

# Biochar-based materials for the sustainable catalysis and photocatalysis

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## Abstract

Applications of biochar-based materials in catalytic and photocatalytic processes are presented in this work. Sawdust from a soft wood was used to prepared biochars by carbonization, thermochemical and physical activation and these biochars were used as a co-support for the H<sub>2</sub> photoproduction on Au-TiO<sub>2</sub>/biochars under visible irradiation. A remarkable increase in the photocatalytic activity of the composite up to a factor about 3 times higher than the commercial catalyst free of biochars was found and ascribed to the surface pH of biochars. Biomass-derived molecules such as furfural, chitosane, and saccharose were used as carbon source to prepare hybrid C-TiO<sub>2</sub> materials by solvothermal synthesis. It was found that carbonized hybrid TiO<sub>2</sub>-C supports led to an important enhancement in the catalytic activity of Pd-based catalysts in the electrooxidation of formic acid with a maxima density power up to 3.3 times higher than the same catalyst supported on a commercial carbon. In addition, Pd-based catalysts showed that hybrid Biochar-TiO<sub>2</sub> supports can be designed to control the selectivity of phenol hydrogenation (up to 100% yield) to cyclohexanone or cyclohexanol by controlling the chemical nature of the biochar-based supports. Enhancements up to a factor about 2 and 5 times higher photocatalytic activity that the commercial semiconductor were found in the photodegradation of methylene blue under visible irradiation by using S-doped and N-doped Biochar-based/TiO<sub>2</sub> materials [1].

## 1. Introduction

Biochar-based materials have gained an important role in the sustainable society of XXI century [1]. This is mainly due to the effective application in different catalytic [2,3] and photocatalytic [4] processes. For example, the use of biochar-TiO<sub>2</sub> hybrid materials showed an additional approach because these materials are in agreement with the green chemistry principles [5]. For example, these materials have showed important and potential application in hydrogen photoproduction by using solar irradiation [6], polluted water and air remediation [7-12], and in selective photooxidation [10]. C-TiO<sub>2</sub> is a non-toxic and biocompatible material and it is relatively cheap and easy to prepare in one-step procedure [7,13]. 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.

## 2. Experimental

Synthesis of non-doped and S- or N-doped biochars have been described elsewhere [1,6,8,12]. Au-TiO<sub>2</sub>/AC photocatalysts preparation was performed as follows [6]. Au was firstly deposited at basic pH on a commercial TiO<sub>2</sub> (Avonik, ex-Degussa) and then Au-TiO<sub>2</sub>/C hybrid materials were prepared by a slurry method [9,10]. C-doped TiO<sub>2</sub> hybrid materials were prepared by solvothermal synthesis from mixtures of furfural, chitosan and saccharose with titanium isopropoxide [2,3,7]. Characterization was performed by N<sub>2</sub> adsorption-desorption isotherms, X-ray photoelectronic spectroscopy (XPS), surface pH (pHPZC), infrared spectroscopy (FTIR), X-ray diffraction (XRD), UV-vis/diffuse reflectance spectra (UV-Vis/DR), and electron microscopy (TEM/STEM). Experimental conditions for the H<sub>2</sub> photoproduction, and methylene blue (MB) photodegradation tests have been carefully described elsewhere [6-8,11-12].

## 3. 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 TiO<sub>2</sub> alone. The photoactivity of the biochar depends both on the texture and on the S and N content [11,12]. The photoactivity was confirmed by PS and CV analysis [11] suggesting that S incorporations decrease the energy band gap in carbon-based materials. S- [11] and N-doped [12] carbons are not only photoactive but also they photoassist to TiO<sub>2</sub> by electron transference of electrons from π\* orbital in S- or N-doped biochars to the conduction band of the TiO<sub>2</sub>.

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

Sample	$v_0^a$ (μmol.L <sup>-1</sup> .min <sup>-1</sup> )	$v_{rel}^b$	$k_{app} \times 10^{-3} c^c$ (min <sup>-1</sup> )	R <sup>d</sup>	$\phi_{photo}^e$
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 <sub>2</sub> (62.5mg)	0.281	1.0	4.61	0.9849	1.0

<sup>a</sup>Initial rate:  $C_{00} \cdot k_{app}$ . <sup>b</sup>Initial activity relative to TiO<sub>2</sub>:  $v_0 \cdot AC / v_0 \cdot TiO_2$ . <sup>c</sup>Apparent rate constant ( $k_{app}$ ). <sup>d</sup>Square regression factor. <sup>e</sup> $\phi_{photo}$  defined as  $k_{app-AC} / k_{app-TiO_2}$

Table 2. Adsorption in the dark ( $Ads_{dark}$ ) of MB, apparent first-order rate constants ( $k_{app}$ ), square regression factor ( $R^2$ ), photocatalytic activity relative to TiO<sub>2</sub> ( $\phi_{photo}$ )

Photocatalyst	$Ads^a$ (%)	$k_{app} \times 10^{-3} (\text{min}^{-1})$	R <sup>2</sup>	$\phi_{photo}^b$
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 <sub>2</sub>	22	4.5	0.9858	1
TiO <sub>2</sub> -PK	28	22.5	0.9871	5.0
TiO <sub>2</sub> -PN	23	17.1	0.9931	3.8
TiO <sub>2</sub> -PNA	15	23.9	0.9887	5.3
TiO <sub>2</sub> -PNO	16	16.2	0.9914	3.6

<sup>a</sup>After 60min adsorption. <sup>b</sup> $\phi_{photo} = (k_{app} / k_{app-TiO_2})$ .

H<sub>2</sub> photoproduction results are given in Table 3. It can be seen an increase up to 3 times higher photoactivity on Au-TiO<sub>2</sub>/C than that on Au-TiO<sub>2</sub> and clearly much higher than that on neat TiO<sub>2</sub> which is non-photoactive under visible irradiation. This increase was attributed to an increase in the plasmon resonance of gold [8] due to the transference of electron density from the conduction band in TiO<sub>2</sub> modified by the interaction with oxygen functional groups on AC [8,11,12]. The stability of photocatalytic activity of these materials was studied following the kinetics of H<sub>2</sub> production during consecutive photocatalytic runs and No gold lixiviation 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 <sup>-1</sup> )	R <sup>2</sup>
TiO <sub>2</sub> -P25	b	b
Au-TiO <sub>2</sub> -P25	0.044	0.9790
Au-TiO <sub>2</sub> /AC <sub>CO2</sub>	0.115	0.9840
Au-TiO <sub>2</sub> /AC <sub>N2</sub>	0.094	0.9965
Au-TiO <sub>2</sub> /AC <sub>ZnO2</sub>	0.062	0.9730
Au-TiO <sub>2</sub> /AC <sub>H3PO4</sub>	0.052	0.9890

<sup>a</sup> $k_{reac}$  obtained from the kinetics of hydrogen production. <sup>b</sup>No photoactivity was detected.

Table 4. Kinetic results of phenol hydrogenation on Pd-based catalysts. Initial activity, maxima phenol conversion ( $Ph_{conv}$ ), selectivity of cyclohexanone ( $S_{C=O}$ ) and cyclohexanol ( $S_{OH}$ ).

Catalyst	Pd <sup>a</sup> (wt %)	Activity <sup>b</sup> (μmol.gPd <sup>-1</sup> .s <sup>-1</sup> )	$Ph_{conv}$ (%)	$S_{C=O}$ (%)	$S_{OH}$ (%)
Pd/TiO <sub>2</sub> -P25	1.1	45.5	99	98	2
Pd/Fu-TiO <sub>2</sub> -C	1.0	71.0	99	97	3
Pd/Sac-TiO <sub>2</sub> -C	0.9	40.3	99	93	7
Pd/Fu-TiO <sub>2</sub> -C-C	0.9	156.2	99	9	91
Pd/Sac-TiO <sub>2</sub> -C-C	1.0	60.8	99	8	92
Pd/TiO <sub>2</sub> -AC <sub>CO2</sub>	0.9	62.1	99	24	76
Pd/TiO <sub>2</sub> -AC <sub>N2</sub>	1.0	48.3	99	19	81
Pd/TiO <sub>2</sub> -AC <sub>ZnO2</sub>	0.9	91.1	99	96	4
Pd/TiO <sub>2</sub> -AC <sub>H3PO4</sub>	0.9	62.2	99	89	11

<sup>a</sup>wt % of palladium measured by ICP chemical analysis. <sup>b</sup>Phenol converted (μmol)/Pd<sub>weight</sub>.sec.

The results of selective phenol hydrogenation [3] on Pd-based catalysts supported on TiO<sub>2</sub>-C are given in Table 4. The nature of the support can be modified to direct the reaction either to cyclohexanol (~100% yield) or to cyclohexanone (~96% yield). High selectivity to cyclohexanone is obtained with Pd on more polar TiO<sub>2</sub>-C supports (4), while when these are transformed into hydrophobic TiO<sub>2</sub>-C the catalyst becomes selective to cyclohexanol. This remarkable change in selectivity was attributed to the stabilization of charges in the semiconductor by the electron transference from carbon materials, which is clearly enriched when it is thermal treated at high temperatures, thus becoming in a basic and hydrophobic support. In short, selective phenol hydrogenation is easily controlled by controlling the functionalization of the hybrid support. Figure 1, shows the mechanism proposed for the selective hydrogenation of phenol to cyclohexanone [3].

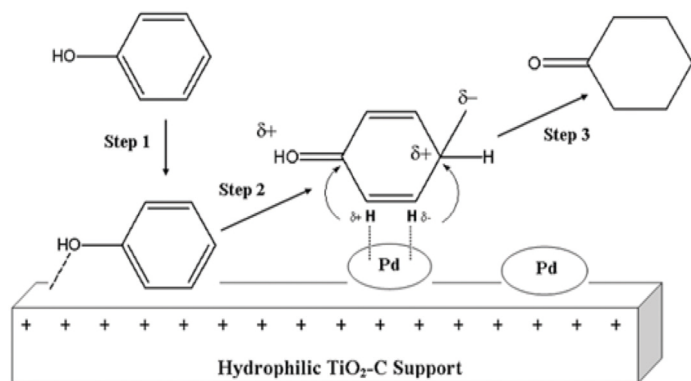


Figure 1. General pathway for selective hydrogenation of phenol to cyclohexanone [3].

Finally, we have found in a recent work [2], that carbonized hybrid TiO<sub>2</sub>-C supports prepared by solvothermal synthesis from mixture of titanium alcoxides and biomass-derivative molecules such as furfural, chitosan, and saccharose, led to an important enhancement in the catalytic activity of Pd-based catalysts in the electrooxidation of formic acid with a maxima density power up to 3.3 times higher [2] than the same catalyst prepared on a commercial carbon. This results can be seen from figure 2.

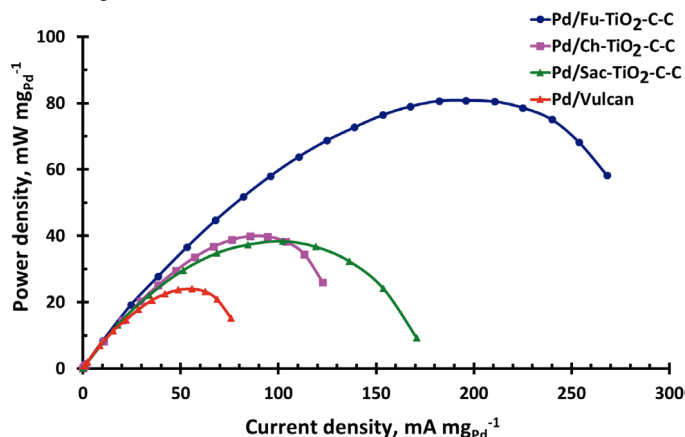


Figure 2. Power density developed on Pd-based catalysts as a function of current for the different Biomass-derived-TiO<sub>2</sub> supports and comparison against a commercial carbon.

### Conclusions

Different biochars and hybrid biochar-TiO<sub>2</sub> materials were prepared by different methods and studied in several catalytic and photocatalytic processes. An important increase in the photocatalytic activity of Au-based catalysts supported on TiO<sub>2</sub>-C materials was found in the H<sub>2</sub> photoproduction under visible irradiation. The composite showed up to a factor about 3 times higher than the commercial catalyst free of biochars was found and ascribed to the surface pH of biochars. It can be concluded that biomass-derived molecules such as furfural, chitosane, and saccharose are usefull to prepare hybrid C-TiO<sub>2</sub> materials by solvothermal synthesis and these hybrid TiO<sub>2</sub>-C supports led to an important enhancement in the catalytic activity of Pd-based catalysts in the electrooxidation of formic acid and at the same time, hybrid Biochar-TiO<sub>2</sub> supports can be designed to control the selectivity of phenol hydrogenation (up to 100% yield) to cyclohexanone or cyclohexanol. Enhancements up to a factor about 2 and 5 times higher photocatalytic activity that the commercial semiconductor were found in the photodegradation of methylene blue under visible irradiation by using Biochar-based/TiO<sub>2</sub> materials. In summary, it can be concluded that biochars-based materials show new perspectives for the sustainable catalysis and photocatalysis related with clean energy production, green and selective catalytic processes, and for the environmental remediation of polluted water by solar technology. This approach is showed in a schematic way in the Figure 3.

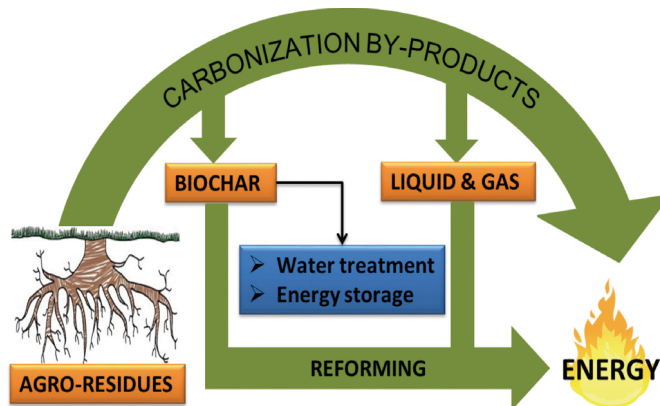


Figure 3. Production of biochar-based materials and applications for the clean energy production, green and selective catalysis, and for the environmental remediation of polluted water by solar technology.

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### References

- [1] J. Matos. (2015). Eco-friendly Heterogeneous Photocatalysis on Biochar-based Materials under Solar Irradiation. Topics in Catalysis, DOI: 10.1007/s11244-015-0434-5.
- [2] J. Matos, A. Borodzinski, A.M. Zychora, P. Kedzierzawski, B. Mierzwa, K. Juchniewicz, M. Mazurkiewicz, J.C. Hernández-Garrido. (2015). Direct formic acid fuel cells on Pd catalysts supported on hybrid TiO<sub>2</sub>-C materials. Appl. Catal. B: Environ. 163 (1), 167-178.
- [3] J. Matos, A. Corma. (2011). Selective phenol hydrogenation in aqueous phase on Pd-based catalysts supported on hybrid TiO<sub>2</sub>-Carbon materials. Appl. Catal. A: Gen. 404 (1-2), 103-112.
- [4] J.M. Herrmann, C. Duchamp, M. Karkmaz, B.T. Hoai, H. Lachheb, E. Puzenat, C. Guillar. (2007). Environmental green chemistry as defined by photocatalysis. J. Hazard. Materials 146 (3), 624-629.
- [5] P.T. Anastas, J. C. Warner. (1998). Green Chemistry: Theory and Practice, Oxford Press, NY.
- [6] J. Matos, T. Marino, R. Molinari, H. García. (2012). Hydrogen photoproduction under visible irradiation of Au-TiO<sub>2</sub>/activated carbon. Appl. Catal. A: General 417-418 ( ), 263-272.
- [7] J. Matos, A. García, L. Zhao, M. M. Titirici. (2010). Solvothermal carbon-doped TiO<sub>2</sub> photocatalyst for the enhanced methylene blue degradation under visible light. Appl. Catal. A: General 390, 175-182.
- [8] J. Matos, M. Rosales, A. García, C. Nieto-Delgado, J. R. Rangel-Mendez. (2011). Hybrid Photoactive Materials from Municipal Sewage Sludge for the Photocatalytic Degradation of Methylene Blue. Green Chemistry 13, 3431-3439.
- [9] J. Matos, E. García-López, L. Palmisano, A. García, G. Marci. (2010). Influence of activated carbon in TiO<sub>2</sub> and ZnO mediated photo-assisted degradation of 2-propanol in gas-solid regime. Appl. Catal. B: Environ. 99, 170-180.
- [10] J. Matos, A. García, T. Cordero, J. M. Chovelon, C. Ferronato. (2009). Eco-friendly TiO<sub>2</sub>-AC photocatalyst for the selective photooxidation of 4-chlorophenol. Catal. Letters 130, 568-574.
- [11] T.J. Bandoz, J. Matos, M. Seredych, M. S. Z. Islam, R. Alfano (2012). Photoactivity of S-doped nanoporous activated carbons: a new perspective for harvesting solar energy on carbon-based semiconductors. Appl. Catal. A: General 445-446, 159-165.
- [12] J. Matos, M. Hofman, R. Pietrzak. (2013). Synergy effect in the photocatalytic degradation of methylene blue on a suspended mixture of TiO<sub>2</sub> and N-containing carbons. Carbon 54, 460-471.
- [13] J. Matos, P. Atienzar, H. García, J. C. Hernández-Garrido. (2013). Nanocrystalline carbon-TiO<sub>2</sub> hybrid hollow spheres as possible electrodes for solar cells. Carbon 53, 169-181.