Phthalocyanines-TiO_2: a New Efficient and Tunable Catalysts for CO_2 Reduction in Water

Alberto De Riccardis[1], Giuseppe Mele[1], Lucia D'Accolti[2], Leonardo Palmisano[3], Giuseppe Vasapollo[1]

[1]Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via Monteroni, 73100 Lecce

[2]Dipartimento di Chimica, Università degli Studi di Bari "Aldo Moro", via Orabona 4, 70126 Bari

[3]Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici, DEIM, Università di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo

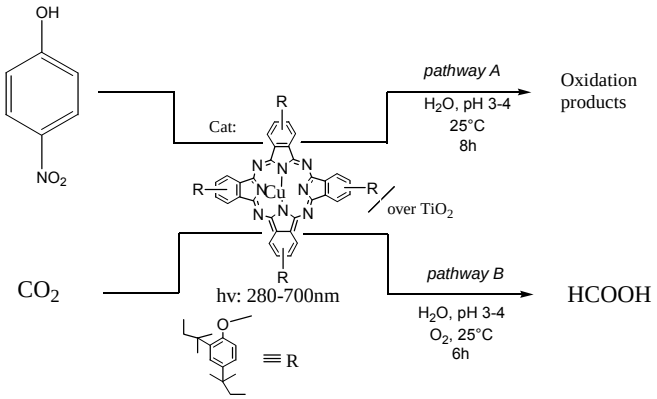
Email: alberto.dericcardis@unisalento.it

ABSTRACT

Organic sensitizer loaded over TiO_2 (anatase), in particular Cu(II) tetrakis [4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)]phthalocyanines was proved to be active in the photoreduction of CO_2 to formic acid (HCO_2H) in water under UV-Vis light. Because of their low environmental impact, low potential cost, and efficient power conversion, these multipurpose materials show promise in the setup of sustainable methods for CO_2 valorization

Keywords: CO_2 reduction, photocatalysis, phthalocyanines, porphyrins

The combination of TiO_2 with different kinds of sensitizers allowed to obtain extremely versatile composite sensitized materials having oxidizing properties suitable to photodegrade organic pollutants in water [1]. More recently, the reductive properties to photo-reduce CO_2 in aqueous medium have been investigated [2].



In this work, composites materials prepared by loading polycrystalline TiO_2 powders with lipophilic highly branched Cu(II)- and metal-free phthalocyanines or porphyrins, which have been used in the past as photocatalysts for photo degradative processes, have been successfully tested for the efficient photoreduction of carbon dioxide in aqueous suspension affording significant amounts of formic acid. The results indicated that the presence of the sensitizers is beneficial for the photoactivity, confirming the important role of Cu(II) co-ordinated in the middle of the macrocycles. A comparison between Cu(II) phthalocyanines and Cu(II) porphyrins indicated that the Cu(II)- phthalocyanine sensitizer was more efficient in the photoreduction of CO_2 to formic acid probably due to its favorable reduction potential.

We have employed the highly hydrophobic Cu(II)tetrakis [4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)] phthalocyanine (CuPc) in order to avoid the dissolution on sensitizer in water .
Typically, the loaded samples used as photocatalysts for the photoreactivity experiments were prepared by impregnating TiO_2 (Tioxide, Huntsman anatase phase) with various amounts of CuPc (4,5, 6.65 and 8,5 μmol/g TiO_2.The sensitizers were dissolved in 5 mL of CH_2Cl_2 and 500 mg of finely ground TiO_2 was added to this solution. The mixture was stirred for 6 h and the solvent was removed under vacuum.The reaction conditions are mild: 0.05 g of catalyst in water at pH 3 at room temperature under UV-Vis light (the experimental set-up is shown in Fig. 1).

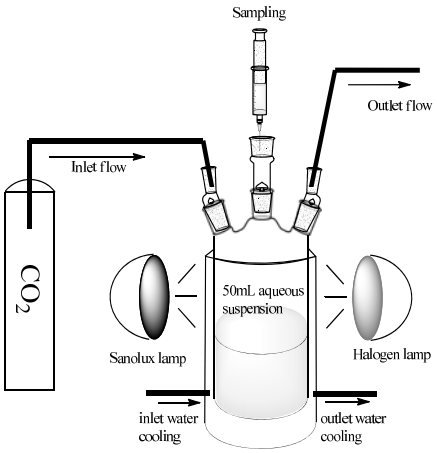


Figure 1: Experimental set-up

TiO_2 (anatase) samples impregnated with functionalized 6.65 μmol CuPc /1g TiO_2 CuPc results to be 62% more effective compared to bare TiO_2 in the production of formic acid. The maximum yield for 8 hours of reaction was 210 μmol·g.cat^{-1}
The possibility to work under similar experimental conditions (acid pH, amount of catalyst, opportune combination of irradiation sources) for the photo-oxidation and the photo-reduction reactions implies that it is possible to switch from one reaction to another by changing only the substrate and replacing O_2 with CO_2 in the photoreduction process. This new class of multipurpose materials in very mild conditions could be considered among the affordable technologies because of their relatively low potential costs and environmental impact.

References

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