

Faraday Discussions

Accepted Manuscript



This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

Register now to attend! Full details of all upcoming meetings: <http://rsc.li/fd-upcoming-meetings>



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Novel windows for “solar commodities”: A device for CO₂ reduction using plasmonic catalyst activation

Alexander Navarrete^a, Sergio Muñoz^a, Luis M. Sanz-Moral^a, Juergen J. Brandner^b, Peter Pfeifer^b, Ángel Martín^a, Roland Dittmeyer^b and María J. Cocero^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A novel plasmonic reactor concept is proposed and tested that works as a visible energy harvesting device while allowing to carry out reactions to transform CO₂. Particularly the Reverse Water Gas Shift (RWGS) reaction has been tested as a means to introduce renewable energy into the economy. The development of the new reactor concept involved the synthesis of the new composite capable of plasmonic activation with light; the development of an impregnation method to create a single catalyst-reactor entity; finally, the assembly of a reaction system to test the reaction. The composite developed was based on a Cu/ZnO catalyst dispersed into transparent aerogels. This allows efficient light transmission and a high surface area for the catalyst. An effective yet simple impregnation method was developed that allowed to introduce the composites into glass microchannels. The activation of the reaction was made using LEDs that cover all the sides of the reactor allowing high power delivery. The results of the reaction show a stable process capable of low temperature transformations.

A Headings are the primary heading type e.g. Introduction, Results and discussion, Experimental

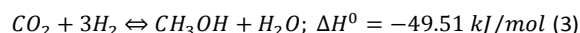
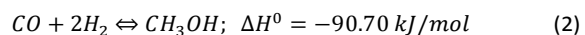
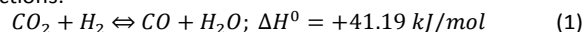
Introduction

CO₂ as a renewable energy vector

One of the most industrially promising heterogeneous catalytic processes is carbon dioxide hydrogenation. In the process of catalytic hydrogenation, hydrogen obtained from carbon neutral energy sources (e.g. wind or solar) is reacted with CO₂ to obtain products such as fuels¹. Thus, this process will then serve a double purpose: first, as a chemical storage of the surplus energy generated by the fluctuating renewable energies; and second, to reduce the emissions of CO₂.

Successful introduction of the CO₂-use technologies require of plausible and profitable processes that use efficiently renewable energy. The most abundant and evenly distributed

of such energies is the one provided by sun. If stored in the form of “solar commodities” such as methanol or olefins new opportunities for use of CO₂ could be opened². The production of methanol from CO₂ and hydrogen involves the following reactions:



In order to capture that energy in chemical bonds there are several useful methods for reactions. From the chemical point of view, they can be grouped into photocatalytic, thermal and electrical routes. In electrical routes, the solar energy is first converted into electricity and then, the resultant electrical energy is used in the chemical transformations of CO₂³⁻⁷; the thermal routes concentrate the solar radiation and convey that energy directly into the reactor⁸⁻¹⁰. Photocatalytic CO₂ conversion involves either the water splitting connected to a CO₂ reduction reaction, or a process combining both in one “single pot”¹¹⁻¹³.

Selective use of visual light with plasmon catalysts

Surface Plasmon Resonance (SPR) phenomenon is commonly found in metallic (or carbon) nanostructures and allows to increase the range of the solar spectrum used on a given photoinduced process¹⁴. This effect is the result of the response of the conduction electrons to the oscillations of the electric field of the light radiation. An increased energy absorption by the electrons is possible at selected wavelengths under the proper particle size and shape of the nanoparticles

^a University of Valladolid, Department of Chemical Engineering and Environmental Technology, High Pressure Processes Group, Paseo Prado de la Magdalena s/n, 47005 Valladolid, Spain

^b Institute for Micro Process Engineering, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany.

^c Address here.

^d Address here.

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

for a given surrounding media (fluid or catalyst). This phenomenon produces high light concentration up to the point that a reduction in the amount of semiconductor of three orders of magnitude for the same amount of light has been possible¹⁵. On the other hand, increased light capture with SPR for photothermal conversions are leading to breakthroughs in energy systems such solar collectors¹⁶.

This work explores the reduction of CO₂ to CO as a first step in a solar-based process to produce methanol. Thus, it is based on the Reverse Water Gas Shift (RWGS) reaction as described by the equation (1). Recent approaches have used gold and semiconductor composites for plasmonic enhancement of the reduction^{17, 18}.

Yet, this process is commonly activated in industry using Cu/ZnO based catalysts¹⁹. Here, we have developed plasmonic catalytic composites in mesoporous silica structures (Aerogels). For this, we have used the plasmon-tuneable Cu/ZnO catalyst reported by Tan et al (2013)²⁰.

A plasmonic microreactor as a light harvesting device

The efficiency of the chemical reactions is not ruled only by the catalytic material but also for the reactor configuration and their mass and energy transport characteristics. Many times promising catalytic materials fail to reach industrial success owing to the disconnection between the catalytic structure and the reactor-level phenomena^{21, 22}.

Here we propose a novel concept for visual energy harvesting: a plasmonic microreactor device. It integrates plasmon catalyst, and reactor as one entity with a sole response to light (Figure 1).

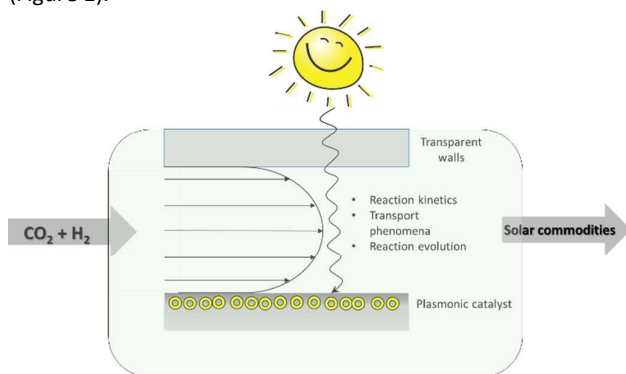


Figure 1. Concept of the plasmonic microreactor device

Microreactors allow efficient energy and mass transport while are easily scalable (numbering up). Thus, the combination of efficient microstructured devices and direct plasmonic absorption of solar energy by the catalyst would represent a major breakthrough in the CO₂-use field.

During this work, a plasmon-tuneable composite is integrated with a microchannel based reaction system under visual LED illumination for the RWGS reaction. This has involved the synthesis of the new composite; the development of an impregnation method to create a catalyst-reactor entity; finally, the assembly of a reaction system to test the reaction.

Methods

Plasmo-catalytic composites synthesis

The chemicals used during this stage are detailed: Zinc acetate dihydrate (>98%), oleylamine (70%), tetramethyl orthosilicate (98%), ammonia (28-30%), triethylenglicol (99%) were purchased from Sigma-Aldrich. Ethylenglicol (99.5%) (Merck). Copper acetate monohydrate (99.9%) was purchased from Alfa Aesar. Methanol (99.8%) (Panreac). All chemicals were used without further purification.

Synthesis of Cu/ZnO bimetallic catalyst

This bimetallic (Cu:ZnO, 1:2) catalyst was synthesised following the procedure proposed by Tan et al (2013)²⁰.

Briefly, first ZnO nanorods were prepared. Zinc acetate (3 mmol) was added to 1.3 mmol of oleylamine in a two necked flask. The oleylamine has not a high purity (70%), requiring a step where the reactants were degassed at 80 °C for 45 min in vacuum atmosphere. Then, the temperature was increased to 220 °C under nitrogen purging. During the heating process, the solution turns white upon reaching 180°C. After 15 min of heating, the mixture was cooled to atmospheric temperature, washed with ethanol and centrifuged in order to isolate the precipitate. It was washed with 6 ml of ethanol three times to ensure complete removal of the reactants or byproducts.

ZnO nanorods prepared above were then redispersed in 20 ml of triethylenglicol by sonication for two hours, followed by stirring under room conditions overnight. Ethylenglicol (2ml) was added to the ZnO dispersion, and the mixture was degassed at room temperature for 5 min before heating to 190°C. Simultaneously, a second solution of copper acetate monohydrate was prepared dissolving in ethylenglicol. This mixture required sonication in order to dissolve well the copper acetate in the liquid. This mixture was added to the ZnO mixture in a dropwise manner during 10 min. After this, 5 min more at 190°C were allowed before the composite was washed with isopropanol, centrifuged during 15 minutes at 4500rpm (centrifuge Kubota 5100, Japan) and isolated from the mixture.

Synthesis of mesoporous silica composites

Light transmission to the catalytic structures is essential while enough surface area has to be provided in order to have enough metal loads to capture light. Transparent aerogels are mesoporous materials combining high surface areas and good light transmission²³.

Aerogels were synthesised following the sol-gel route. The precursor for the silica hydrogel selected was the tetramethyl orthosilicate (TMOS). The molar ratio TMOS: CH₃OH: H₂O: NH₄, was 1 : 2.3 : 3.84 : 0.012 .

First, methanol was used to disperse the nanoparticles formed in the catalyst synthesis. Sonication (15 min) was applied to ensure a good dispersion of the nanoparticles in the liquid phase. Methanol with the particles and TMOS were mixed together. While this solution was stirred, a second solution of ammonium hydroxide and water was prepared and stirred. After a few minutes of stirring, both solutions were mixed, and the gelation process began.

In this moment, the gelation process of the silica hydrogel has started, but it is still liquid for a few minutes. This time lapse, before gelation, must be used to impregnate the solution inside the microchannels of the microreactors.

Integration of composites and microreactor

In order to have a single integrated device it is necessary to integrate light transmission and composite activation in the same structure. Here, we have developed a method to integrate transparent aerogels in glass microchannels. The method used to make the impregnation of the sol-gel that showed best results was the suction of the liquid with a syringe, which was previously adapted to the microreactor on its top (Figure 2). With this method, placing the microreactor in vertical position, it was very easy to fill the microchannel placing the tip in the liquid. After a short time, the gelation process finished and the hydrogel formed had a good adherence inside the microchannels.

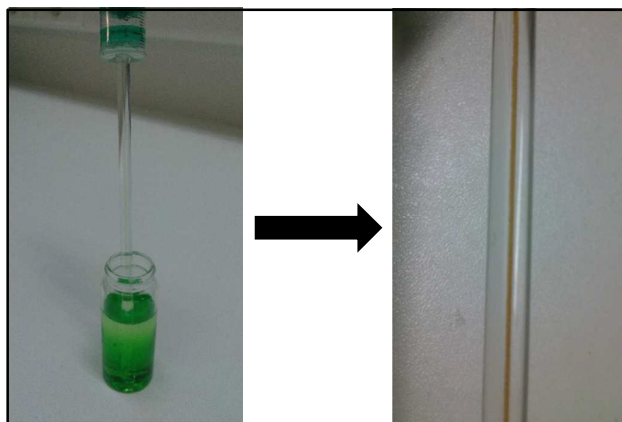


Figure 2. Syringe filling microchannels

It is worth to mention that one of the most important parameters during this step is the amount of ammonia, as it acts as the catalyst for the gelation process. It is necessary to use an amount of ammonia low enough that allows to have

enough time to impregnate the hydrogel inside the microreactor, because it must be still a fluid. On the other hand, the amount of ammonia cannot be very low, because if the gelation process is too slow, the nanoparticles start to precipitate and they will not be inside the silica net. Finding an equilibrium between this two factors is the key to achieve a good impregnation of the nanoparticles supported in the silica gels inside the microreactors.

In order to ensure a good adherence of the aerogel to the walls of the microchannels, it is necessary to perform a pretreatment to the glass microreactors (15.0 cm) to clean the walls of the microchannels. For this cleaning process, the most common option is to use a piranha solution, which reacts violently with most organic materials. The solution used was a mixture of sulfuric acid and hydrogen peroxide that can be prepared in different proportions, the most usual 4:1 in concentrated sulfuric acid. From 15 to 30 minutes the material is submerged in the solution, then removed, washed with plenty Milli-Q water and dried carefully.

The empty glass microreactors were put inside a glass pot, and the sulfuric acid was first added. Then, the hydrogen peroxide was also added with extreme care because the reaction is very exothermic, the temperature is suddenly increased and some vapors can be formed. After 20 minutes, the slides were removed from the piranha solution, washed with Milli-Q water and dried carefully.

After introduction of the nanoparticles in the sol-gel and its introduction into the microreactors, these were put in a vessel with methanol for aging. This vessel was carefully closed to avoid methanol evaporation, and it was heated to 50°C in an oven. With this procedure the water contained in the silica net was replaced with methanol, resulting into alcogels.

After 24 hours of heating, the alcogels were dried using supercritical carbon dioxide. The microreactors were put in a high pressure vessel, and this vessel was filled completely with methanol. Carbon dioxide was introduced slowly in the vessel to allow a good diffusion into the methanol. The pressure was raised to 100 bar and the temperature to 40 °C, above the critical point of carbon dioxide. Three cycles of 45 minutes were performed, renewing the carbon dioxide between each cycle to complete the drying process²⁴. After this, silica aerogels were correctly obtained, keeping the adherence to the walls of the microchannels.

Proof-of-concept setup

Once Cu/ZnO based plasmonic composites are integrated into the glass microchannels, a test of these devices is made. In order to test the reactor concept, a reaction system has been built that included visual LED illumination and control of temperature the reaction while a precise control of flow and pressure is provided. A scheme of the experimental plant is presented in Figure 3.

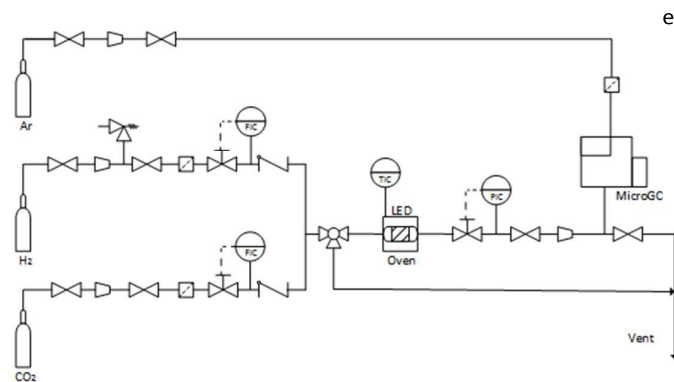


Figure 3. Schematic flow diagram of the plant.

Hydrogen and carbon dioxide are introduced in the system, and their flows are controlled with two different flow mass meter/controllers (EL-Flow F-200, Bronkhorst) with ranges from 0,02 to 1 ml/min.

Before the reaction was initiated, hydrogen and carbon dioxide are mixed in a 3:1 proportion, and sent to the vent while both flows are stabilized.

When the flows are correctly controlled, the mixture of the gases goes to the second part of the setup. In this part the gases are heated, together with the glass microreactor, in a gas chromatography oven (Agilent 7890). The microreactor consists on a 0.5 mm ID glass capillary with an external diameter of 5 mm (Schott Duran, USA).

A second vent is used to take out the gases while the pressure is increasing to 20 bar. Pressure is controlled by a pressure meter/controller (EL-Press series, Bronkhorst). When pressure is and flows are stable at 20 bar, the valve for extraction is closed, and the oven and LEDs are turned on.

Visual light stimulation was provided by 36 LEDs (Superbright, inspired LED) surrounding the microreactor as, shown in Figure 4. In total, they provided the equivalent to a nominal power of 9780 W/m² of white light.



Figure 4. LED light configuration. Left, detail of the inner LED distribution. Right, microreactor in the oven surrounded by the LEDs.

The reaction begins and the products of the reaction are measured in a Micro Gas Chromatograph (CP-4900, Varian)

equipped with two columns: a poraplot 10m and a 5A olsieve. Before the micro GC, the pressure of the gas stream reduced to less than 5 bar.

Composites characterization

Analyses of the bimetallic catalysts to check absorbance of visual light were carried out in a UV-Vis spectrometer (UV 2550, Shimadzu). XRD analysis were carried out in a Bruker Discover D3 diffractometer. The porosity measurements were carried out in a Surface Area and Porosity Analyzer (ASAP 2020, Micromeritics)

Results and discussion

Composites Characterization

After the synthesis UV-Vis scans were made in order to check the absorption of visual light from both the ZnO nanorods and the bimetallic Cu/ZnO catalyst (Figure 5)

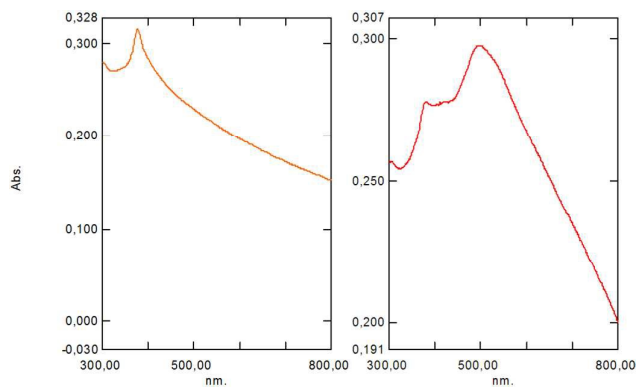


Figure 5. Absorption spectra of ZnO (left) and Cu/ZnO (right)

It can be seen that the bimetallic catalyst have a peak at 498 nm. This correspond to the absorption of the range close to the green colour²⁵. The transparent aerogels change and acquire colour once the composite is formed (Figure 6). It can be seen that the bimetallic catalyst have a peak at 498 nm. This correspond to the absorption of the range close to the green colour²⁵. The transparent aerogels change and acquire colour once the composite is formed (Figure 6).

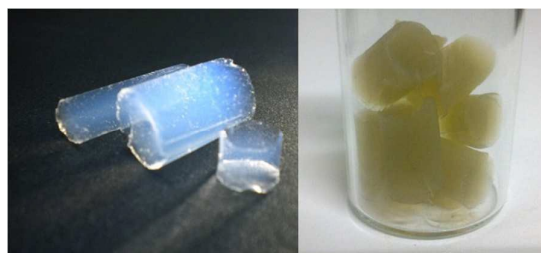


Figure 6. Silica aerogel before (left) and after (right) catalyst impregnation

The XRD shows the presence of the ZnO and metallic copper in the silica amorphous structure. The ZnO planes 100

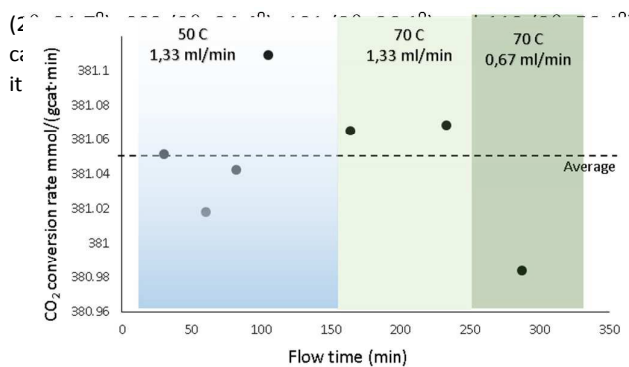


Figure 7. XRD pattern of the plasmonic composite

BET surface area and pore volume of the samples were calculated from N_2 isotherm. The adsorption-desorption curve show a type IV isotherm curve typical for mesoporous silica aerogels²⁶ (Figure 7). The BET surface area is $945.8 \text{ m}^2/\text{g}$ which indicates that the inclusion of the bimetallic catalyst does not have a significant influence on the textural properties of the aerogel. The BJH pore volume is equal to $2.29 \text{ cm}^3/\text{g}$ reinforcing that the structure is not affected.

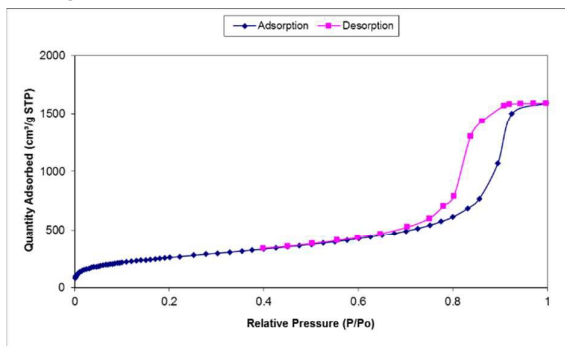
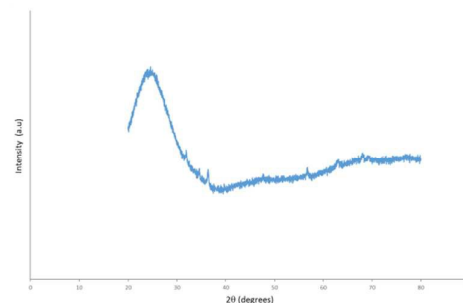


Figure 7. Adsorption-desorption isotherms of the composites

Reaction test of the concept

The full power of the LED was applied and the evolution of the compounds were followed. In order to test the influence of the main variables of the process, changes in flow and temperature were made during the reaction (Figure 8).

It could be observed that the reaction was stable at 50C at during more than 100 minutes. Then the temperature was increased at 70C and tested during the same time span. Finally, the flow was reduced to half of the initial condition. No significant changes were observed during almost 300 minutes. Which indicates the suitability of this system to test several catalyst loads and thermodynamic conditions.



It is important to note that the average conversion rate is similar to the one obtained in other works at temperatures around 200 C^{17} . Thus, the integrated plasmonic reactor concept proposed here opens new avenues to couple low temperature solar collectors and chemistry as a mean to introduce renewable energy in the economy. Particularly, for the conversion of CO_2 .

Conclusions

A novel plasmonic composite was developed that can absorb light from the visible spectrum. Its characterization evidenced a high surface area and a proper integration with the metallic components of the catalyst.

It was then possible to introduce this composite into glass microchannels in order to obtain a single entity that acts as both a light-harvesting device and as a reactor. This is possible owing to the development of a simple yet effective impregnation method that allows the synthesis of the aerogels "in situ".

The microreactor obtained was tested for RWGS in a system that allowed not only to control the reaction variables such pressure, temperature and flow. But also, delivers visual light in an elegant way.

The CO_2 conversion rates were in accordance to other works testing plasmonic catalysts at higher temperatures. This can be owed to the increased light energy delivery, the high surface area of the material and to the integrated and efficient way to deliver the radiant energy possible in this reactor. This is then a novel opportunity to gain understanding on the field of CO_2 use applying solar energy.

Acknowledgements

The authors acknowledge the kind support of the FP7 Shyman European project (Project reference: 280983)

References

- G. Centi, E. A. Quadrelli and S. Perathoner, *Energy & Environmental Science*, 2013, **6**, 1711-1731.
- G. Centi and S. Perathoner, in *Green Carbon Dioxide: Advances in CO₂ Utilization*, eds. G. Centi and S. Perathoner, 2014, vol. John Wiley & Sons
- K. Ogura, H. Yano and T. Tanaka, *Catalysis Today*, 2004, **98**, 515-521.
- R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313-315.
- H. Li, P. H. Opgenorth, D. G. Wernick, S. Rogers, T.-Y. Wu, W. Higashide, P. Malati, Y.-X. Huo, K. M. Cho and J. C. Liao, *Science*, 2012, **335**, 1596.
- B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis and R. I. Masel, *Science*, 2011, **334**, 643-644.
- E. E. Barton, D. M. Rampulla and A. B. Bocarsly, *Journal of the American Chemical Society*, 2008, **130**, 6342-6344.
- G. P. Smestad and A. Steinfeld, *Industrial & Engineering Chemistry Research*, 2012, **51**, 11828-11840.
- I. Ermanoski, J. E. Miller and M. D. Allendorf, *Physical Chemistry Chemical Physics*, 2014, **16**, 8418-8427.
- M. Forster, *Journal of CO₂ Utilization*, 2014, **7**, 11-18.
- A. Dhakshinamoorthy, S. Navalon, A. Corma and H. Garcia, *Energy & Environmental Science*, 2012, **5**, 9217-9233.
- P. D. Tran, L. H. Wong, J. Barber and J. S. C. Loo, *Energy & Environmental Science*, 2012, **5**, 5902-5918.
- Ş. Neaţu, J. Maciá-Agulló and H. Garcia, *International Journal of Molecular Sciences*, 2014, **15**, 5246.
- S. Linic, P. Christopher and D. B. Ingram, *Nat Mater*, 2011, **10**, 911-921.
- C. Hägglund, S. P. Apell and B. Kasemo, *Nano Letters*, 2010, **10**, 3135-3141.
- M. A. Garcia, *Journal of Physics D: Applied Physics*, 2011, **44**, 283001.
- A. A. Upadhye, I. Ro, X. Zeng, H. J. Kim, I. Tejedor, M. A. Anderson, J. A. Dumesic and G. W. Huber, *Catalysis Science & Technology*, 2015, **5**, 2590-2601.
- C. Wang, O. Ranasingha, S. Natesakhawat, P. R. Ohodnicki, M. Andio, J. P. Lewis and C. Matranga, *Nanoscale*, 2013, **5**, 6968-6974.
- M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlögl, *Science*, 2012, **336**, 893-897.
- Z. Y. Tan, D. W. Y. Yong, Z. Zhang, H. Y. Low, L. Chen and W. S. Chin, *The Journal of Physical Chemistry C*, 2013, **117**, 10780-10787.
- J. Gascon, J. R. van Ommen, J. A. Moulijn and F. Kapteijn, *Catalysis Science & Technology*, 2015, **5**, 807-817.
- B. Louis, G. Laugel, P. Pale and M. M. Pereira, *ChemCatChem*, 2011, **3**, 1263-1272.
- G. M. Pajonk, *Journal of Non-Crystalline Solids*, 1998, **225**, 307-314.
- L. M. Sanz-Moral, M. Rueda, R. Mato and Á. Martín, *The Journal of Supercritical Fluids*, 2014, **92**, 24-30.
- NASA, What Wavelength Goes With a Color?, http://science-edu.larc.nasa.gov/EDDOCS/Wavelengths_for_Colors.html.
- R. Al-Oweini and H. El-Rassy, *Applied Surface Science*, 2010, **257**, 276-281.

Context, what are the characters we are studying? What information is necessary to understand the work, why is important and will contribute? What is the challenge? Objectives, hypothesis, etc.