

B04-0755: (Invited) Biomass-Derivative Molecules for the Sustainable Synthesis of Carbon-Doped High-Performance Nanostructured Materials

Thursday, 30 May 2019

09:00 - 09:20

 Dallas Sheraton Hotel - City View 5

Within the framework of the green chemistry, a review of some examples reported by our group [1-7] related to the solvo- and hydrothermal synthesis of Carbon-doped materials is presented. Special attention is paid in catalysis, photocatalysis, solar cells and fuel cells applications.

The photodegradation of methylene blue (MB) and phenol (PhOH) on a Carbon-doped TiO_2 and on pure TiO_2 was studied [1,2]. Both nanomaterials exhibited mesoporous textures and the TiO_2 frameworks consist mainly of Anatase phase. SEM images showed spherical microparticles while the TEM images showed hierarchically nanostructured morphologies on both samples. C- TiO_2 exhibited higher first-order apparent rate constants for the degradation of MB and PhOH than those on pure TiO_2 . The photoactivity of carbon-doped TiO_2 was higher than that of TiO_2 suggesting a red-shift in the semiconductor and the photo assistance of carbon functional groups from carbon quantum-dots to the semiconductor. DFT theoretical estimations confirms both phenomena.

The catalytic activity of a Pt-Ru alloy supported on hydrothermal carbon for dry methane reforming (DMR) and for the partial oxidation of methane (POM) was studied [3]. Upon removal of the carbon support a mixture of Pt and Ru oxide was obtained. For DMR the initial activity in both samples was high but the catalysts were readily deactivated in time. Regarding the POM, the Pt-Ru alloy supported on hydrothermal carbon showed a lower initial activity but a better catalytic stability than its oxidized analogous, suggesting that hydrothermal carbon-supported Pt-Ru alloys could be employed as a catalyst in catalytic oxidations.

Carbon-doped TiO_2 -based were prepared and the activity and selectivity of Pd-based catalysts on phenol hydrogenation in aqueous phase was studied [4]. The reaction can be directed either to cyclohexanol (~100% yield) or to cyclohexanone (~96% yield). High selectivity to cyclohexanone is obtained with Pd on more polar TiO_2 -C supports, while when these are transformed into hydrophobic TiO_2 -C supports the resultant catalyst becomes selective to cyclohexanol. Thus, product distribution during the selective phenol hydrogenation in aqueous phase is easily controlled by controlling the functionalization of the hybrid support.

The electrooxidation of formic acid was performed on Pd-based catalysts supported on hybrid TiO_2 -C materials prepared from different carbon origins by solvothermal [5]. The carbonized hybrid TiO_2 -C supports with mesopore texture and high anatase:rutile ratio in the TiO_2 framework led to about three times higher activity per Pd mass unit than the catalyst prepared on a commercial Vulcan XC-72 carbon black, which will allow to reduce considerably the amount of expensive noble metal at the anode of DFAFC. The rate of electrooxidation of formic acid on Pd/ TiO_2 -C catalysts, calculated per one surface Pd atom (TOF), is for $\text{TOF} < 1 \text{ s}^{-1}$ independent of Pd particle size and morphology of the supports.

C-doped TiO_2 hybrid hollow spheres were prepared from mixtures of furfural, chitosan or saccharose with titanium isopropoxide. The origin of the carbon influences the texture, the crystalline framework, and the optical and photoelectrochemistry properties of the TiO_2 . The results indicate that the carbon- TiO_2 hybrid hollow spheres may be used as TiO_2 -based film electrodes for use in solar cells [6]. The microwave-assisted solvothermal synthesis of C-doped TiO_2 and ZnO hybrid materials was also performed [7]. Saccharose, titanium isopropoxide and zinc acetate were used as organic and inorganic sources for the synthesis. The influence of temperature and reaction time on the textural and optoelectronic properties of the hybrid materials was verified. Carbon quantum-dots of TiO_2 and ZnO nanostructured spheres were obtained in a second pot by controlled calcination steps of the precursor hybrid materials. It was found a red-shift in the energy band gap of the semiconductors with values of 3.02 eV and 3.13 eV for the TiO_2 -C and ZnO-C, respectively, clearly lower than those on bare semiconductors, which is associated with the C-doping effect. From the photo-electrochemistry characterization can be concluded that the present materials have potential applications as photoelectrodes for quantum-dots sensitized solar cells.

Solvo- and hydrothermal synthesis by using biomass-derivative molecules opens a new, low cost and eco-friendly method for the preparation of high-performance applications.

References

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[7] Jose R. Rangel-Mendez, Juan Matos, et al. Applied Surface Science 434 (2018) 744-755.

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