

## Colloidal strategies for Cu-V-O nanocrystals as photocatalysts for solar-to-fuel conversion

**V. Mantella,<sup>a</sup> M. Strach,<sup>a</sup> R. Buonsanti<sup>a</sup>**

<sup>a</sup>Department of Chemistry and Chemical Engineering, École Polytechnique Fédérale de Lausanne, Sion, CH-1950

With the boosting CO<sub>2</sub> levels in the atmosphere, the importance of developing technologies to efficiently exploit renewable energy sources is higher than ever. A very promising approach to fuels generation is the conversion of water and CO<sub>2</sub>, using solar radiation as source of energy, known as artificial photosynthesis. [1] Currently, the development of efficient and stable light absorbing and catalyst materials to carry such chemical transformations are among the scientific challenges preventing practical implementation of water splitting and CO<sub>2</sub> reduction devices. As for the light absorbers, required properties are high photo and chemical stability, a band gap around 1.7-2eV, good charge transport properties, and ideally the possibility of using abundant and non-toxic elements. Multinary metal oxides might be ideal candidates, yet their synthetic development is still at earlier stages compared to II-VI semiconductors. [2] In the pursuit for efficient solar-to-chemical energy conversion, copper vanadates, such as Cu<sub>2</sub>V<sub>2</sub>O<sub>7</sub>, have been recently highlighted as promising photoanodes possessing a band gap < 2eV and suggested to be stable in a wide range of operational conditions relevant for water splitting. [3] One of the hurdles which remains to be overcome is to simultaneously control the crystalline phase, stoichiometry and morphology, so to identify the optimal parameters governing the materials' performance as photoanodes.

In this work, a colloidal strategy to access ternary Cu-V-O semiconductor nanocrystals was developed. In order to achieve control on the crystalline phase, several synthesis parameters were adjusted (i.e. the reactivity of precursors, ligands, temperature, and concentration) with the ultimate goal of understanding the mechanistic path governing the nucleation and growth of such complex metal oxides. An in-situ FTIR probe was used to monitor the reaction mechanism. The as-obtained nanocrystals were thoroughly characterized using X-Ray diffraction and electron microscopy techniques. The composition was confirmed by elemental analysis using ICP-OES. The dependence of their optoelectronic properties on the crystalline structure, stoichiometry and size was investigated by UV-Vis spectroscopy.

Obtaining this material in the form of colloidal nanocrystals will allow us to achieve a higher degree of compositional and morphological tunability compared to other approaches, which have been currently used (such as sol-gel or solid state chemistry). [3,4] Variation of band gap might be observed, compared to their bulk counterparts, as a result of quantum effects or strain. Heterostructured nanocomposites might also be accessed to improve charge separation, as already demonstrated in the group for bismuth vanadate. [4] Furthermore, the easy processability of colloidal nanocrystals will facilitate their integration in baggie-type water splitting reactors and to optimize device performance through structural and compositional modifications. [2]

1) J. H. Montoya et al., *Nature Materials*, **2017**, 16, 70.

2) C.Gadyiar, A. Loiudice, R. Buonsanti., *J. Appl. Phys. D* **2017**, accepted.

3) A. Loiudice, J. Ma, W. S. Drisdell, T. M. Mattox, J. K. Cooper, T. Thao, C. Giannini, J. Yano, L.- W Wang, I. D. Sharp, and R. Buonsanti., *Adv. Mater.* **2015**, 27, 6733.

4) A. Loiudice, J. K. Cooper, L. H. Hess, T. M. Mattox, I. D. Sharp, and R. Buonsanti., *Nano Lett.* **2015**, 15, 7347.