

CO₂ photoreduction through TiO₂@SiO₂(HIPE) self-standing foams: a new paradigm of a real 3D photoconversion behavior

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In the current context of harvesting novel energy sources while minimizing the environmental impact, two main issues have to be circumvented: global warming due to critical levels of atmospheric carbon dioxide (CO₂), and continuous increasing demand in energy.^[1,2,3] Among several strategies, solar fuel production from CO₂ photoconversion is appearing both as a smart and convenient option able to contribute in solving simultaneously the aforementioned issues.^[4]

The main drawback of solar-based energy conversion technologies is the need of a huge active surface to meet a world scale production of energy.^[5] To reduce the process footprint, two main considerations are likely to be investigated. On one hand, an improvement of the intrinsic photocatalytic activity would enhance the solar energy conversion per area unit. On the other hand, an increase of the photocatalyst loading per area unit would also reach higher energy efficiency. If the first point is often encountered in the literature, the latter is yet only poorly studied, mainly because of an expected too low productivity threshold due to light shading effect.^[7]

To overcome this drawback while evolving beyond the typical boundary as regards loading per area unit, we propose to take advantage of inorganic monolithic systems with controlled porosity. Indeed, we assume that specific porosity may improve photon harvesting.

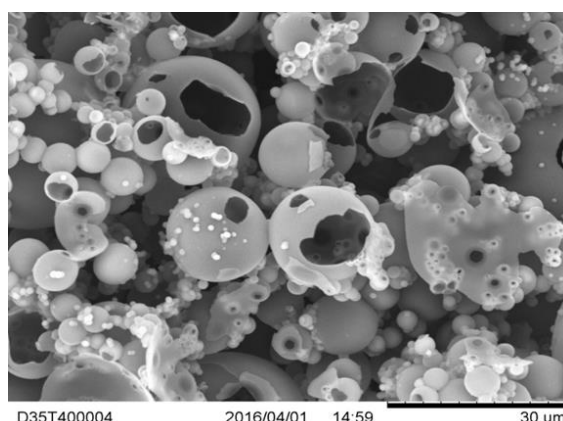


Figure 1. SEM image of TiO₂@SiO₂(HIPE) at 40 wt% of titania

According to these considerations, novel 3D macrocellular self-standing monoliths were synthesized and employed for the CO₂ photoreduction with water. Thereby, TiO₂/SiO₂ based monoliths bearing hierarchical porosity have been synthesized following a novel two steps sol-gel synthesis method. Via a direct O/W emulsion template and taking benefit of

silica polycondensation, high internal phase emulsion (HIPE) based SiO_2 foam is first obtained.^[6] Secondly, titanium dioxide (TiO_2) post-impregnation allows the generation of $\text{TiO}_2@/\text{SiO}_2$ (HIPE) porous monoliths (Fig. 1). TiO_2 , anchored at the silica walls matrix, present an anatase/rutile allotropic proportion similar to the P25 Degussa titanium dioxide, a well-known commercial powder employed for its high photocatalytic activity.

The photocatalytic performances of those 3D solids were carried out under soft conditions (T_{amb} , P_{atm}), with CO_2 and H_2O as gaseous reactants and under UV-Visible irradiation. As made self-standing monoliths were compared in terms of photocatalytic activity with conventional TiO_2 P25 Degussa powdered bed. Whereas this commercial TiO_2 powder shows a maximum varying the mass, for $\text{TiO}_2@/\text{SiO}_2$ (HIPE), consumption of photo-generated electrons still continue to increase with the mass of the monolith, i.e. with the thickness (Fig. 2).

These results can be regarded as a real breakthrough concerning footprint reduction of solar fuel photocatalytic processes, where a better efficiency is now obtained for thicker materials, leading thus to a new paradigm of a real 3D photoconversion behavior.

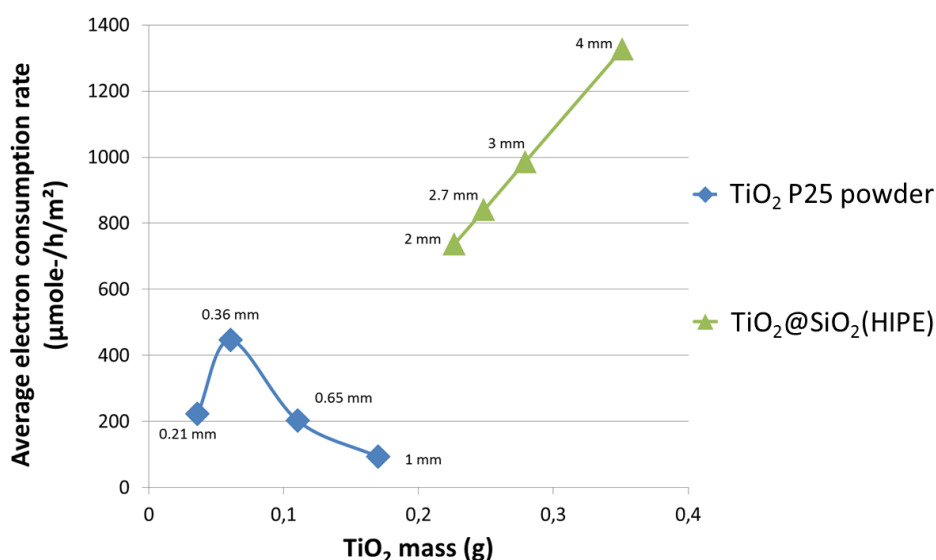


Figure 2: Comparison of $\text{TiO}_2@/\text{SiO}_2$ (HIPE) and TiO_2 P25 powder behavior in terms of average electron consumption rate

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