Stable and luminescent colloidal ALD-grown quantum dot@metal-oxide hybrids

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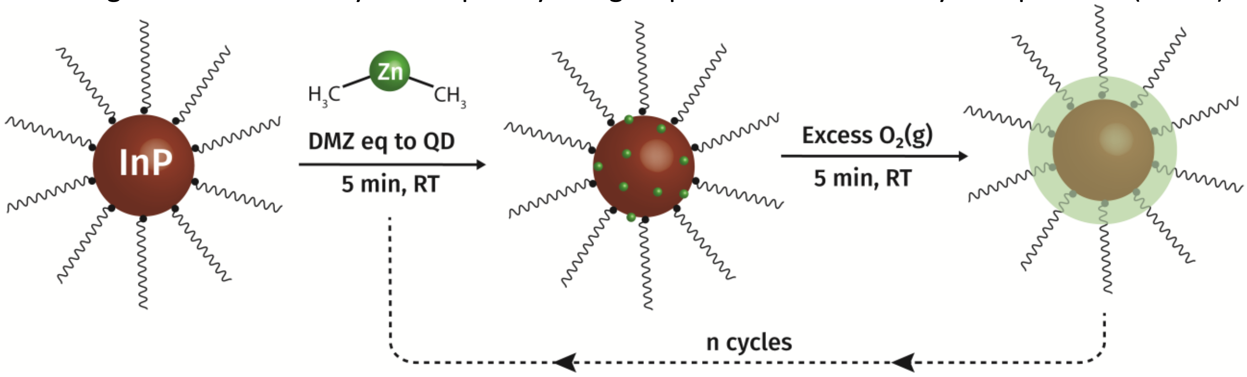
Colloidal quantum dots (QDs) have been used in applications spanning from medicine to catalysis and optoelectronics. Yet, their stability under ambient and processing conditions remains a challenge. In particular, InP QDs are highly sought for their low toxicity and suitable emission tunability within the visible range, however the surface of such QDs is vulnerable to ambient condition. We propose the growth of inert and stable metal-oxide shells to overcome this issue.[1,2] To this aim, we have grown ZnO shells on InP QDs using a method recently developed by our group: colloidal atomic layer deposition (c-ALD).



Solution and solid-state NMR spectroscopy unveiled that the formation of a metal-oxide shell by c-ALD is driven by a precursor-ligand interaction at the QD surface.[3] Further synchrotron X-ray absorption spectroscopy (XAS) and XRD measurements allowed us the reconstruct the structure of the ZnO shell and interface with the InP surface. We found that the deposition of a ZnO shell by c-ALD results in the formation of surface InPOx which permits the deposition of ZnO. We then study the effect of shell growth conditions and thickness on the stability and optical properties of our InP@ZnO core@shell particles. First, we unveiled the delicate balance between surface oxidation and electronic defect passivation that leads to enhanced emission (QY≈60%). Secondly, we demonstrated that these new core@shell heterostructures are colloidally and chemically stable in ambient conditions whereas the as-synthesized InP QDs rapidly degrade and precipitate. We foresee c-ALD as a methodology to grow a variety of metal oxide shells on different QDs for improved chemical protection in harsh conditions, such as aqueous solutions in a range of pH conditions, which are important for biological imaging or photocatalysis, while preserving or improving their luminescent properties.

[1] Loiudice, A.; Strach, M.; Saris, S.; Chernyshov, D.; Buonsanti, R. *J. Am. Chem. Soc.* **2020**, *141*, 8254–8263.
[2] Loiudice, A.; Segura Lecina, O.; Bornet, A.; Luther, J. M.; Buonsanti, R. *J. Am. Chem. Soc.* **2021**, *143*, 13418–13427.
[3] Segura Lecina, O.; Hope, M. A.; Venkatesh, A.; Björgvinsdóttir, S.; Rossi, K.; Loiudice, A.; Emsley, L.; Buonsanti, R. *J. Am. Chem. Soc.* **2022**, *144*, 3998–4008.