Surfactant-free and stable colloidal metal oxide ultra-small quantum dots via plasma-liquid electrochemistry

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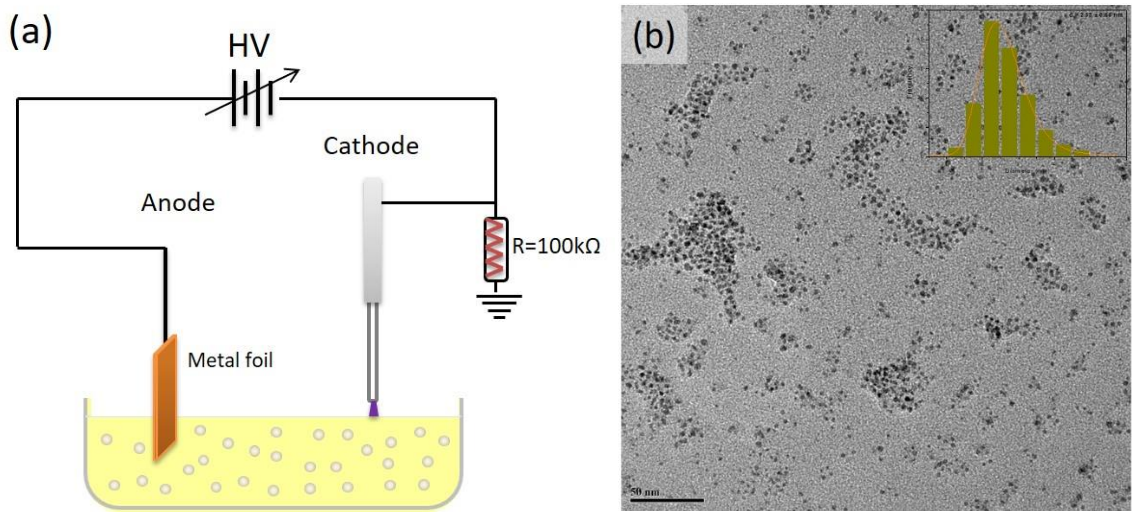
Abstract:

Metal oxides are materials of great importance and interest with exceptional chemical stability, tunable optical and electrical properties and, importantly, meeting cost and environmental requirements for a sustainable future.[1-3] For these reasons metal oxides nanoparticles are being investigated for a very wide range of applications that include energy harvesting and solar conversion and for exploiting nanoscale effects. However, due to synthesis challenges, the properties of ultra-small and quantum confined metal oxide nanoparticles, or quantum dots (QDs), are still very little understood while expected to offer exciting opportunities. Here we demonstrate that the synthesis of metal oxide QDs can be achieved by plasma-liquid electrochemistry with exceptional control of the size distribution even for particles well below 2 nm in diameter. Plasma-induced chemistry[4,5] initiated at the plasma-liquid interface allows for rapid and simple production of highly stable colloidal suspension in ethanol of surfactant free metal oxide QDs, where a solid metal foil acts as the metal precursor.[6] We provide an overview of these capabilities for a range of metal oxides that include Cu, Ni, Co, Mo and Zn oxides. We then study in detail the synthesis mechanisms leading to cupric oxide (CuO) QDs providing a range of experimental evidence that clarifies chemical reaction pathways due to the plasma interacting with ethanol. For a better understanding of the plasma chemistry, the process was also studied with different electrodes so to assess the impact of QDs formation in the overall plasma-ethanol chemistry. We have carried out extensive material characterization for the QDs and we have also analysed liquid products at different conditions by Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, nuclear magnetic resonance, mass-spectroscopy etc. Our work points at the role of different species in the synthesis of QDs. We believe that some of these chemical pathways may be general and applicable to the formation of other metal oxide QDs, however in some cases (e.g. for Mo-oxide) we expect some deviations. Overall our work discloses

important general aspects of plasma-liquid interactions, in particular when ethanol is used. The study of the properties of our metal-oxide QDs uncovers quantum confinement effects that can become particularly useful in many application and suggest exciting opportunities in the control of defects and achieving phases that are difficult to produce with other methods.



(a) Schematic of hybrid plasma-liquid electrochemical cell, (b) Transmission electron microscopy of CuO QDs with inset of particle size distribution

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