

Colloidal Chemistry to Advance Studies in Artificial Photosynthesis

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Abstract: This article presents an overview of our research in the field of colloidal nanocrystal synthesis and their implementation into water splitting and CO₂ reduction electrochemical cells. We discuss our approaches to tailor-made novel material platforms to advance our knowledge in energy storage in chemical bonds, namely artificial photosynthesis. Herein, we focus on complex metal oxides as light absorbers to drive water splitting, nanocrystal hybrids and metals as electrocatalysts for carbon dioxide conversion. Our approach to solve the synthetic challenges so to achieve very precise control on size, shape and composition of such materials is highlighted.

Keywords: CO₂ reduction · Colloidal synthesis · Device assembly · Nanocrystals · Water splitting



Raffaella Buonsanti has started her position as Tenure-Track Assistant Professor at the Institute of Chemical Sciences and Engineering (ISIC) of the École polytechnique fédérale de Lausanne (EPFL) in November 2015. She received her Master Degree in Chemistry from the University of Bari in 2006. In 2010, she graduated in Chemistry from the University of Salento working at the National Nanotechnology Laboratory (NNL, in Lecce-Italy). After two years as a postdoctoral researcher at LBNL (2010–2012), she was promoted to Project Scientist, a non-tenure track scientist position, in the Molecular Foundry. From 2013 to 2015 Raffaella was a tenure-track Staff Scientist in the Department of Materials Science within the Joint Center for Artificial Photosynthesis at LBNL, before moving to EPFL. Here, through her core expertise in colloidal synthesis, she develops novel approaches to complex materials to drive chemical transformations, with particular emphasis on energy-related reactions such as CO₂ reduction and water oxidation.

1. Introduction

Colloidal synthesis is a wet-chemistry approach which affords a superb control and tunability on the morphology and the composition of nanocrystalline materials (Fig 1).^[1–10] Such a material engineering at the atomic-scale is critical when searching for design specifications which will eventually lead to optimal performance in energy devices. Yet, the potential of colloidal chemistry is far from being fully explored in energy research. Nonetheless, many groups are devoting their efforts towards this direction. To cite only a few examples, Kovalenko and his team are utilizing colloidal nanocrystals to advance battery research,^[11] the Milliron group is developing a new smart window technology based on doped metal oxide nanocrystals,^[12] Wood is searching for non-toxic quantum dots for light-emitting devices,^[13] Sargent continues to push the limit of quantum dot-based photovoltaics,^[14] and Cargnello is employing colloidal chemistry to design catalysts which drive high-pressure and high-temperature chemical transformations.^[15] Our group aims at exploiting the full potential of colloidal chemistry to advance energy storage in chemical bonds, otherwise named as artificial photosynthesis.

Storage of intermittent renewable energy in chemical bonds is an important research area to build a more sustainable society. Artificial photosynthesis mimics natural photosynthesis by converting sunlight, water and carbon dioxide into value-added chemicals (such as fuels for transportation like hydrogen or hydrocarbons but also useful chemicals like ethylene, which is a feedstock for petrochemicals).

In this account, we will highlight some of the contemporary synthetic challenges in colloidal chemistry, our general approach to address them and our recent

results. Firstly, we will focus on complex metal oxide nanocrystals, which are important as light absorbers to drive water oxidation among different applications. Secondly, we will discuss our very recent efforts in interfacing colloidal nanocrystals with building blocks of different chemical nature (such as metal organic frameworks) in a controlled manner. Finally, our strategies to build unambiguous structure/properties relations in electrochemical CO₂ conversion using atomically-defined nanocrystals as catalysts will be disclosed.

2. Current Challenges in Colloidal Chemistry

Colloidal nanocrystals (NCs) are synthesized in solution in the presence of organic surfactants (*i.e.* oleic acid, oleylamine, trioctylphosphine).^[1–10] The latter play a key role in colloidal synthesis. Surfactants bind unsaturated surface atoms and contribute to define the NC size and shape by modulating the surface free energy.^[2] Furthermore, they confer solubility and colloidal stability to the NCs in a large variety of solvents. Such colloidal dispersions are easily employed as ‘inks’ for processing of the NCs as thin film electrodes.^[4,5,8,9,12,14] At this time, the synthesis of nanocrystals containing one or two elements is pretty much mature and readily available, to the point that nanocrystals can be used as ‘artificial atoms’ to create nanocrystal solids.^[16] Yet, we are still far from having an extensive library of chemical reactions that permits to rationally target NCs with the desired size, shape and composition, in a similar manner of organic chemistry for example. The lack of deterministic and by-design synthetic paths becomes more significant when we go from single or binary particles to more complex

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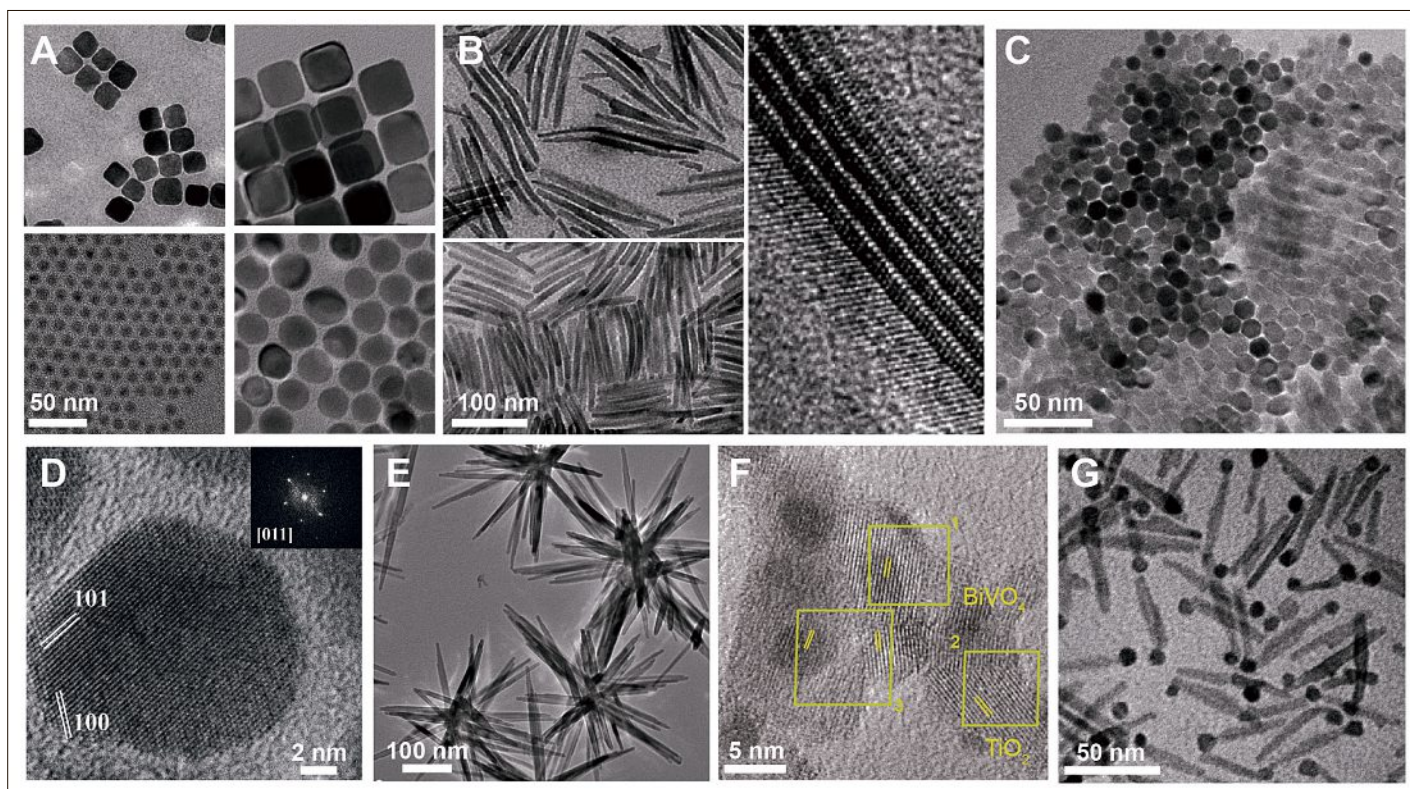


Fig. 1. Overview of transmission electron microscopy (TEM) images corresponding to colloidal nanocrystals with different composition, size and shape: (A) Cu nanospheres and nanocubes (Reprinted with permission from *Angew. Chem. Int. Ed.* **2016**, *55*, 5789. Copyright 2016 Wiley-VCH); (B) TiO₂ brookite nanorods (Reprinted with permission from *J. Am. Chem. Soc.* **2008**, *130*, 11223. Copyright 2008 American Chemical Society); (C) CuZnTeSn nanorods oriented perpendicularly to the substrate; (D) Al-doped ZnO NCs (Reprinted with permission from *Nano Lett.* **2011**, *11*, 4706. Copyright 2011 American Chemical Society); (E) N-doped TiO₂ nano-urchins (Reprinted with permission from *J. Phys. Chem. C* **2015**, *119*, 7443. Copyright 2015 American Chemical Society); (F) BiVO₄/TiO₂ heterostructures (Reprinted with permission from *Nano Lett.* **2015**, *15*, 7347. Copyright 2015 American Chemical Society); (G) γ -Fe₂O₃/TiO₂ NC hybrids (Reprinted with permission from *J. Am. Chem. Soc.* **2010**, *132*, 2437. Copyright 2015 American Chemical Society)

compositions. The latter comprise ternary, quaternary and quinary NCs as well as hybrid constructs. The specific synthetic challenges associated with multinary metal oxides and hybrids are described in the following sections.

Presently, our strategy to progress toward a synthesis-by-design of complex nanomaterials is to provide a better understanding of the chemical transformations behind nucleation and growth of the NCs (Fig. 2). We aim at achieving this goal through a combination of spectroscopic techniques spanning from liquid-NMR (Nuclear Magnetic Resonance) to *in situ* ATR-FTIR (Attenuated Total Reflectance-Fourier Transform Infrared) spectroscopies. Such chemical understanding will be complemented with *in situ* XRD studies, which will give insight into nucleation and

growth mechanism from a structural standpoint.

2.1 Multicomponent Metal Oxide Nanocrystals

Colloidal synthesis of metal oxide NCs is one of the core expertise of our group. We are currently relaying this knowledge to develop complex metal oxide light absorbers to drive the water oxidation reaction.

Water oxidation plays a key role in artificial photosynthesis. In fact, it is the only scalable anodic reaction to pair with the cathodic fuel-forming reactions (H₂O reduction to hydrogen fuel and CO₂ reduction to value-added chemicals). Yet, light absorbers that can efficiently convert photons into charge carriers that drive this oxidative chemistry, while being stable in

the harsh environment required to carry the water oxidation reaction, are largely missing.

Many of the promising candidates suggested by theoretical calculations and some experimental results consist of multication oxides (see discussion below). The synthetic challenge associated with accessing these materials with systematic and precise definition of both composition and morphology is significant; it relies on establishing control over the reactivities of three or more metal precursors and on identifying the conditions required to form composition and structure with the desired function, without phase segregation occurring. In the context of complex multi-element materials, colloidal chemistry has allowed for much progress in the class of metal chalcogenides (*i.e.* CuZnSSe, CuZnSnS, PbSeS, CuZnTeSe), which have been widely used for ink-based photovoltaics.^[17] Synthetic routes to achieve an exquisite control on crystalline phases, stoichiometry, size and shape have been established and these structural properties demonstrated to correlate with the photovoltaic performance.^[17] Specifically, the superior control on phase transformations, grain size and grain orientation compared to vacuum-based methods and other molecular

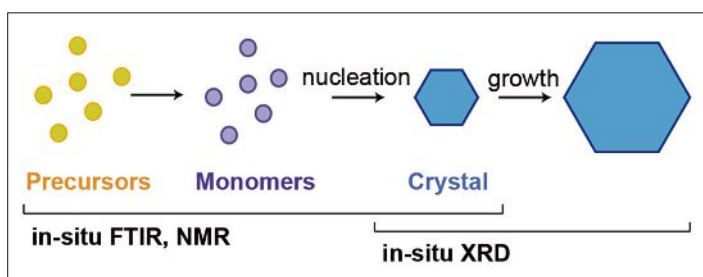


Fig. 2. Simplified schematic of nanocrystal nucleation and growth and miscellanea of techniques that our group will use to study those.

solution approaches has often resulted in much higher performance devices for this class of materials.^[17] More recently Yarema *et al.* have been developing and elucidating the chemistry to access ternary I-II-VI NC light emitters.^[13] On the contrary, the synthesis of ternary and quaternary oxide NCs is far less developed, despite the applications of this material class into a broader range of applications ranging from catalysis, to batteries and memory devices.^[18] The aim of our group is to contribute to develop the chemistry of complex oxide colloidal NCs by focusing on specific materials to advance the field of solar-to-fuels conversion. If successful, our work will open the pathway to photo-physical investigation in a similar manner to the on-going studies for colloidal II-VI NCs and their hetero-structures with hydrogen evolution catalysts.^[19] In the future, dual bed baggie-reactors consisting of colloidal nanocrystals may be envisioned.^[20]

The first class of interest in the group is represented by oxynitrides (*i.e.* $\text{TiO}_3\text{O}_3\text{N}_2$, $\text{La}_2\text{TiO}_2\text{N}_2$, $\text{Li}_5\text{MoO}_4\text{N}$), which have been identified as promising photoanodes.^[21] They have smaller band gaps than the corresponding metal oxides because of the valence band lifting resulting from the substitution of oxygen 2p orbitals with nitrogen 2p levels. One of the most common approaches to oxynitrides and nitrogen doping remains high temperature annealing in ammonia. Such an approach does not allow for control on the nitrogen content, on the N-atom location (interstitial vs. substitutional, surface vs. bulk). These parameters have all been identified to impact the electronic structure and photoactivity of the N-doped oxides and oxynitrides.^[18] Thus, achieving control on those would be desirable to establish unambiguous structure/properties correlations. We have started to explore a new chemistry for this class of light absorbers by starting from the simplest system: N-doped TiO_2 .^[18] The vast amount of literature on N- TiO_2 provided us a knowledge base for unambiguous verification of our synthetic approach through established spectroscopic methods. We have proposed a colloidal-based route where the rational selection of reaction conditions and precursors has allowed for the tuning of the nitrogen dopant concentration (over a wider range of concentrations compared to previous work) and, more importantly, lattice sites in TiO_2 . We found that ternary amines favor substitutional nitrogen and overall higher doping content compared with primary amines. A nucleation-doping mechanism, triggered by tertiary amines, and a growth-doping mechanism, which dominates when primary amines are used instead, were hypothesized to account for the introduction of nitrogen impurities in substitutional or in-

terstitial sites, respectively. In the former, the Ti–N bond forms during the nucleation phase; instead in growth-doping the nitrogen dopants are mainly introduced during the growth as a result of the generation of ammonia in the reaction flask. The reaction scheme is depicted in Fig. 3 and it was supported by FTIR and NMR investigations.^[18] This newly developed chemistry allowed us to correlate the change of the band gap and the photoelectrochemical behavior of the doped TiO_2 nanostructures to the nature of the dopants. The substitutionally doped TiO_2 possessed a much higher activity under visible light compared to the interstitially doped sample. This result suggested that the band gap reduction in the substitutionally doped TiO_2 is accompanied by actual delocalized valence band states that enable generation and transport of chemically active charges upon visible light illumination. Instead, probably only intra-band defects are introduced when nitrogen occupies interstitial lattice sites. Our aim is now to exploit the full potential of this chemistry and to demonstrate that it can be extended to a wider range of oxynitride materials.

Our second class of interest is represented by ternary and quaternary vanadates. In the last years, monoclinic BiVO_4 has attracted much attention as a photoanode for solar fuel applications.^[22] The best performance for this material has been obtained by nanostructuring and by interfacing with wider band gap oxide semiconductors.^[22] We have developed a BiVO_4 NC ink that facilitates the assembly of BiVO_4 /metal oxide (MO) (MO = TiO_2 , WO_3 , and Al_2O_3) nanocomposites in which the morphology

of the metal oxide building blocks is finely tailored (Fig. 4).^[9] The BiVO_4 NC ink was constituted by $\text{Bi}_2\text{O}_{2.7}/\text{VO}_x$ heterodimers. The latter were synthesized through an *in situ* seed-mediated growth where Bi nanosheets, generated in the reaction flask, act as nucleation seeds of a noncentrosymmetric vanadium oxide shell (Fig. 4A,B). We used bismuth chloride (BiCl_3) as a bismuth source and vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) as a vanadium source, while oleylamine was used as surfactant and solvent. BiCl_3 was reduced to elemental bismuth in the form of nanosheets by the amine. The reaction of the nanosheets with $\text{VO}(\text{acac})_2$ led then to the formation of the $\text{Bi}_2\text{O}_{2.7}/\text{VO}_x$ heterodimers. Tunable nanostructured BiVO_4/MO were obtained by annealing thin films deposited from mixed solution of the NC heterodimers with TiO_2 , Al_2O_3 and WO_3 NC of different size and shape (Fig. 4C,D). We used a combination of transient absorption spectroscopy – spanning from picoseconds to second timescales – and photoelectrochemical measurements to reveal that the achieved structural tunability is key to understanding and directing charge separation, transport, and efficiency in these complex oxide heterostructured films (Fig. 4E,F). For example, in the $\text{BiVO}_4/\text{WO}_3$ nanocomposite, better photoelectrochemical performance was found for smaller WO_3 nanorods (Fig. 4E,F). This behavior resulted from an improved efficiency of electron injection from BiVO_4 to WO_3 deriving from a more extended interfacial area between BiVO_4 and WO_3 , compared to nanocomposites comprising bigger WO_3 nanorods. These results highlight the significant potential

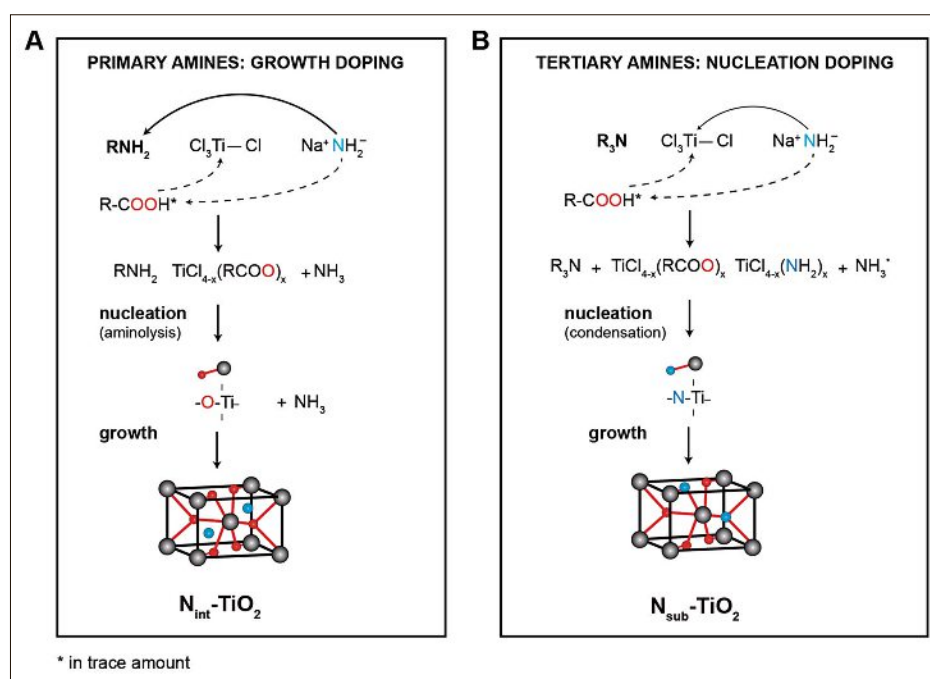


Fig. 3. Reaction schemes for the nitrogen doping of TiO_2 nanostructures in A) interstitial and B) substitutional lattice sites in the presence of primary and tertiary amines, respectively.^[18]

afforded by the assembly of such oxide nanocomposites and unveil relationships between MO properties and PEC performance. While the focus of this initial study was on BiVO_4/MO nanocomposites, the generality of this facile method for the assembly of preformed building blocks, which avoids tedious growth optimization and long preparation times, will enable access to a wide range of tailored heterojunctions. At the same time, we learned that accessing multicomponent vanadates with uniform composition is a non-trivial task.

Balancing precursor reactivities is the key to access homogeneous composition; some understanding of the reaction mechanism is needed to properly choose the precursors.^[23] The nucleation and the growth of metal oxides are usually initiated by heating up the reaction mixture, instead of the hot-injection technique which is more common for II-VI and III-V NCs.^[1,2] A possible explanation of this different approach might rely on the reactivity of the precursors. Common precursors for metal oxides are chlorides, acetates, acetylacetonates, oleates, amino-complexes, which often form *in situ* in the reaction mixture during the heating stage. Frequently used ligands include long chain (C8–C18) amines, carboxylic acids and diols. Common reaction paths for metal oxides include thermal decomposition of

the precursors, aminolysis and alcoholysis reactions.^[6–8] We have shown that FTIR is a great tool to corroborate hypotheses about the reaction mechanism.^[6–8]

As for BiVO_4 , bismuth is a border line Lewis acid and vanadium is a hard Lewis acid. Therefore, bismuth acetate is expected to be less reactive than vanadium acetate. In our attempt to obtain colloidal BiVO_4 NCs, when bismuth chloride was substituted with bismuth acetate or ethylhexanoate, 300 nm bismuth aggregates formed before bismuth could react with the vanadium precursor. This suggests that our hypothesis regarding reactivity was wrong and that we need to develop a deeper understanding of the chemistry behind the nucleation and growth of these vanadates. We plan to do so by looking also at different cations (such as copper or manganese), so to be able to further manipulate the band gap while elucidating the reaction mechanisms.

As an alternative approach to colloidal chemistry, we are investigating a NC-seed mediated growth of thin film vanadate light absorbers. The seeding process has been traditionally employed to reduce the crystallization temperature in ceramic ferroelectric materials, such a lead zirconate titanate, to facilitate their integration in flexible electronics as a result of the decreased crystallization temperature.^[24]

Recently, our group has utilized colloidal NCs with variable composition as seeds for the nucleation and growth of vanadate thin films (Fig. 5).^[25] Specifically, we employed $\text{Bi}_x\text{Sb}_{1-x}$ colloidal NCs with variable composition x to discover a new light absorber, $\text{BiV}_{1-x}\text{Sb}_x\text{O}_4$. The $\text{Bi}_{1-x}\text{Sb}_x$ NCs were converted into Sb-BiVO_4 films by reacting them with vanadyl acetylacetonate upon annealing (Fig. 5A). This novel two-step synthetic approach allowed for a precise compositional tuning while preserving the same morphology and crystalline structure up to a 20% antimony content. It is important to note that attempts to synthesize Sb-BiVO_4 by more conventional approaches such as sol-gel, solid solution, and spray pyrolysis were unsuccessful and resulted in phase separation, even for low percentage Sb alloys. X-ray characterization techniques revealed the substitution of V^{5+} with Sb^{5+} in the monoclinic BiVO_4 lattice. Thanks to the broad compositional range covered by our approach, a combination of theoretical prediction and experimental validation has showed that this photoanode possesses a band gap that linearly decreases with increasing Sb content up to 20% when the band gap is 0.2 eV smaller than the one of the undoped counterpart (Fig. 5A). While this material is still far from being optimal, the results of this work, derived from close coupling of theoretical

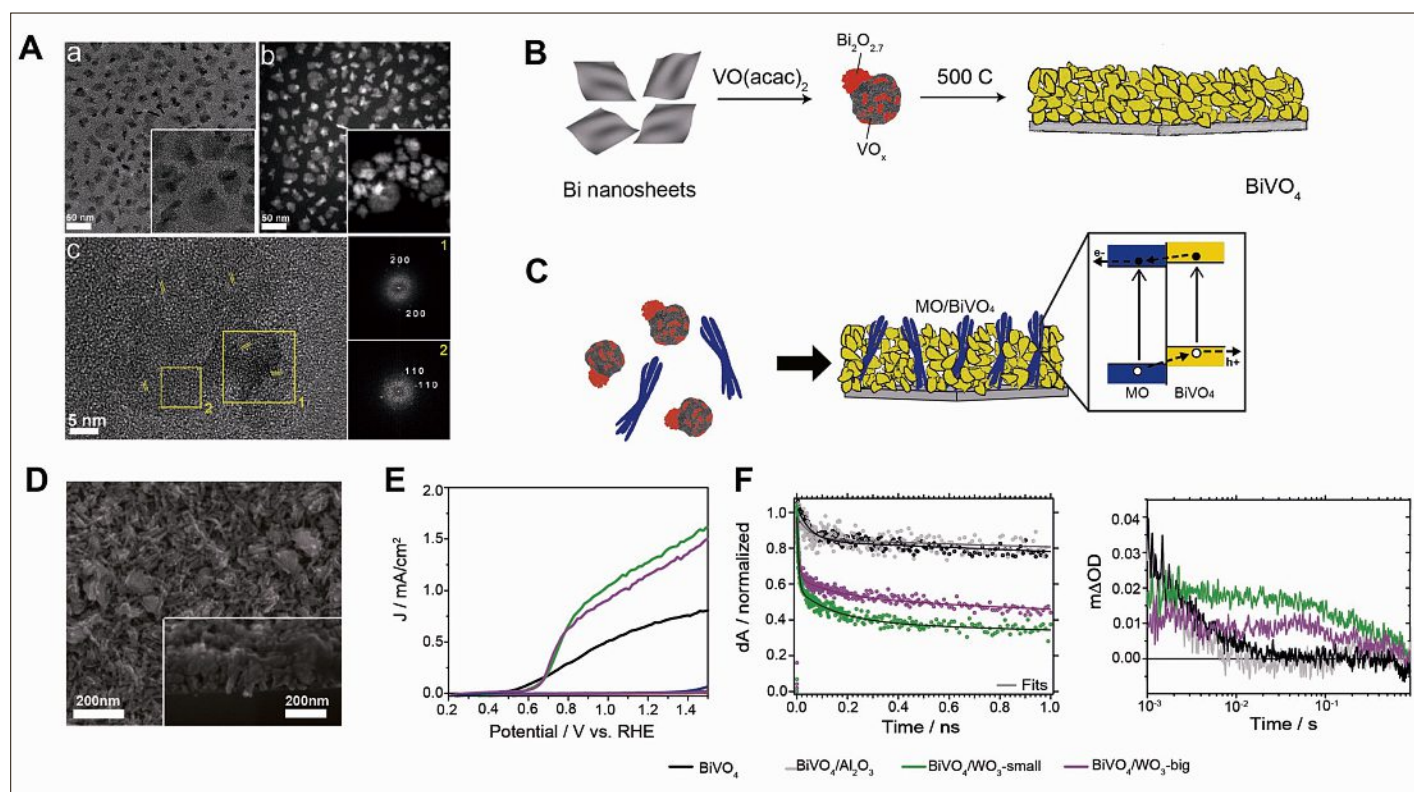


Fig. 4. Overview of assembly and photocarrier dynamics of heterostructured BiVO_4/MO heterostructured nanocomposite photoanodes: (A) TEM analysis of the heterodimers; (B,C) schematic representation of the $\text{Bi}_2\text{O}_{2.7}/\text{VO}_x$ heterodimers and their assembly with metal oxide NCs to form the nanocomposites, respectively; (D) scanning electron microscopy images of $\text{BiVO}_4/\text{TiO}_2$ nanocomposites; (E, F) photoelectrochemical and photophysical characterization of $\text{BiVO}_4/\text{Al}_2\text{O}_3$ and $\text{BiVO}_4/\text{WO}_3$, the latter assembled from the $\text{Bi}_2\text{O}_{2.7}/\text{VO}_x$ heterodimers and two different sizes of WO_3 nanorods.^[9] Reprinted with permission from *Nano. Lett.* 2015, 15, 7347. Copyright 2015 American Chemical Society.

understanding and advanced synthesis approaches, provide a path to the design of other metal oxides alloys with desirable band gaps and band edge positions for solar water splitting. To demonstrate the general applicability of the NC-seeded growth approach, other high surface area ternary oxide light absorbers were targeted (Fig. 5B). Bi_2WO_6 , CuWO_4 , SnWO_6 , and InVO_4 were synthesized and structurally characterized by XRD by using Bi, Cu, Sn and In_2O_3 NC seeds, respectively (Fig. 5B). Presently, we are targeting various quaternary vanadates, which we expect to possess a tunable band gap in the visible range. At the same time we are developing *in situ* techniques to gain a better understanding on the conversion mechanism of the NC seeds into the thin films. We aim at controlling grain size and orientation of the films, which are expected to impact performance, by tuning NC size and shape.

2.2 Nanocrystal Hybrids

The assembly of colloidal NCs with building blocks of different chemical nature (*i.e.* polymers, glasses and carbon-based materials) show considerable promise to satisfy the demand for complexity of several applications ranging from gas storage to energy storage to catalysis.^[26,27] The functionalities of such hybrid materials are dictated not only by the intrinsic properties of the single units but also by the morphology of the hybrids, the reciprocal spatial distribution of their constituents and the interfaces between them.^[26,27] Therefore, it is crucial to develop synthetic approaches to control these features.

Our group is studying NC-based hybrids which will eventually be utilized as multifunctional catalytic platforms to advance CO_2 conversion studies. The goal here is to establish novel synthetic schemes to achieve an exquisite control and tunability of these hybrid materials across multiple length. Firstly, we need to establish rules of design to synthesize such hybrids in a programmable manner.

In our recent work, we have focused on NC/metal organic framework (MOF) hybrids. Beautiful work has been done by the team led by Fischer based on wet- and gas-impregnation of pre-synthesized MOF.^[28] Here, small and naked NCs are embedded into the frameworks; however the control of size, shape, and composition of the NCs themselves is highly constrained by the pre-formed frameworks. Solvo-chemical conversion of metal oxide NCs developed in Falcaro's group has enabled the assembly of two- and three-dimensional MOF architectures on various substrates.^[29] Despite the demonstrated potential of chemical conversion, the synthesis of metal NC@MOFs by such an approach still

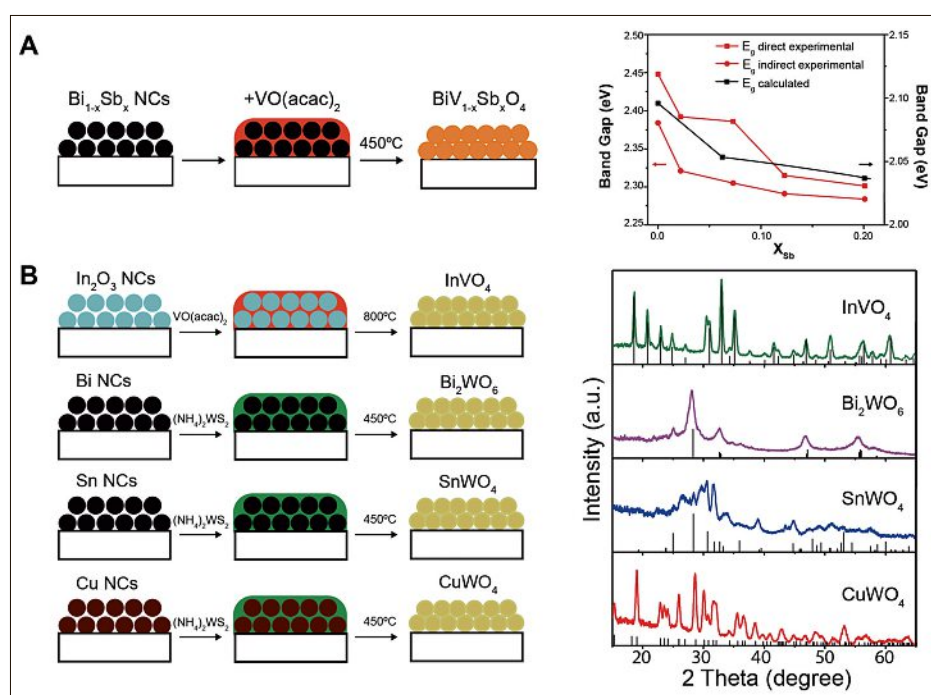


Fig. 5. NC-seed mediated growth of thin films metal oxide light absorbers: (A) schematic for growth of Sb-alloyed BiVO_4 and corresponding theoretical and experimental band gap variation; (B) applicability of the NC-seeded growth to other metal oxides.^[25] Reprinted with permission from *Adv. Mater.* **2015**, *27*, 6733. Copyright 2015 Wiley-VCH.

remains an underexplored area compared to the oxide counterpart.

We have reported a one-step synthetic strategy to encapsulate ligand-free (naked) Cu NCs into a carboxylate based MOF (Cu-MOF-74).^[30] Cu@Cu-MOF-74 hybrids were synthesized *via* a partial conversion of naked Cu NCs into Cu-MOF-74 in the presence of H_4dobdc (2,5-dihydroxyterephthalic acid, the MOF ligand) in a solvent mixture of dimethylformamide (DMF) and ethanol (EtOH) (Fig. 6).

One of the hurdles to realizing metal NC@MOF hybrids with uniform morphology and with a homogeneous NC spatial distribution by chemical transformation is to precisely match the metal dissolution and the MOF crystallization rate. Our study defined and rationalized the parameter space that provides control of the NC dissolution rate so to find the optimal window (Fig. 6). The initial Cu NCs uniformly dissolve during the conversion and this results in a narrow size distribution of the NCs in the final material. By explaining the role played by the solvent polarity, the reaction temperature, and the reactant concentration, we have contributed to gain knowledge toward a more rational approach to the synthesis of metal NC@MOF hybrids rather than more traditional trial and error methods.

To disclose the potentiality of the Cu@Cu-MOF-74 hybrids for device integration, we have demonstrated that the seeding approach reported here works on different substrates commonly used in

electrocatalysis, such as glassy carbon and carbon paper.^[30] Charge transport studies and structural stability will be object of future studies.

Nowadays, a huge compositional library of NCs is accessible by colloidal chemistry and we foresee the extension of the metal NC-to-MOF conversion to NCs with different sizes and shapes and to more complex systems, such as bimetallic NCs. Furthermore, the access to a pristine interface between inorganic NCs and MOFs will pave the way towards exploring new synergistic effects at the interface, especially in catalysis or gas adsorption where surface interactions dictate the material properties.

3. Colloidal Chemistry to Advance CO_2 Conversion Studies

CO_2 is an under-utilized resource for chemicals and fuels. With gigatons of this gas released in the atmosphere each year, any technology which uses CO_2 as a raw material can make a huge impact on climate change. However, the thermodynamic stability of the CO_2 molecule implies that high temperatures, highly reactive reagents (*i.e.* hydrogen) or a different source of energy are required to carry out its conversion. The exploitation of intermittent renewable sources (*i.e.* solar) emerges as a win-win solution, considering the need for seasonal storage. While progress has been made, one of the main challenges is to find

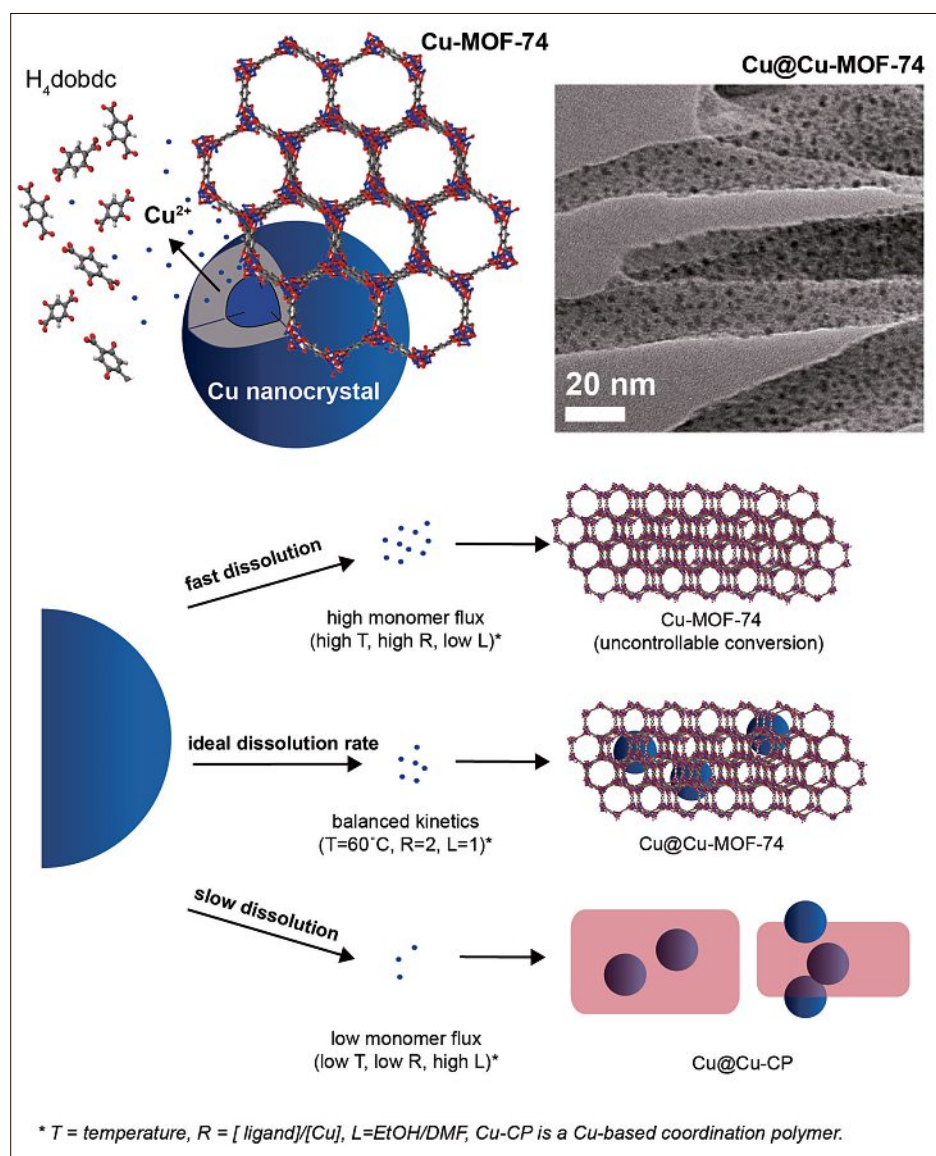


Fig. 6. Proposed formation mechanism and one representative TEM image of the Cu@Cu-MOF-74 hybrids (top) and impact of NC dissolution rate on the growth of the same (bottom).^[30] Reprinted with permission from *Chem. Mater.* **2016**, *28*, 3839. Copyright 2016 American Chemical Society.

catalysts that can electrochemically reduce CO₂ with high efficiency and selectivity towards a specific product.^[31]

We believe that colloidal chemistry offers a huge potential in advancing CO₂ conversion studies. The material tunability afforded by such technique is ideal to build unambiguous relations between the catalyst structure and its activity and to understand the relevant parameters to modulate activity and selectivity.

Currently, Cu is the only catalyst with propensity to form hydrocarbons, which are high energy dense molecules and therefore desirable products.^[31] In the conversion pathway from CO₂ to hydrocarbons, oxygen-containing intermediates, such as CHO, and the hydrogenation reaction to form those, have been identified as potential limiting steps.^[32–34] This means that the reaction barrier of CO₂ reduc-

tion would decrease and the selectivity towards hydrocarbons would increase if these oxygen-containing intermediates are stabilized. On metal surfaces the binding energy of CO and the downstream oxygen containing intermediates are linearly correlated (Fig. 7C), as they all bind through the carbon atom.^[32–34] As a consequence, on pure metal surfaces, it is not possible to stabilize CHO without stabilizing CO and thus poisoning the catalyst surface. Copper is more efficient and selective than other metals only because it has a slightly better than average ability to perform the hydrogenation of the adsorbed CO. Norskov *et al.* have suggested that more efficient and selective catalysts should decouple the adsorption energies of CO and CHO.^[32–34]

In our recent work, we have explored the effect of both size and shape of Cu NCs on their electroreduction activity and product selectivity.^[5] It is known that catalyst morphology can modulate catalytic activity and selectivity, yet this remains a relatively underexplored area in electrochemical CO₂ reduction. Two different sizes of Cu NC spheres (7.5 nm and 27 nm) and three different sizes of Cu NC cubes (24 nm, 44 nm, and 63 nm) were synthesized by the same colloidal chemistry-based method (Fig. 7A). Within the same morphology, we found that smaller NCs exhibit higher activity; however overall, the cube-shaped NCs were more intrinsically active than the spheres. An unexpected non-monotonic selectivity trend was observed, with an 80% selectivity for carbon products, 40% of which corresponded to ethylene, for the best case Cu NC cubes with 44 nm side length (Fig. 7B). While increased selectivity for ethylene at (100) step sites of Cu was anticipated by previous literature, the size-dependence was quite surprising, as smaller particles are commonly the most

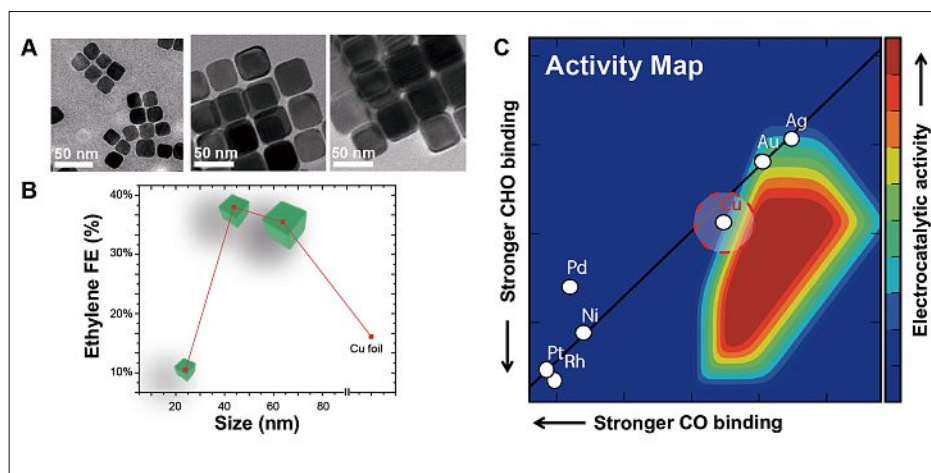


Fig. 7. Colloidal Cu nanocrystals as electrocatalysts for CO₂ reduction: (A) TEM images of Cu cubes with an average edge length of 24, 44, 63 nm; (B) corresponding faradaic efficiencies towards ethylene (the complete product analysis can be found in reference [5]); (C) kinetic volcano adapted from reference [34]. Reprinted with permission from *J. Phys. Chem. Lett.* **2013**, *4*, 388. Copyright 2013 American Chemical Society.

reactive ones. Our hypothesis is that atoms at the edges and on the (100) planes behave as different catalytic sites and that an optimal ratio between them ($N_{\text{edge}}/N_{100} = 0.25$ for $d = 44$ nm, where N indicates the number of atoms at the edge or on the planes) is crucial to maximize CO_2 reduction products and ethylene specifically. We are now verifying such a hypothesis and also studying the morphological evolution of the catalyst over time under operational conditions.

The activity map in Fig. 7C has been calculated for ideal flat metallic surfaces. Our work and others now show that morphology allows to gain some degree of freedom on the map. Yet, we are still far from being able to tune single metal catalysts so to maximize their electrocatalytic activity towards a specific product.

In the future, the group will continue to look at colloidal catalysts with different composition and morphologies in order to gain more insights into the CO_2 conversion mechanism and to maximize the hydrocarbon production. The next challenge will be to synthesize and to investigate hybrid materials with thoroughly bi-functional sites.

4. Conclusion and Outlook

Our research is highly multidisciplinary as it spans from synthesis of new atomically-defined materials to their implementation into proof-of-concept devices so to derive unambiguous structure/properties relations. While addressing synthetic challenges in colloidal chemistry, we focus on materials for storing energy in chemical bonds. Because we are integrating nanocrystals into electrochemical devices, we face challenges which are common in many applications involving NCs, from batteries to solar cells and smart windows. The primary one is to assure electrical connection between the NCs and the substrate and between the individual NCs. In fact, the pristine ligands are insulating. Currently, we are adopting previously developed strategies such as thermal decomposition or chemical stripping of the native ligands. One requirement, which is specific to material implementation into water splitting and CO_2 electrochemical cells, is to assure their stability in water and under highly oxidative or reducing conditions. We have recently started some work on capping NC semiconductor thin films with thin metal oxide layers by atomic layer deposition as a way to passivate the surface of water-sensitive materials and to explore different mechanisms of energy transport in NC networks. Overall, in the next years we aim at contributing to the broader nanoscience field with our research on colloidal NCs for energy storage into chemical bonds.

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