

PAPER

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

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A novel plasmonic reactor concept is proposed and tested to work as a visible energy harvesting device while allowing reactions to transform CO₂ to be carried out. 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 a new composite capable of plasmonic activation with light, the development of an impregnation method to create a single catalyst reactor entity, and 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 introduction of the composites into glass microchannels. The activation of the reaction was made using LEDs that covered all the sides of the reactor allowing a high power delivery. The results of the reaction show a stable process capable of low temperature transformations.

Introduction

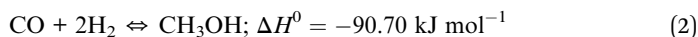
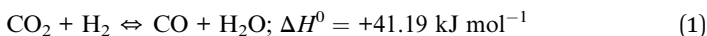
CO₂ as a renewable energy vector

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 fuels.¹ Thus, this process serves a double purpose: firstly, as chemical storage of the surplus energy generated by fluctuating renewable energies; and secondly, to reduce emissions of CO₂.

^aUniversity of Valladolid, Department of Chemical Engineering and Environmental, Technology, High Pressure Processes Group, Paseo Prado de la Magdalena s/n, 47005 Valladolid, Spain. E-mail: anm@iq.uva.es

^bInstitute for Micro Process Engineering, Karlsruhe Institute for Technology, Eggenstein-Leopoldshafen, Germany

The successful introduction of CO₂-use technologies requires plausible and profitable processes that use efficiently renewable energy. The most abundant and evenly distributed of such energies is the one provided by the Sun. If stored in the form of “solar commodities” such as methanol or olefins new opportunities for the use of CO₂ could be considered.² 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. From a 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 transformation of CO₂.^{3–7} The thermal routes concentrate solar radiation and convey that energy directly into the reactor.^{8–10} Photocatalytic CO₂ conversion involves either 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

The surface plasmon resonance (SPR) phenomenon is commonly found in metallic (or carbon) nanostructures and allows the range of the solar spectrum used on a given photoinduced process to be increased.¹⁴ This effect is the result of the response of the conduction electrons to the oscillations of the electric field of the light radiation. Increased energy absorption by the electrons is possible at selected wavelengths under the proper particle size and shape of the nanoparticles for a given surrounding media (fluid or catalyst). This phenomenon produces a 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 possible.¹⁵ On the other hand, increased light capture with SPR for photothermal conversions is leading to breakthroughs in energy systems such as solar collectors.¹⁶

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 eqn (1). Recent approaches have used gold and semiconductor composites for plasmonic enhancement of the reduction.^{17,18}

This process is commonly activated in industry using Cu/ZnO based catalysts.¹⁹ 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 by the reactor configuration and their mass and energy transport characteristics. On many occasions, promising catalytic materials have failed to reach

industrial success due 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 a plasmon catalyst and reactor as one entity with a sole response to light (Fig. 1).

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.

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

Methods

Plasmo-catalytic composite synthesis

The chemicals used during this stage are detailed: zinc acetate dihydrate (>98%), oleylamine (70%), tetramethyl orthosilicate (98%), ammonia (28–30%) and triethyleneglycol (99%) were purchased from Sigma-Aldrich. Ethyleneglycol (99.5%) (Merck) and copper acetate monohydrate (99.9%) were purchased from Alfa Aesar. Methanol (99.8%) was provided by Panreac. All chemicals were used without further purification.

Synthesis of the 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 was not of high purity (70%), requiring a step where the reactants were degassed at 80 °C for 45

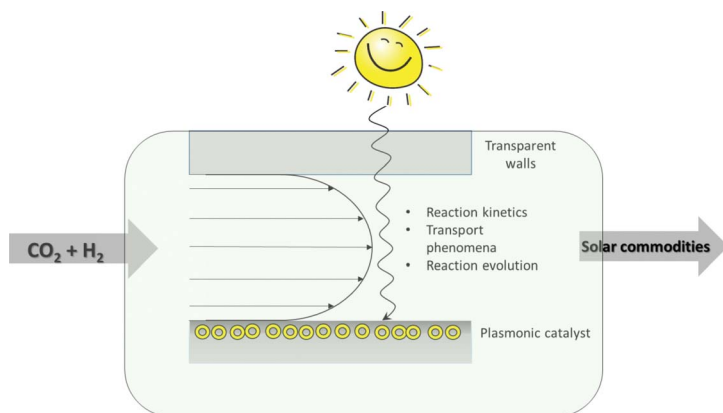


Fig. 1 Concept of the plasmonic microreactor device.

min under a vacuum atmosphere. Then, the temperature was increased to 220 °C under nitrogen purging. During the heating process, the solution turned 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.

The ZnO nanorods thus prepared were then redispersed in 20 ml of triethyleneglycol by sonication for two hours, followed by stirring under room conditions overnight. Ethyleneglycol (2 ml) 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 by dissolving in ethyleneglycol. This mixture required sonication in order to dissolve the copper acetate in the liquid. This mixture was added to the ZnO mixture in a dropwise manner over 10 min. After this, 5 more min heating at 190 °C was allowed before the composite was washed with isopropanol, centrifuged for 15 minutes at 4500 rpm (centrifuge Kubota 5100, Japan) and isolated from the mixture.

Synthesis of the 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 loading to capture light. Transparent aerogels are mesoporous materials combining high surface areas and good light transmission.²³

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

Firstly, 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 the 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 impregnate the sol–gel that showed the best results was the suction of the liquid with a syringe, which was previously adapted to the microreactor on its top (Fig. 2). With this method, placing the microreactor in a 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.

It is worth mentioning that one of the most important parameters during this step is the amount of ammonia, as it acts as a catalyst for the gelation process. It is

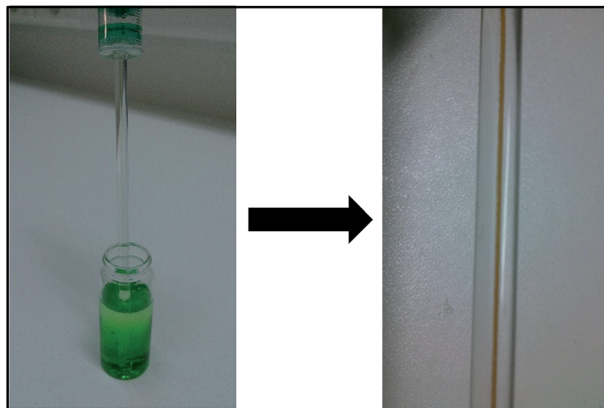


Fig. 2 Syringe filling of the microchannels.

necessary to use an amount of ammonia low enough that allows 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 remain inside the silica net. Finding an equilibrium between these two factors is the key to achieving good impregnation of the nanoparticles supported in the silica gels inside the microreactors. The microreactor consisted of a 0.5 mm ID glass capillary with an external diameter of 5 mm (Schott Duran, USA).

In order to ensure 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 being 4 : 1 in concentrated sulfuric acid. For 15 to 30 minutes the material is submerged in the solution, then removed, washed with plenty of 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 added with extreme care because the reaction is very exothermic; the temperature is suddenly increased and some vapor can be formed. After 20 minutes, the slides were removed from the piranha solution, washed with Milli-Q water and dried carefully.

After the 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 in 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 process.²⁴ After this, silica aerogels were correctly obtained, keeping the adherence to the walls of the microchannels.

Composite characterization

Scans of the bimetallic catalysts to check absorbance of visual light were carried out using a UV-vis spectrometer (UV 2550, Shimadzu). XRD analysis was carried out using a Bruker Discover D8 diffractometer. The porosity measurements were carried out using a Surface Area and Porosity Analyzer (ASAP 2020, Micromeritics).

Proof-of-concept setup

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

Hydrogen and carbon dioxide were introduced in the system, and their flows were controlled with two different flow mass meter/controllers (EL-Flow F-200, Bronkhorst) with ranges from 0.02 to 1 ml min⁻¹.

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

When the flows were correctly controlled, the mixture of the gases moved to the second part of the setup. In this part the gases were heated, together with the glass microreactor, in a gas chromatography oven (Agilent 7890).

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

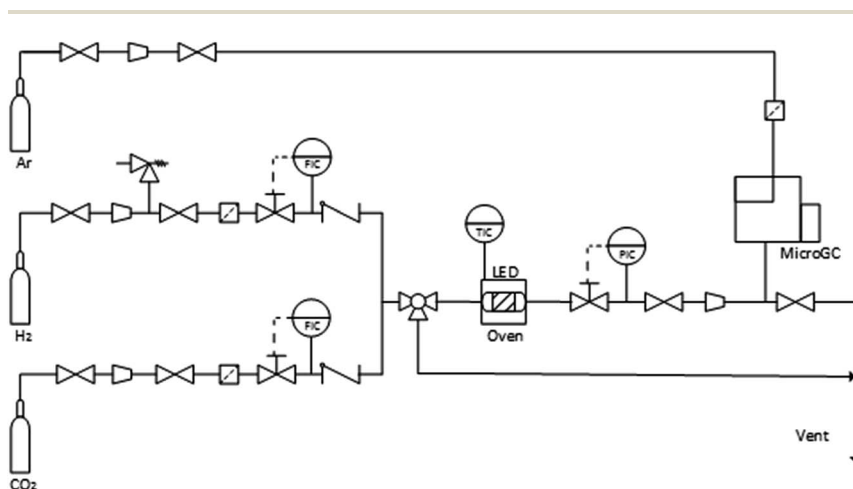


Fig. 3 Schematic flow diagram of the plant.

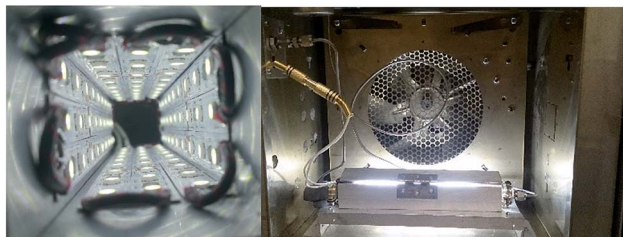


Fig. 4 LED light configuration. Left, detail of the inner LED distribution. Right, microreactor in the oven surrounded by the LEDs.

Visual light stimulation was provided by 36 LEDs (superbright, inspired LED) surrounding the microreactor as shown in Fig. 4. In total, they provided the equivalent of a nominal power of 9780 W m^{-2} of white light.

The reaction began and the products of the reaction were measured in a Micro Gas Chromatograph (CP-4900, Varian) equipped with two columns: a poraplot 10 m and a 5A molsieve. Before the micro GC, the pressure of the gas stream was reduced to less than 5 bar.

Results and discussion

Composite characterization

After the synthesis UV-vis scans were carried out in order to check the absorption of visual light from both the ZnO nanorods and the bimetallic Cu/ZnO catalyst (Fig. 5).

It can be seen that the bimetallic catalyst has an absorption peak at 498 nm. This corresponds to absorption in the range close to the green colour.²⁵ The transparent aerogels change and acquire colour once the composite is formed (Fig. 6).

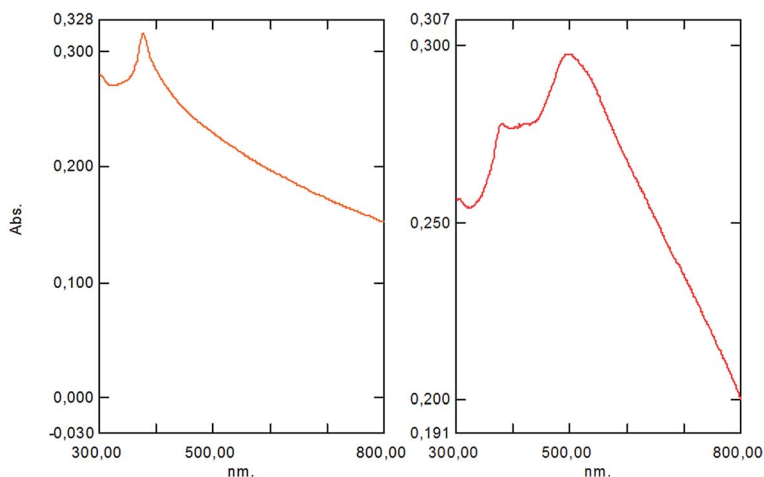


Fig. 5 Absorption spectra of ZnO (left) and Cu/ZnO (right).



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

The XRD pattern shows the presence of ZnO and metallic copper in the silica amorphous structure. The ZnO planes 100 ($2\theta = 31.7^\circ$), 002 ($2\theta = 34.4^\circ$), 101 ($2\theta = 36.1^\circ$) and 110 ($2\theta = 56.4^\circ$) can be identified in Fig. 7. Copper cannot be seen due to its lower proportion in the structure.

BET surface area and pore volume of the samples were calculated from N_2 isotherms. The adsorption–desorption curve shows a type IV isotherm curve typical for mesoporous silica aerogels²⁶ (Fig. 8). The BET surface area is $945.8 \text{ m}^2 \text{ g}^{-1}$ 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 $2.29 \text{ cm}^3 \text{ g}^{-1}$ reinforcing that the structure is not affected.

Reaction test of the concept

The full power of the LEDs 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 (Fig. 9).

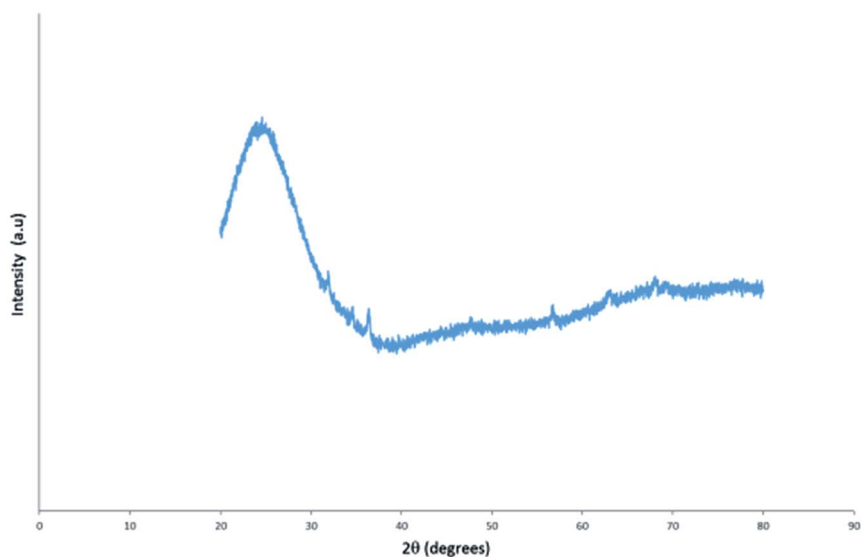


Fig. 7 XRD pattern of the plasmonic composite.

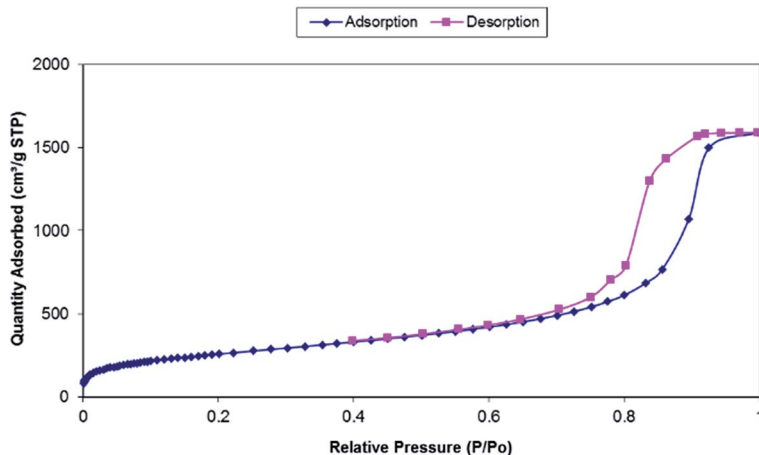


Fig. 8 Adsorption–desorption isotherms of the composites.

It could be observed that the reaction was stable at 50 °C during more than 100 minutes. Then the temperature was increased at 70 °C and tested during the same time span. Finally, the flow was reduced to half of the initial conditions. No significant changes were observed during almost 250 minutes at constant flow, which indicates the suitability of this system to test several catalyst loads under different thermodynamic and flow conditions.

It is important to note that the average conversion rate at higher flow 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 CO₂.

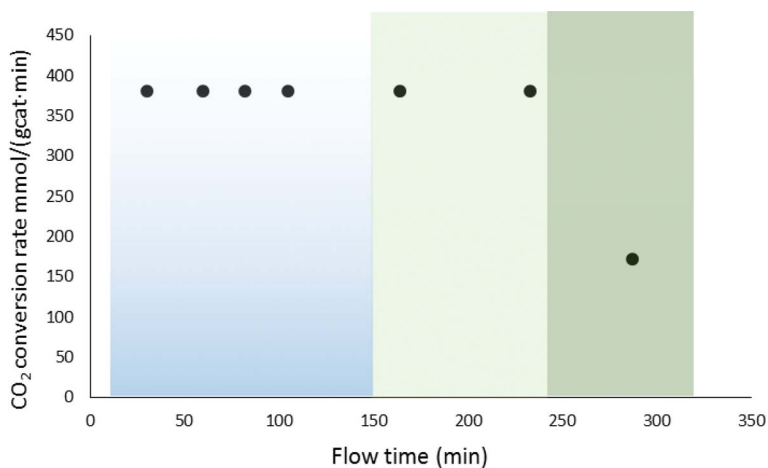


Fig. 9 Evolution of the reaction.

Conclusions

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

It was 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 due 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 control of the reaction variables such as pressure, temperature and flow, but also, delivers visual light in an elegant way.

The CO₂ conversion rates were in accordance with other works testing plasmonic catalysts at higher temperatures. This can be due 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 in the field of CO₂- use by applying solar energy.

Acknowledgements

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