

ZnO@TiO₂ core-shell nanostructures: solvothermal synthesis optimization of the TiO₂ shell.

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Several nanostructured semiconductors with a wide band gap have been employed as ordered electron acceptors in optoelectronic and photovoltaic devices.[1] As one of these, ZnO has attracted significant attention due to its low-cost, direct band gap (3.37 eV), high exciton energy (60 meV), high electron mobility (200 cm²V⁻¹s⁻¹) and low toxicity.[2]

The 1D nanostructured morphology provides a direct and continuous pathways for charge transport whilst maintain a high interfacial surface area. ZnO nanorod arrays can be easily grown by different techniques, such as chemical vapor deposition, magnetron sputtering, hydrothermal and electrochemical deposition methods. Of these, electrochemical deposition is probably the most promising due being eco-friendly, simple to scale-up and low-cost.[3]

When the nanostructured ZnO is coupled with another material to form a composite, like core-shell materials, a variety of properties different from the original ZnO emerge. One such proposed structure is the coverage of ZnO nanorods with a thin TiO₂ layer (TiO₂ has similar band edge positions). The objective in this case is to benefit from the conjugation of the efficient electron transport in ZnO with the chemical stability and lower density of recombination defect states of TiO₂. [4]

Presented here are ZnO nanorods cores prepared by pulsed electrochemical deposition which are then, via a solvothermal synthesis, subsequently coated with a TiO₂ shell. Parameters such as temperature and the presence of additives were varied and their effects on the resultant films characterized by XRD, SEM and photochemical response.

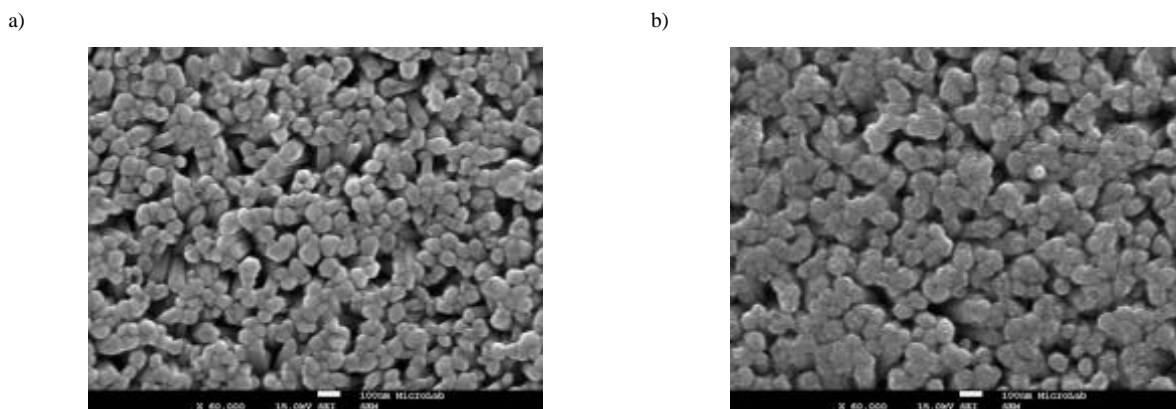


Figure 1 – a) Electrodeposited ZnO nanorods before and b) after solvothermal treatment.

[1] QF Zhang et al., Adv. Funct. Mater., 2008, 18, 1654

[2] M Mehrabian et al., J. Opt. Soc. Korea, 2014, 18, 307

[3] CZ Yao J. Rare Earths, 2011, 29, 133

[4] M Law et al., J. Phys. Chem. B, 2006, 110, 22652.

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State-of-the-art

The 1D nanostructured morphology provides a direct and continuous pathway for charge transport whilst maintaining a high interfacial surface area. When the ZnO nanostructure is coupled with another material to form a composite, like core-shell materials, a variety of properties different from the original ZnO emerge. One such proposed structure is the coverage of ZnO nanorods with a thin TiO₂ layer (TiO₂ has similar band edge positions). The objective in this case is to benefit from the conjugation of the efficient electron transport in ZnO with the chemical stability and lower density of recombination defect states of TiO₂ [1].

The use of complexing agents, such as acetylacetonate (ACAC), in solvothermal synthesis of TiO₂ nanoparticles has proven to be promising in the control of nanoparticle size. However, there is a limit in the molar ratio of ACAC to titanium isopropoxide (TTIP) without significant effect to the formation of TiO₂ [2]. Also, the aging of the sol-gel solution seems to obtain a better homogenized solution of titanium precursor [3]. Consequently, the aging of the sol-gel solution decreases the pH of the solution after solvothermal synthesis which is not beneficial when used for coating ZnO nanostructures.

The present work tested the hypotheses of aging and no aging the sol-gel solution applied in solvothermal treatments, and how the concentration of ACAC affects the formation of TiO₂ shell.

Experimental

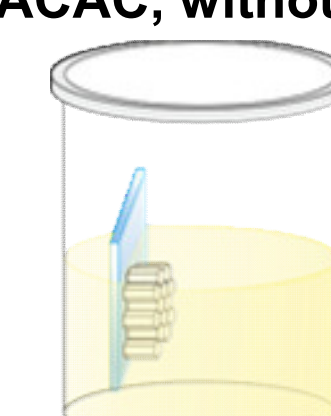
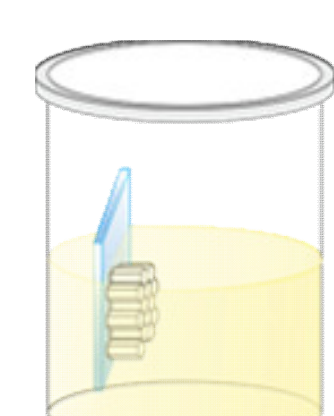
Pulsed electrodeposition of ZnO nanorods

- FTO/TiO₂/ZnO seed-layer substrates
- Bath composition: 10 mM Zn(NO₃)₂ + 5 mM KCl
- Bath temperature: 70 °C
- E_{on} = -1,0 V vs Ag/AgCl, t_{on} = 0,25 s; E_{off} = 0,0 V vs Ag/AgCl, t_{off} = 1,00 s
- n° of cycles = 2880
- Post-treatment: annealed at 450 °C for 1 h (heating rate of 5 °C/min)

ZnO@TiO₂ core-shell nanostructures prepared by solvothermal treatment

Sol-gel solution after 1 day aged

Sol-gel solution with different amounts of ACAC, without aging



150 °C for different times

180 °C for 6 h

Annealing at 450 °C for 2 h (heating rate of 1 °C/min)

Synthesis of titanium precursor

Ti(OⁱPr)₄ + PrOH



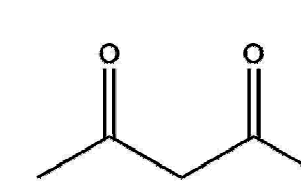
2h stirring

Acetylacetonate (ACAC)

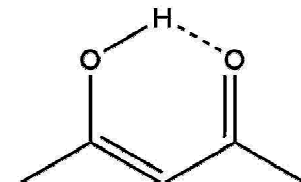


30 min stirring

Keto-enol tautomerism of acetylacetonate

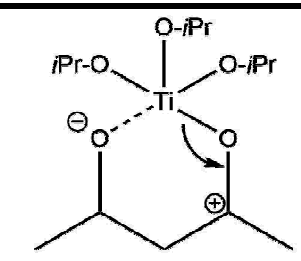
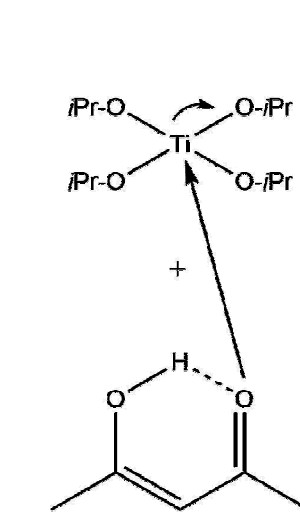


(stable in aqueous solutions)



(stable in organic solutions)

Formation of titanium complex



titanium alkoxide complex (formed at room temperature)

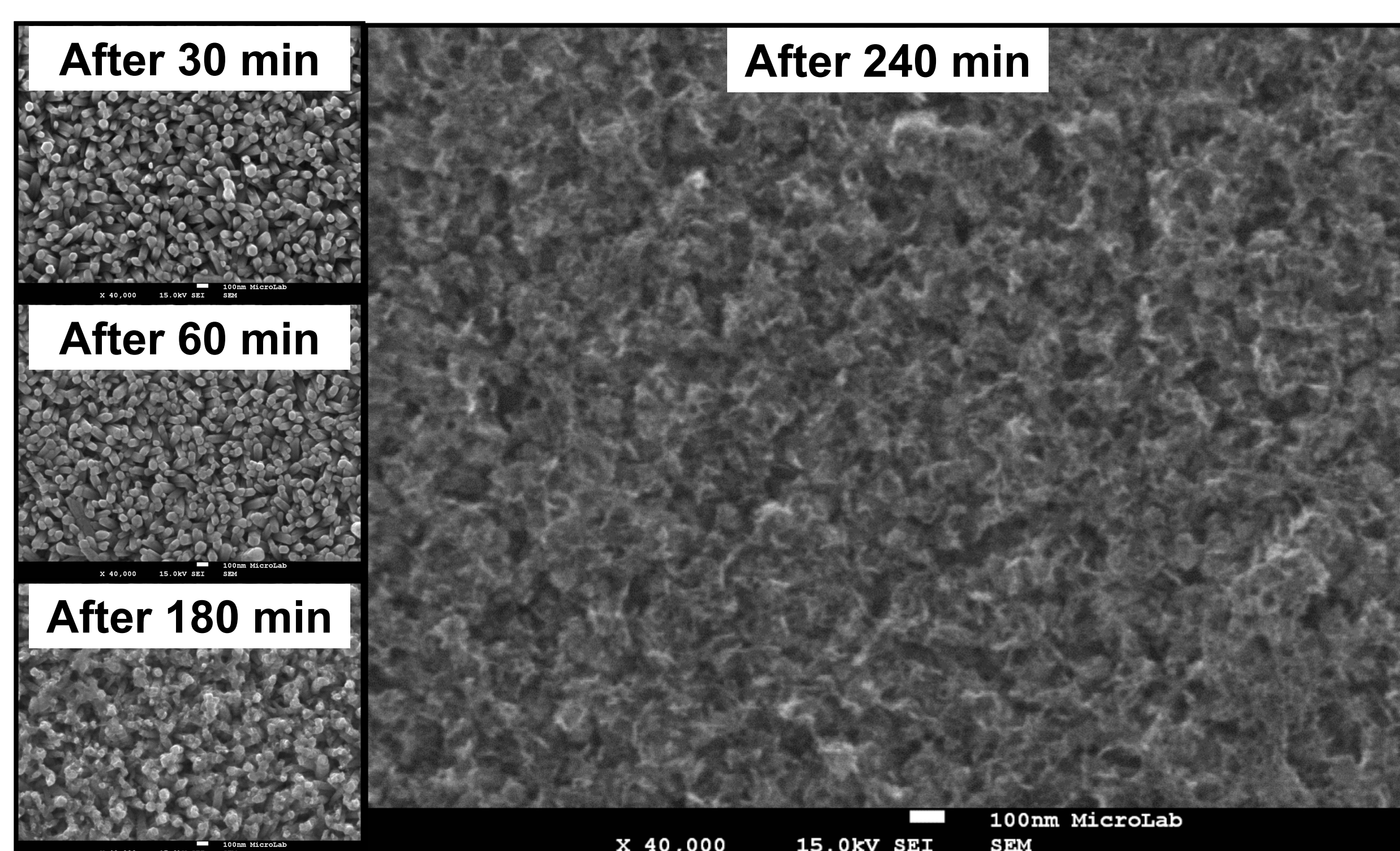
Results and Discussion

Aging versus no aging

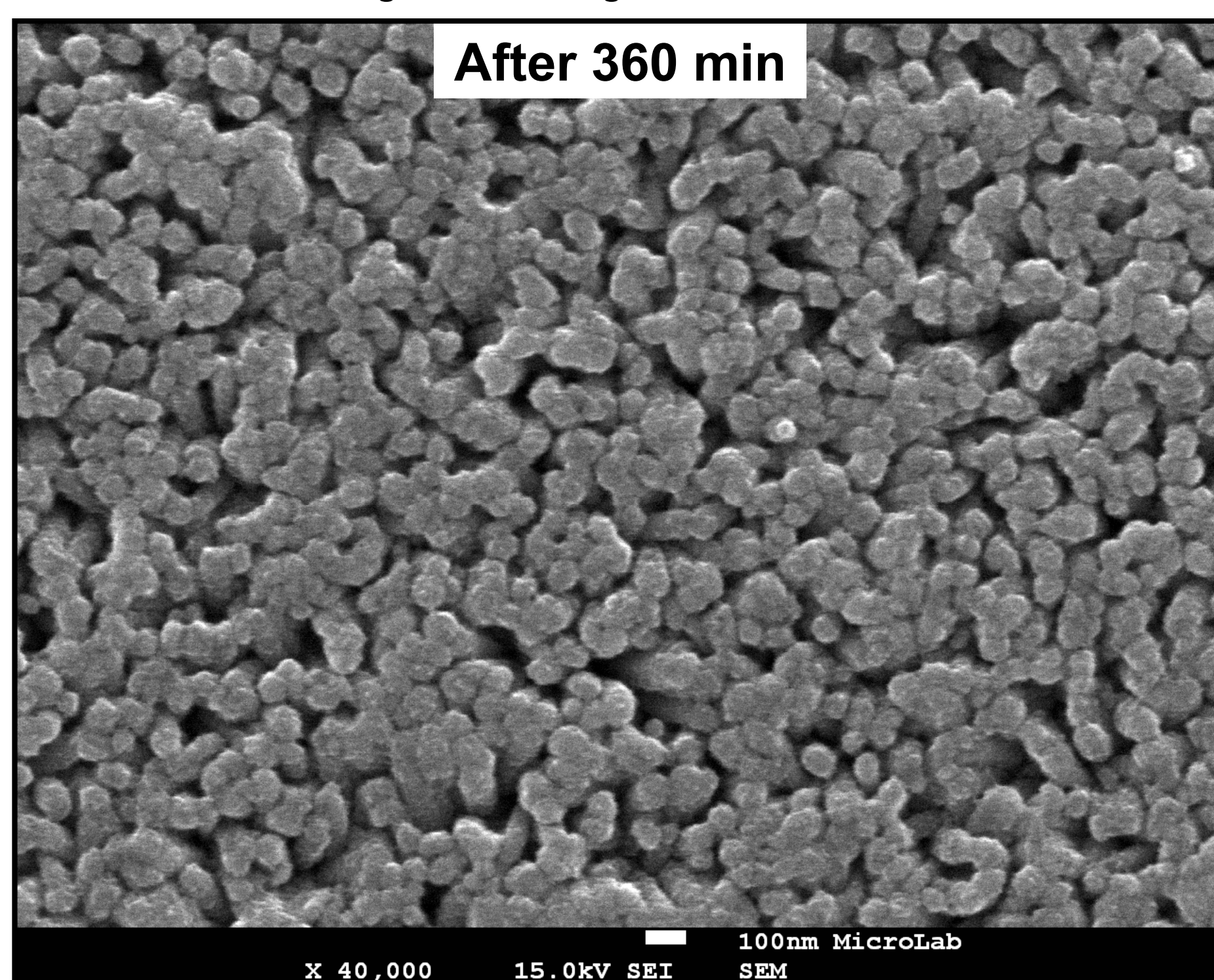
Effect of the amount of acetylacetonate

Aging

ZnO as-deposited

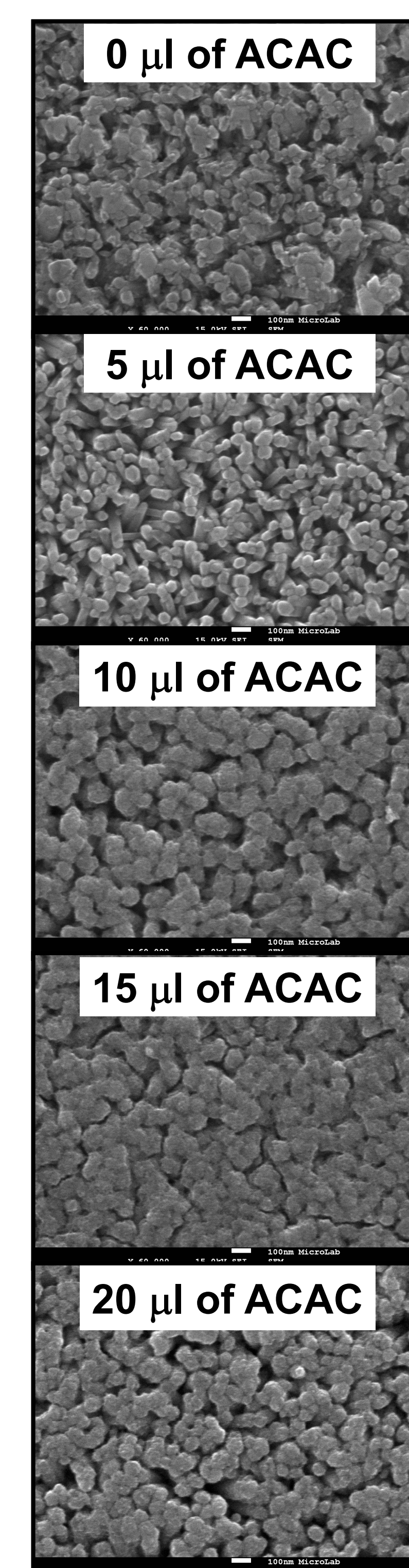


SEM image of ZnO@TiO₂ core-shell nanostructures after solvothermal treatment in sol-gel solution aged, at 150 °C for different times

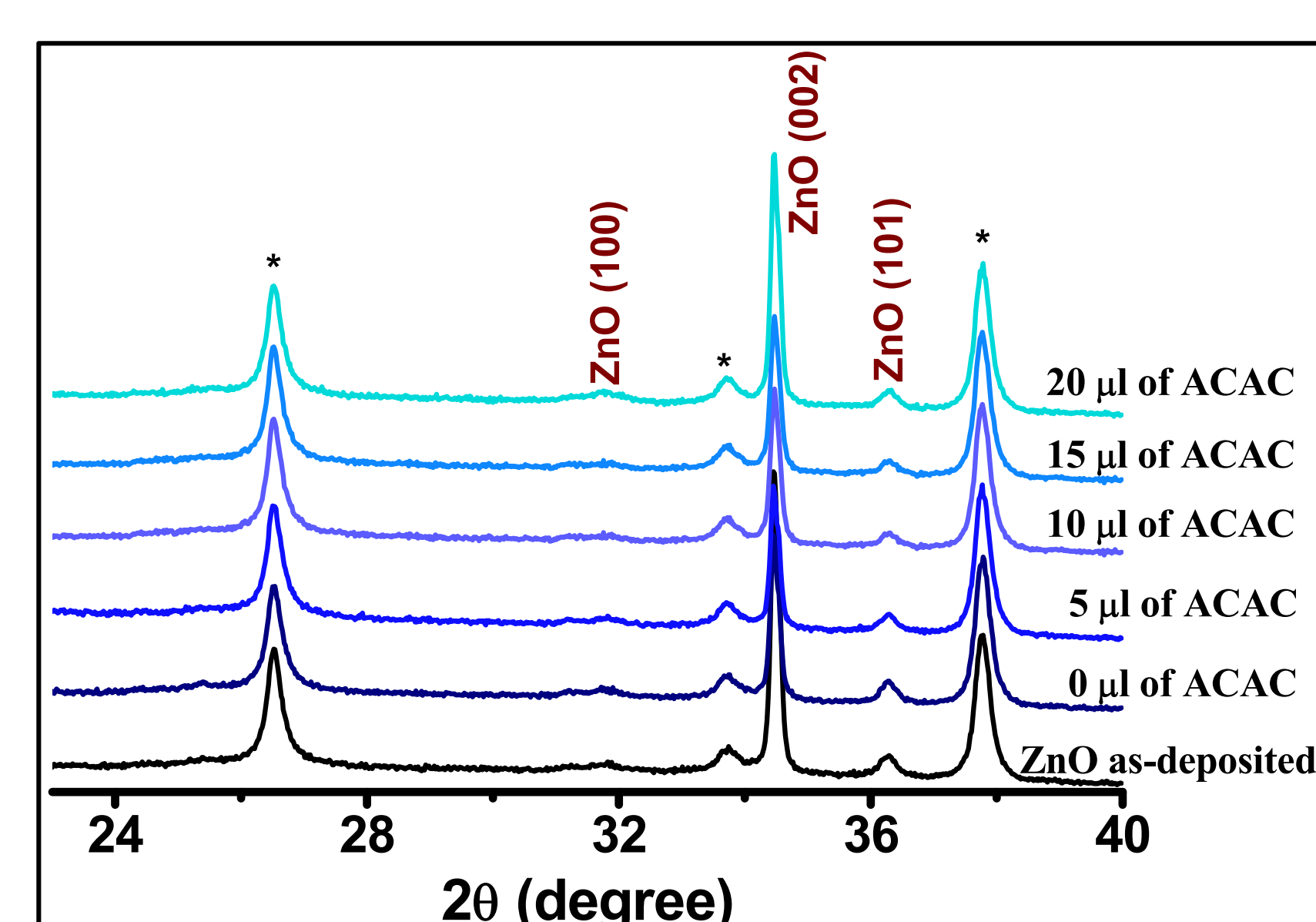


SEM image of ZnO@TiO₂ core-shell nanostructures after solvothermal treatment in sol-gel solution without aging, at 180 °C for 360 min

- The aging of the sol-gel solution seems to affect the ZnO nanostructures, leading to ZnO nanorod dissolution during solvothermal treatment.
- Without aging of the sol-gel solution, the ZnO nanostructure appears to remain intact even when solvothermal treatment lasts for longer and at higher temperature.



SEM image of ZnO@TiO₂ core-shell nanostructures after solvothermal treatment in sol-gel solution without aging, with different amounts of ACAC added, at 180 °C for 360 min



Diffraction patterns of ZnO as-deposited and after solvothermal treatment in sol-gel solution without aging, with different amounts of ACAC added, at 180 °C for 360 min

- The addition of acetylacetonate allows for better control of the formation of TiO₂ nanoparticles, which then coat ZnO nanorods to form the shell.
- Only when 20 µl of ACAC (in a 1:1 molar ratio with titanium isopropoxide), was each ZnO nanorod coated with a thin TiO₂ shell.
- The XRD analysis confirms the presence of ZnO nanostructures after the solvothermal treatment, i.e. it does not dissolve.

Final Remarks

- Aging the sol-gel solution decreases the pH during the solvothermal treatment which dissolves the ZnO nanostructures.
- No aging the sol-gel solution allows higher temperature of synthesis and longer treatment times.
- Smaller amounts of ACAC does not seem to significantly affect the formation of TiO₂.