

BIOCHARS-BASED MATERIALS FOR HETEROGENEOUS PHOTOCATALYSIS

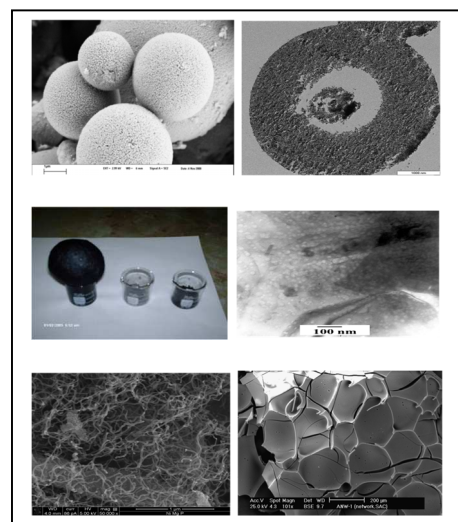
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ABSTRACT

Biochar-based photocatalysts have been prepared from biomass derivatives and studied in photocatalytic processes concerning with environmental remediation such as phenol and methylene blue photodegradation, and in clean energy production such as hydrogen photoproduction. A carefully design of the pyrolysis/activation processes permit the control both the texture and chemistry surface of carbons. Biomass precursor is a master key to control both the crystalline framework and optical and electronical properties of photoactive semiconductors such as TiO₂, ZnO and Nb₂O₅. The influence of heteroatoms-doped biochars and the influence of noble metal upon TiO₂-based photocatalysts will be also presented.



INTRODUCTION

An important challenge for science is to develop green chemistry processes [1]. An interesting alternative is the use of C-TiO₂ hybrid materials because they concerns with the green chemistry principles [2]. C-TiO₂ properties can be design to be used in photocatalytic processes such as H₂ photoproduction [3], polluted water and air remediation [4-9], and in selective photooxidations [7]. C-TiO₂ is a non-toxic and biocompatible material and it is relatively cheap and easy to prepare in one-step procedure [4,10]. The objective of this work is to show that heteroatoms-doped biochar-based hybrid materials prepared under eco-friendly conditions can be used in different photocatalytic processes related to polluted water remediation and clean energy production.

METHODOLOGY

Synthesis of non-doped and S- or N-doped biochars have been described elsewhere [3,5-9]. Au-TiO₂/AC photocatalysts preparation was performed as follows [3]. Au was firstly deposited at basic pH on a commercial TiO₂ (Avonik, ex-Degussa) and then Au-TiO₂/C hybrid materials were prepared by a slurry method [6,7]. C-doped TiO₂ hybrid materials were prepared by solvothermal synthesis from mixtures of furfural and

titanium isopropoxide [4]. Characterization was performed by N₂ adsorption–desorption isotherms, X-ray photoelectronic spectroscopy (XPS), surface pH (pH_{PZC}), infrared spectroscopy (FTIR), X-ray diffraction (XRD), UV-vis/diffuse reflectance spectra (UV-Vis/DR), and electron microscopy (TEM/STEM). Experimental conditions for the H₂ photoproduction, and methylene blue (MB) photodegradation tests have been carefully described elsewhere [3-5,8-9].

RESULTS AND DISCUSSION

A summary of the kinetic results of MB degradation are given in Table 1 and 2. In presence of S- and N-doped biochars, the photoactivity increased up to about 2 and 5 times higher than on TiO₂ alone. The photoactivity of the biochar depends both on the texture and on the S and N content [8,9]. The photoactivity was confirmed by PS and CV analysis [8] suggesting that S incorporations decrease the energy band gap in carbon-based materials. S- [8] and N-doped [9] carbons are not only photoactive but also they photoassist to TiO₂ by electron transference of electrons from π* orbital in S- or N-doped biochars to the conduction band of the TiO₂.

Table 1. Summary of kinetic results for the MB photodegradation on S-doped carbons

Sample	v ₀ ^a (μmol.L ⁻¹ .min ⁻¹)	v _{rel} ^b	k _{app} x10 ^{-3c} (min ⁻¹)	R ^d	φ _{photo} ^e
C (6.3 mg)	0.291	1.04	6.00	0.9740	1.3
C-S (6.3 mg)	0.579	2.1	10.28	0.9693	2.2
B (6.3 mg)	0.262	0.93	4.00	0.9870	0.9
B-S (6.3 mg)	0.536	1.9	8.56	0.9917	1.9
TiO ₂ (62.5mg)	0.281	1.0	4.61	0.9849	1.0

^aInitial rate: C_{eq}.k_{app}. ^bInitial activity relative to TiO₂: v_{0-AC}/v_{0-TiO₂}. ^cApparent rate constant (k_{app}).

^dSquare regression factor. ^eφ_{photo} defined as k_{app-AC}/k_{app-TiO₂}

Table 2. Adsorption in the dark (Ads_{dark}) of MB, apparent first-order rate constants (k_{app}), square regression factor (R²), photocatalytic activity relative to TiO₂ (φ_{photo}).

Photocatalyst	Ads ^a (%)	k _{app} x 10 ⁻³ (min ⁻¹)	R ²	φ _{photo} ^b
PK	4	1.7	0.9078	0.38
PN	2	2.0	0.9376	0.44
PNA	5	2.3	0.9840	0.51
PNO	2	1.3	0.9637	0.29
TiO ₂	22	4.5	0.9858	1
TiO ₂ -PK	28	22.5	0.9871	5.0
TiO ₂ -PN	23	17.1	0.9931	3.8
TiO ₂ -PNA	15	23.9	0.9887	5.3
TiO ₂ -PNO	16	16.2	0.9914	3.6

^aAfter 60min adsorption . ^bφ_{photo}= (k_{app-i}/k_{app-TiO₂}).

H₂ photoproduction results are given in Table 3. It can be seen an increase up to 3 times higher photoactivity on Au-TiO₂/C than that on Au-TiO₂ and clearly much higher than that on neat TiO₂ which is non-photoactive under visible irradiation. This increase was attributed to an increase in the resonance plasmon of gold [5] due to the transference of

electron density from the conduction band in TiO₂ modified by the interaction with oxygen functional groups on AC [5,8,9]. The stability of photocatalytic activity of these materials was studied following the kinetics of H₂ production during consecutive photocatalytic runs and No gold lixiaviation during reaction was detected and photoactivity remains constant at least for three consecutive runs.

Table 3. First-order rate-constants (k_{reac}) for the hydrogen photoproduction

Sample	k_{reac}^a (mM.min ⁻¹)	R ²
TiO ₂ -P25	b	b
Au-TiO ₂ -P25	0.044	0.9790
Au-TiO ₂ /AC _{CO2}	0.115	0.9840
Au-TiO ₂ /AC _{N2}	0.094	0.9965
Au-TiO ₂ /AC _{ZnCl2}	0.062	0.9730
Au-TiO ₂ /AC _{H3PO4}	0.052	0.9890

^a k_{reac} obtained from the kinetics of hydrogen production. ^bNo photoactivity was detected.

CONCLUSIONS

TiO₂-based hybrid materials were designed for efficient photocatalytic processes. H₂ was photoproduced on Au-TiO₂/C under visible light up to 3 times higher than the commercial photocatalysts. Enhancements in the MB photodegradation under UV-vis irradiated hybrids C-TiO₂ and S- and N-doped carbons showed that the harvesting of solar energy for environmental and green chemistry applications is possible by using even free-metal carbon-based materials.

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