

NANOPOROUS CARBONS FOR SOLAR FUELS PRODUCTION

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Introduction

Solar fuels are a promising strategy since they are produced from simple and abundant molecules using a renewable energy source such as sunlight. However, the efficiency of photocatalysts is still low and far from the practical application. The H₂ production by direct water splitting¹ using TiO₂ and the CO₂ reduction² are the two main reactions concerning with solar fuels. It has been widely showed that noble metal/graphene-based catalysts are suitable for these reactions^{1,2}. A third way poorly studied correspond to the photo assisted valorization of molecules such as furfuryl alcohol (FA) and 5-hydroxymethyl furfural (5-HMF) because they are important products of the biorefinery industry³. In addition, glycerol (Gly) is the main by-product of biodiesel industry⁴ with an important economic devaluation⁵. The FA and Gly photo assisted valorisation to selectively produce aldehydes or ketones is an important strategy to obtain more valuable compounds such as five or six-member dioxane-based carbocycles. In this sense, this work explores a photocatalytic approach for the valorization of FA, 5-HMF and Gly by using C-doped and Cu-containing TiO₂-based catalysts, under solar light.

Materials and Methods

C-doped TiO₂ photocatalyst was prepared by solvothermal synthesis by mixing furfural and titanium isopropoxide in ethanol. The solution was sealed inside an autoclave and heated at 180 °C for 16 h. The solid was filtered and washed in absolute ethanol and dried under static-air at 100 °C for 2 h. The material was denoted as TiO₂-C. Cu-containing photocatalyst was prepared by adding Cu(acac)₂ to the mixture of furfural and Ti-alkoxide (5 wt.% Cu) and proceeding as above. The sample was denoted as Cu@TiO₂-C. The catalysts were characterized by XRD, TEM, gas adsorption, and surface pH. The photocatalytic tests were performed using a Pyrex open-to-air photoreactor with 125 mL of FA or Gly solution and 125 mg of catalyst. Irradiation was provided by a solar simulator (250W Xe-lamp). FA and 5-HMF solutions were used from the remnant liquid from the solvothermal synthesis. For the Gly photocatalytic tests, a solution of 20% v/v was prepared in distilled water. UV-vis spectroscopy was used to follow the reaction in both target molecules and for the case of Gly, the appearance of the product was followed by changes in the transmittance peaks observed in FTIR.

Results and Discussion

Table 1 displays some properties of the catalysts. The amount of Cu measured was ca. 4.3 wt%, very close to the nominal value (ca. 5 wt%). Cu leads to a decrease in C content in the hybrid material and to a remarkable increase in the surface pH from 3.8 up to 6.2.

Table 1. Chemical composition, surface pH and selected textural parameters the photocatalysts evaluated from N₂ adsorption isotherms at 77 K.

Sample	S _{BET} ^a (m ² g ⁻¹)	V _{total} ^b (cm ³ g ⁻¹)	V _{micro} ^c (cm ³ g ⁻¹)	Ti + O ^d (wt.%)	C ^d (wt.%)	Cu ^d (wt.%)	pH ^e
TiO ₂	145	0.162	0.032	79.8	20.2	---	3.8
Cu@TiO ₂ -C	127	0.117	0.033	78.2	17.5	4.3	6.2

^aBET surface area; ^bTotal pore volume at p/po ≈ 0.99; ^cMicropore volume, Dubinin-Raduskevich equation; ^dTiO₂, C and Cu content; ^eSurface pH.

Fig. 1A shows the N₂ adsorption-desorption isotherms at 77 K. Both materials show type IV isotherms⁶, characteristic of mesoporous materials. Differences in the hysteresis loop (type H₂) indicate a wider distribution of mesopores sizes for TiO₂-C than Cu@TiO₂-C. Contribution of micropores to the total pore volume is ca. 20% and 28% for TiO₂-C and Cu@TiO₂-C, respectively. Cu promotes a slight enhancement in the micropore contribution and a decrease in C content from ca. 20.2 to 17.5 wt.%. TEM images (Fig. 1B and 1C) show the materials are constituted by micrometric spheres which distribution of sizes increased in the presence of Cu (ca. 4.0 μm and 5.2 μm) suggesting that Cu nanoparticles are intercalated within the TiO₂-C matrix. The XRD patterns (Fig. 1D) shows that anatase is the main crystalline phase of TiO₂ (ca. 90%) with a mean crystal size about 9.3 nm in both samples. In addition, XRD pattern of Cu@TiO₂-C sample presents two peaks at 43.2° and 50.6° that can be attributed to elemental Cu nanoparticles -with a mean size of ca. 9.7 nm-.

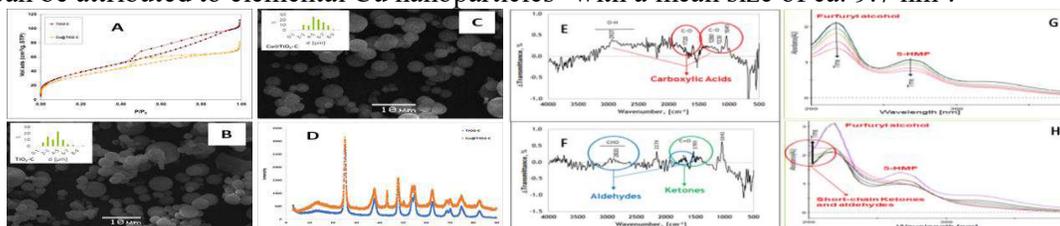


Fig 1. (A): N₂ adsorption/desorption isotherms at 77 K. **(B)-(C):** TEM images. **(D):** XRD patterns. **(E)-(F):** Differential transmittance from the FTIR spectra after 120 min irradiation of Gly on TiO₂-C and Cu@TiO₂-C. **(G)-(H):** Photocatalytic conversion of FA on TiO₂-C and Cu@TiO₂-C.

Fig. 1E and 1F show the differential transmittance data obtained from the FTIR spectra after 120 min irradiation of Gly. Carboxylic acids are formed on TiO₂-C sample while ketones and aldehydes along with carboxylic acids, are formed on Cu@TiO₂-C. These results agree with the surface pH of samples: the photooxidation of Gly to carboxylic acid occurs on TiO₂-C catalysts due to its acidic surface pH, while reduction of alcohols groups on Gly occur on the neutral Cu@TiO₂-C, where the high electron affinity of Cu is the driving force for the reduction reaction. Fig. 1G and 1H show the photoconversion of the FA and 5-HMF mixture. In absence of Cu, the absorbance peaks in the UV-vis spectrum decreased as function of time indicating that the photomineralization of the FA + 5-HMF mixture is promoted. On the contrary, the Cu-containing catalyst leads to a different reaction mechanism which is inferred by the increase in the absorbance below the main peak of FA at 217 nm and the increase for the peak below 268 nm, corresponding to 5-HMF. It may be inferred that short-chain ketones and aldehydes could be formed. A quantitative study is currently ongoing to elucidate the reaction mechanisms for the photocatalytic valorization of Gly, FA, 5-HMF.

Conclusions

Our preliminary results open new perspectives for the development of low cost and selective C-based catalysts for the photoassisted valorization of biomass' derivatives molecules. The catalysts showed activity for the photoconversion of FA and Gly. The incorporation of Cu resulted in a catalyst with a higher selectivity for the electron-donor involved reactions.

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