Final report for project grant # 18-425

"Using sunlight to catalyse demanding reactions"

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The project started with recruitment of a postdoctoral fellow. Due to very long visa waiting times, the selected candidate, Quang Long Le, a Vietnamese national, with a PhD degree from France, was not able to arrive and start working in Sweden until the first few months of 2019. This caused a slight delay in the project's starting phase. However, Dr Le is very efficient and has worked very hard and thus made substantial progress despite the slow start. Dr Le will continue to work on this project for a few more months and we expect that it will result in at least one high impact publication. Below follows a summary of the obtained results, a more detailed summary of the project and a future outlook, together with a financial report.

Summary of key results:

- We have developed a method for synthesis of water soluble PCN quantum dots
- We have shown that PCN quantum dots absorb visible light and that our synthetic procedure produce quantum dots with a low amount of detrimental trap states, also a prerequisite for efficient photocatalysis
- We have shown that irradiation of PCN quantum dots results in ultrafast electron transfer from the conduction band of the PCN quantim dots to model catalysts, another prerequisite for efficient photocatalysis
- We have developed an experimental setup to test the catalytic properties under various atmospheres
- We have been able to show that CO_2 to some extent is consumed by our system but have not yet been able to confirm all the products
- The project has yielded results so interesting that it will continue also after the funding period of this project is over.

1. State-of-the-art photocatalytic CO_2 reduction systems

Carbon dioxide (CO_2) is an important cause of emission of greenhouse gases that are directly involved in the global warming and sea level rise observed in the last decades. Capturing and chemically converting CO_2 to more value-added products is beneficial not only environmentally but also economically, moving towards a net-zero CO_2 emission goal. Sun light is often chosen as a ubiquitous and free energy source to drive the CO_2 reduction reaction. To this end, many researchers have investigated metallic nanoparticulate systems based on noble metals such as Au, Pt, Ag that can function as both light absorber and catalyst to convert CO_2 to mainly CO.[1] Unfortunately, their high cost, low efficiency and low product selectivity prohibit large-scale production and applications. Metallic binary systems consisting of a semiconductor as light absorber and a noble metal as catalyst have recently received a lot of attention due to their increased lifetime of photo-induced charge separated state, which is one of the critical factors for improving the efficiency and selectivity.[1,2] Remarkably, recent reports have shown that oxides of non-noble metals like Cu and Fe, coupled with TiO_2 as light absorber, can replace their noble counterparts to produce more valuable products such as methanol, methane and even ethane, but only as by-products.[1] These heterogeneous photocatalysts are known to be stable and easy to produce in large scale, but improving both efficiency and selectivity remains an important challenge due to the intrinsic and non-tunable nature of the chemical bonding between the metal oxide and CO_2 molecules.

On the other hand, homogeneous catalysts based on non-noble metal complexes have been extensively investigated in recent years owing to their tunable electronic and chemical properties. Consequently, they can exhibit very high efficiency and product selectivity even in aqueous solutions at room temperature conditions.[3] Bio-inspired Fe and Cu porphyrin complexes are currently the most promising for future applications due to their low cost, high performance, high stability and environmental friendliness.[4] They can also be coupled with a molecular visible light absorber to improve their overall performance due to formation of a long-lived charge separated state under sun light.[3] Moreover, the ability to precisely control the composition at atomic level allows researchers to establish structure – property – performance relationships, which then can be used to guide future development. In this regard, the homogeneous catalysts easily outperform the heterogeneous ones; however, low photostability and difficulty in catalyst recycling are among their major challenges.

More recently, hybrid photocatalytic systems where a homogeneous catalyst is immobilized on a heterogeneous substrate have been emerging as promising materials for industrial applications. They combine the photostability and recyclability of heterogeneous systems with versatility and efficiency of homogeneous ones. Various substrates (semiconducting particles, metal organic frameworks, carbon nanostructures to mention a few) and molecular complex catalysts have been reported.[3] However, they are mainly based on TiO_2 semiconductor and noble metal complexes, which can only harvest a small part of the sun light in the UV region. More importantly, prolonged exposure to UV light is known to degrade molecular complexes. Insights into kinetics of photo-induced charge transfer processes and photocatalytic mechanism are still lacking and demanding further research for material developments. Thus, this is the starting point for our project.

2. Our project: Hybrid photocatalytic systems consisting of only earth-abundant elements for CO_2 reduction

We are developing new hybrid photocatalytic systems that (i) are able to harvest the visible light, (ii) do not contain noble or toxic metals and (iii) have promising performance in terms of efficiency, selectivity and stability, even in aqueous solution. We believe this is the next step towards more sustainable photocatalysts that could find applications in near future. To achieve this, we chose metal-free polymeric carbon nitride quantum dots (PCN QDs) as visible light absorbers and third-row transition metal porphyrin complexes as catalysts (**Figure 1**).

PCN nanomaterials have just recently emerged as a low-cost, tunable visible light absorbers to replace conventional but expensive Ru or Ir complexes for multi-electron photocatalytic reactions, such as water or CO_2 reduction.[3] Meanwhile, the third-row transition metal complexes represent a class of earth-abundant, sustainable catalysts that still remain underexplored in comparison with noble-metal catalysts. There are currently just a few sporadic reports on such hybrid materials, in which the kinetics of electron transfer reactions, the pathway to accumulate electrons on the catalytic sites and formation of catalytically active intermediates remain under active investigation.[5]

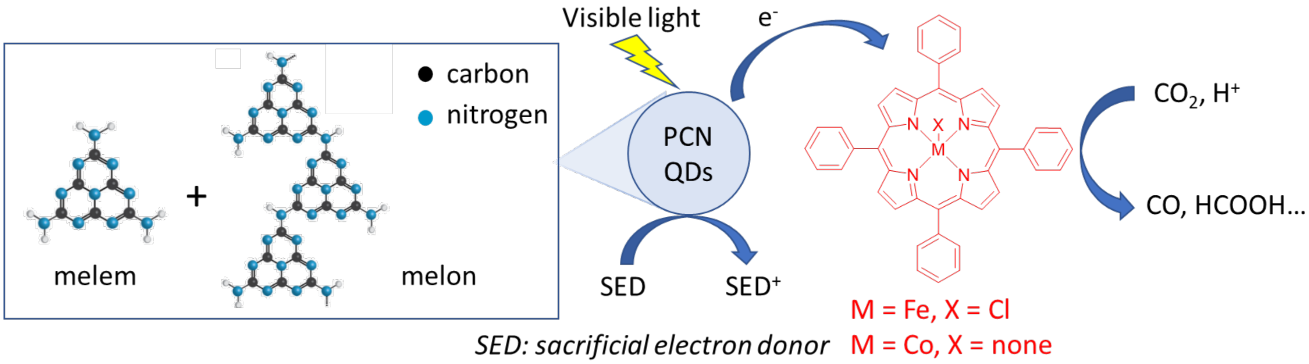

Figure 1. Hybrid photocatalytic systems and photocatalytic CO_2 reduction processes under investigation in this project.

2.1. Synthesis and characterization

QDs ($d < 10$ nm) are first synthesized from cost-effective, water-soluble precursors (guanidine hydrochloride and ethylenediaminetetraacetic acid) following a microwave assisted procedure[6] with minor modifications. In contrast to commercial PCN products, our PCN QDs are entirely soluble in water, which is of great interest for the ability to perform photocatalysis in fully aqueous media. The QDs were then characterized by means of X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) to understand their composition. XPS data show that the QDs contain mainly C, H and O where the ratio of C/N is about 4/6. This is in accordance with a commercially available PCN powder. Detailed analysis of the C and N peaks by a deconvolution method, together with the FTIR analysis, allow us to conclude that the PCN QDs consist mainly of melem and melon units (**Figure 1**). This finding shows that our QDs are synthesized with a low degree of polymerization, which generates high concentrations of polar surface groups (likely -OH and -COOH). The combination of the QDs small size, the polar surface groups and electrostatic repulsion is the key to achieve complete solubility in water, which is not the case for commercial PCN bulk powders.

Photophysical properties of the PCN QDs are then investigated in detail using a wide range of steady state and time-resolved spectroscopies. UV-visible absorption shows that the QDs suspension in water can absorb light up to 600 nm (**Figure 2a**). Tauc plot analysis shows the optical bandgap of ~ 2.5 eV, which is 0.2-0.4 eV lower than bulk PCN powders[7]. It indicates that the QDs have a more extended absorption spectrum than the bulk PCN. Under continuous light irradiation, they emit over a broad wavelength range and with a shape which is dependent on the excitation wavelength (**Figure 2b**). This behavior is characteristic of carbon-related QDs and have attributed to different emissive states with different degree of allowability in agreement with literature reports.[6,8] After excitation by 405 nm-light by a pulsed laser, time-resolved emission decay of PCN QDs in water is recorded and fitted to a multiexponential model to yield three lifetimes (**Figure 2c**). The two short lifetimes (1.27 and 4.52 ns) are attributed to the recombination of free charges while the longest lifetime (12.88 ns) is due to defect sites. The fact that the majority of photogenerated electrons (~ 80 – 90%) are found as free charges in the conduction band implies the high potential to use the QDs in photocatalysis.

In the presence of a metal porphyrin complex (MTPP, M = Fe(III) or Co(II), **Figure 1**) as an electron acceptor, the luminescence of PCN is quenched by an electron transfer reaction to MTPP. Analysis of the Stern-Volmer plot reveals the quenching rate of $3\text{-}4\times10^{13}$ M^{-1} s^{-1}, which is four orders of magnitude higher than the diffusion rate. The results clearly indicate a static quenching mechanism by

MTPP probably due to π-π interaction between the heptazine units of PCN and the porphyrin ligands of the complexes. The ability to facilitate this ultrafast photo-induced electron transfer is one of the prerequisites for a useful photocatalytic system.

2.2 Photocatalytic CO_2 reduction

We have set up the photocatalytic experiments using a continuous flow rate photoreactor coupled with a mass spectrometer (**Figure 3**) so that the gas products can be analyzed in real time. Products in the liquid phase are analyzed at the end of each experiment using nuclear magnetic resonance (NMR) spectroscopy. First, optimization of the setup components (connectors, flowrate, photoreactor size, tubing etc) and calibration of the instruments are conducted. We then irradiate the PCN QDs in aqueous solution under visible light in the presence of sodium ascorbate (NaAsc, 0.1 M) as sacrificial electron donor. No reaction occurs under Ar atmosphere, but H_2 is produced as the only gas product under CO_2 atmosphere. This is explained by the increase of solution acidity under CO_2 favoring proton reduction reaction by the photogenerated electrons on the conduction band of PCN (~ -1.3 V *vs* NHE).[9] Products in liquid phase are still under investigation.

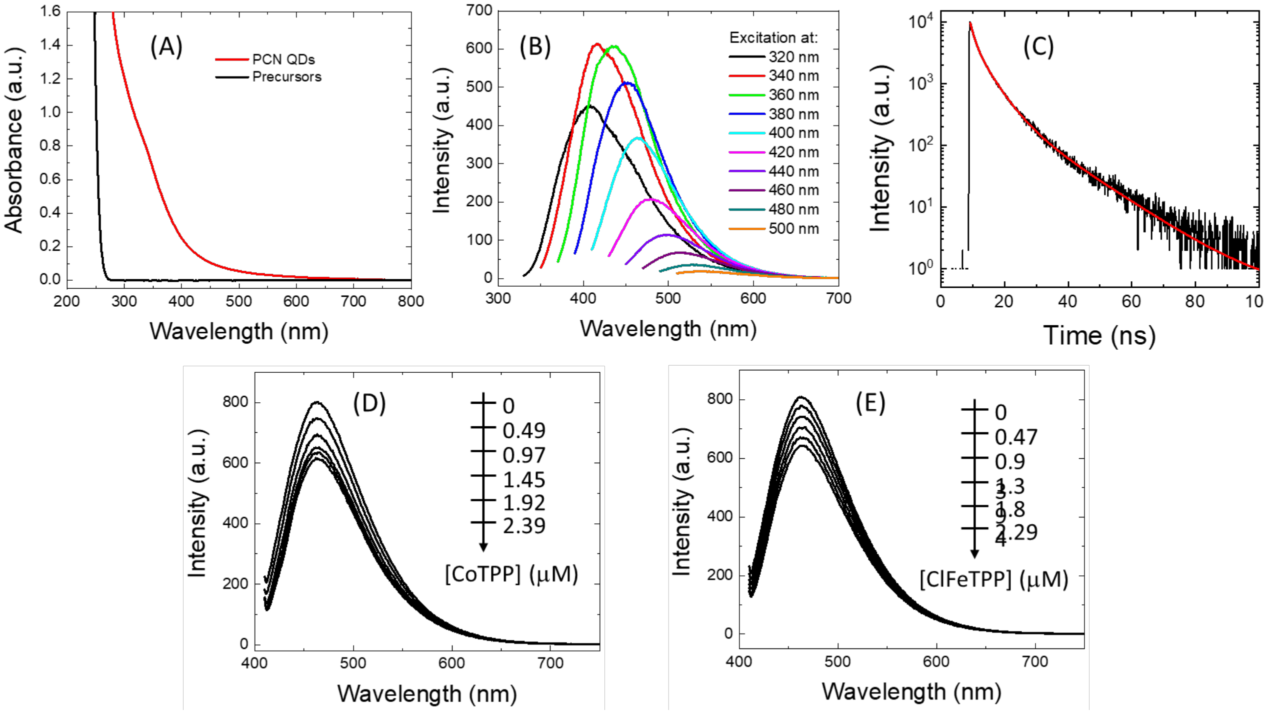

Figure 2. (A) UV-vis absorption, (B) emission and (C) time-resolved emission spectra of PCN QDs in aqueous solution. Quenching of PCN QDs luminescence by (D) CoTPP and (E) ClFeTPP

Subsequently, we moved to PCN and MTPP photocatalytic systems. As MTPP is not soluble in water, we use a mixed solvent of methanol/water (9/1, %v) and obtain a stable suspension. It is noted that the complexes significantly degrade and precipitate if the water content exceeds 15-20%. However, irradiating this solution does not produce any gaseous products. Post-mortem analysis by UV-vis absorption spectroscopy shows that the metal complexes are completely degraded. Attempts to work with a more conventional solution of acetonitrile or dimethylformamide, with or without water, are also not successful due to solubility problem of PCN QDs or precipitation of MTPP.

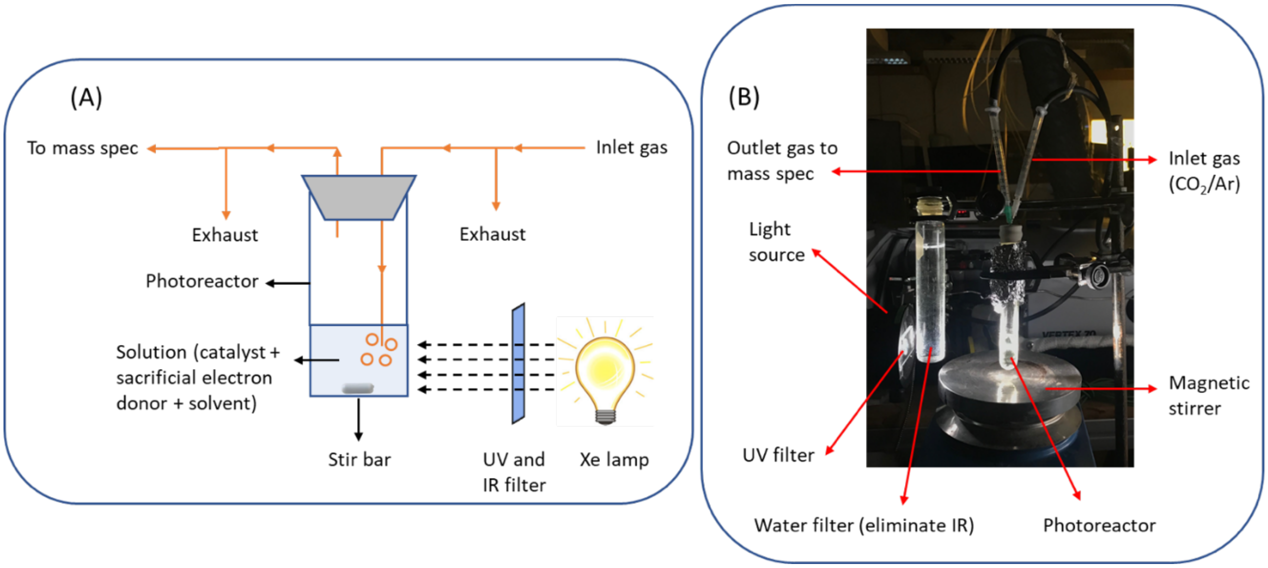

Figure 3. Photocatalytic CO_2 reduction setup: (A) illustration and (B) experiment in progress

3. Work in progress and future outlook

We are trying to modify the ligand of MTPP complexes to make them soluble in water. Photocatalytic CO_2 reduction in water is of broad interest, not only in academia but also in industry, as it represents a leap towards practical applications. Water is not only "greener" than organic solvents that have been largely employed in photocatalysis, it can also act as a sacrificial electron donor and a proton source for the CO_2 reduction process. The main problems of using water as solvent are, (i) CO_2 solubility in water is much lower than in some organic solvents, and (ii) proton reduction is much more thermodynamically favorable than CO_2 reduction. However, recent progresses in photocatalytic systems that can operate in water are encouraging, although some of them still rely on noble metals.[10]

In addition, electrochemical characterization of the photocatalytic systems is also under investigation. This method is expected to give more information on the CO_2 reduction process. Identification of catalytically active species will also be examined using electrochemistry and femtosecond transient absorption spectroscopy.

References

(1) Chem. Rev., **2014**, *114*, 9987; Chem. Rev., **2015**, *115*, 12888; J. Mater. Chem. A, **2017**, *5*, 21625
(2) Chem. Commun., **2018**, *54*, 5289
(3) Chem. Rev., **2019**, *119*, 2752
(4) J. Am. Chem. Soc., **2016**, *138*, 16639; J. Am. Chem. Soc., **2016**, *138*, 8076; Nature, **2017**, *548*, 74; Nat. Commun., **2018**, *9*:415
(5) Appl. Catal. B, **2017**, *200*, 141; Appl. Catal. B, **2018**, *221*, 312; J. Colloid Interface Sci., **2019**, *543*, 201; Green Chem., **2017**, *19*, 5900
(6) Anal. Chem., **2014**, *86*, 4528

(7) Nat. Mater., **2009**, *8*, 76; J. Am. Chem. Soc., **2017**, *139*, 5216; ACS Sustainable Chem. Eng. **2017**, *5*, 7260
(8) J. Am. Chem. Soc., **2006**, *128,* 7756; J. Phys. Chem. C, **2017**, *121,* 28180
(9) Appl. Surf. Sci., **2017**, *391*, 72
(10) J. Am. Chem. Soc., **2016**, *138*, 5159; Angew. Chem., Int. Ed., **2017**, *56*, 4867; ACS Catal., **2018**, *8*, 11815; ACS Catal., **2019**, *9*, 4867

Financial report for the project

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Redovisningsperiod	20180701-20190930
Total anslag	1 308 000 kr

Period	Totalt
Sista datum i aktuell period	20190930
Lönekostnader	748 815
Köpta tjänster	-
Utrustning	-
Material	98 662
Laboratoriekostnad	-
Resor	3 505
Övriga kostnader	68 454
Lokaler	82 823
Indirekta kostnader	325 375
Summa	1 327 634