnO:Ga sample deposited on a Si/SiO₂ wafer.

Table S1. Comparison of grain size, morphology and surface coverage of samples after ZnO-to-MOF conversion under various conditions (SEM micrograph analysis).

Conversion conditions	Apparent "MOF" crystal size / morphology	Estimated Surface Coverage (%)
Water, ZnO:Ga, 100°C, 12h	No MOF	-
DMF, ZnO:Ga, 100°C, 12h	~ 400 nm Pseudo-cubic	95 %
Ethanol, ZnO:Ga, 100°C, 12h	~ 130 nm Poorly faceted (grain clusters)	99 %
Methanol, ZnO:Ga, 100°C, 12h	~ 3 000 nm Pseudo-cubic	57 %
Methanol/water mixture (1:3), ZnO:Ga, 100°C, 1.5h	~ 800 nm Pseudo-cubic + small particles (30 - 100 nm)	88 %
Methanol/water mixture (1:1), ZnO:Ga, 100°C, 1.5h	~ 150 nm Poorly faceted (grains)	97 %
Methanol/water mixture (3:1), ZnO:Ga, 100°C, 1.5h	Unmeasurable Poorly faceted (grains)	96 %
Methanol/water mixture (3:1), Annealed ZnO:Ga, 100°C, 1.5h	~ 300 nm Poorly faceted	75 %
Methanol/water mixture (3:1), Annealed ZnO:Ga, 200 °C for 1.5 h	~ 80 nm Poorly faceted (grain clusters)	94 %
Methanol/water mixture (3:1), Annealed ZnO:Ga, 100 °C for 12 h	Unmeasurable Poorly faceted (grains)	82 %

II. Energy-Dispersive X-Ray Spectroscopy

II.1. Effect of Solvent Physicochemical Properties on ZnO:Ga Conversion to ZIF-8

II.1.1. Water Solvent



Figure S2. EDX spectrum of a ZnO:Ga sample after reaction at 100°C for 12h in water. The absence of Zn and Ga signals confirms the complete removal of the ZnO layer. The Si and O signals originate from the SiO₂-coated silicon wafer substrate while trace amounts of C and N likely result from residual 2-methylimidazole ligand adsorbed on the surface without participating in ZIF-8 formation.

II.1.2 Dimethylformamide Solvent



Figure S3. EDX spectra of a ZnO:Ga sample after conversion at 100°C for 12h in DMF.



Figure S4. EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 12h in DMF.

II.1.3 Ethanol Solvent



Figure S5. EDX spectra of a ZnO:Ga sample after conversion at 100°C for 12h in ethanol.



Figure S6. EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 12h in ethanol.

II.1.4 Methanol Solvent



Figure S7. EDX spectra of a ZnO:Ga sample after conversion at 100°C for 12h in methanol.



Figure S8. EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 12h in methanol.



Figure S9. Cross-sectional EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 12h in methanol.

II.2 Effect of MeOH/H₂O volumetric ratio on ZnO:Ga conversion to ZIF-8

II.2.1 Methanol/water mixture (1:3)



Figure S10. EDX spectra of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 1:3.



Figure S11. EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 1:3.



Figure S12. Cross-sectional EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 1:3.

II.2.2 Methanol/water mixture (1:1)



Figure S13. EDX spectra of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 1:1.



Figure S14. EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 1:1.

II.2.3 Methanol/water mixture (3:1)



Figure S15. EDX spectra of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 3:1.



Figure S16. EDX mapping analysis of ZnO:Ga samples after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 3:1.

II.2.4 Methanol



Figure S17. EDX spectra of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol.



Figure S18. EDX mapping analysis of a ZnO:Ga sample after conversion at 100°C for 1.5h in methanol.

- II.3. Effect of Solvent Physicochemical Properties on ZnO:Ga Conversion to ZIF-8
- II.3.1. Conversion at 100°C for 1.5h



Figure S19. EDX spectra of an annealed ZnO:Ga sample after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 3:1.



Figure S20. EDX mapping analysis of annealed ZnO:Ga samples after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 3:1.

II.3.2. Conversion at 200°C for 1.5h



Figure S21. EDX spectra of an annealed ZnO:Ga sample after conversion at 200°C for 1.5h in methanol/water solvent mixture with ratio 3:1.



Figure S22. EDX mapping analysis of annealed ZnO:Ga samples after conversion at 100°C for 1.5h in methanol/water solvent mixture with ratio 3:1.

III. Synthesis Protocol



Figure S23. Schematic illustration of the two-step process for synthesizing ZIF-8@ZnO on a Si wafer.