

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room Hall B - Session PC+AS+BI+EM+NS+PB+SS-TuP

Processing and Characterization of Gas-Liquid, Solid-Liquid, and Gas-Solid Interfaces

PC+AS+BI+EM+NS+PB+SS-TuP1 Operando Photoelectron Spectroscopic Study of Copper-based Oxide Semiconductor Interface with Water, *Pitambar Sapkota, S. Ptasinska*, University of Notre Dame; *A. Cabrera*, Instituto de Física, Pontificia Universidad Católica de Chile

The quest for suitable semiconductor photoelectrodes to build efficient and stable photoelectrochemical (PEC) cells for solar water splitting is continually growing in the material sciences and solar energy community. Along with good stability in aqueous media, such photoelectrodes should have suitable band-edges and band-gap energies properly matching both the water oxidation-reduction potential and the solar spectrum, respectively. Copper-based oxide semiconductors are promising candidates fulfilling these criteria, but little is known about the interfacial properties of these compounds with H₂O under operational conditions. Therefore, knowledge of their surface dynamics and interfacial reactions under realistic conditions is essential to improve our understanding of water-splitting mechanism, as well as to increase the stability and efficacy of PEC devices. Ambient pressure X-ray photoelectron spectroscopy was used to characterize the semiconductor surface and study the chemical reactions occurring at the interface under the reaction conditions. In this study, thin films of CuFeO₂ and CuFe_{1-x}Ga_xO₂ composites were exposed to various H₂O pressures and temperatures. Water interactions with the Cu-based oxide surface and the electronic structures of the surface atoms were evaluated from the Cu 2p, Fe 2p, C 1s and O 1s photoemission spectra to identify surface species newly formed.

PC+AS+BI+EM+NS+PB+SS-TuP2 Interfacial Water in Silicon-based Catalytic Motors, *Jordi Fraxedas, K. Zhang, B. Sepulveda, M.J. Esplandiu*, Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; *X. Garcia, J. Llorca*, Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Center in Multiscale Science and Engineering. Universitat Politècnica de Catalunya, Spain; *V. Perez-Dieste, C. Escudero*, Alba Synchrotron Light Source, Spain

Self-propelled motors that can harvest chemical energy from their surroundings to convert it in mechanical energy are at the cutting edge of nanotechnology for their appealing applications in e.g., environmental remediation and nanobiomedicine. A full understanding of the propulsion mechanism is crucial to improve their performance and controllability. Recently, a simple motor made of silicon and a noble metal that can operate with visible light has been developed [1]. The photoactivation mechanism and consequent motion is essentially based on the formation of electron/hole pairs. The holes are strong oxidizing agents for the species in the fluid producing protons and the electrons can diffuse towards the metal surface and participate in the counterpart reduction reaction. As a result, a gradient of proton concentration is formed in the fluid which builds-up an electric field driving the motion of the fluid through electro-osmosis. A mechanism that competes with the electro-osmotic process is based on diffusion-osmosis and is triggered by the redox decomposition exclusively at the metal surface and is not light responsive. We have recently shown that it is possible to enhance/suppress one mechanism over the other by tuning the surface roughness of the micromotor metal. Thus, the actuation mechanism can be switched from light-controlled electrokinetics to light-insensitive diffusio-osmosis by only increasing the metal surface roughness [2].

We have recently performed near ambient pressure photoemission studies of Pt/Si micromotor surfaces activated by oxygen plasma in water atmosphere at the NAPP endstation of the CIRCE beamline at the ALBA synchrotron near Barcelona. We have used p-type silicon substrates with one half covered with a Pt film with a thickness of about 50 nm grown by both e-beam and sputtering deposition. The results reveal a chemical gradient at the Si/Pt edge with a reduction of the Pt species. The analysis has to carefully consider the photochemical reactions induced by the combined action of the impinging beam and the water condensed at the surfaces. The beam induced damage evolves in two regimes: an initial preferential reduction of Pt⁴⁺ species and then the reduction of Pt²⁺ species, which increases the metallic character of the surface.

[1] M.J. Esplandiu, A. Afshar Farniya, A. Bachtold, ACS Nano, 9, 11234 (2015).

[2] K. Zhang, J. Fraxedas, B. Sepulveda, M. J. Esplandiu, ACS Appl. Mater. Interfaces 9, 44948 (2017).

PC+AS+BI+EM+NS+PB+SS-TuP3 Chiral Modification of Oxide-Supported Pt Surfaces: An in-situ ATR-IR Study, *Yufei Ni*, University of California, Riverside; *F. Zaera*, University of California, Riverside

The synthesis of enantiopure compounds is of great significance to the designing of pharmaceuticals and agro products. Possible methods for the manufacture of enantiopure chemicals include the separation of racemic product mixtures and reactions with other chiral chemicals, but perhaps the most promising procedure is the use of enantioselective heterogeneous catalysis. Chiral modification of catalytically active metals such as Pt and Ni is believed to be the most feasible approach to produce chiral heterogeneous catalysts. In this context, the use of cinchona alkaloids-modified Pt for the hydrogenation of activated ketones has drawn particular attention in the past few decades. A better understanding of how these chiral modifiers work to bestow enantioselectivity is still a prerequisite for the design of such catalysts.

In this project, we have used attenuated total reflection infrared absorption spectroscopy (ATR-IR) to investigate the details of the adsorption of such cinchona-alkaloid chiral modifiers on the Pt surfaces of supported catalysts in situ at the liquid-solid interface. It was determined that adsorption can be only observed after H₂ pretreatment of the catalyst. A comparison study in terms of adsorption strength was carried out using not only cinchona alkaloids such as cinchonidine and cinchonine but also simpler alternatives such as (R)- or (S)-(-)-1-(1-naphthyl) ethylamine (NEA), naphthylmethyl amine, and dimethyl naphthyl ethylamine. The adsorption strength of the different modifier molecules was found to be quite different among those compounds. This is illustrated by the fact that quinoline can displace s-NEA from Pt but not vice versa, for instance, and by the observation that when Pt is exposed to a solution containing both quinoline and s-NEA only the quinoline's signature peaks can be detected by ATR-IR spectroscopy. The ordering of the modifiers studied in terms of adsorption strength was found to correlate with their ability to chirally modify the Pt catalyst during the hydrogenation of unsaturated aldehydes.

Finally, it was found that NEA bonds to the metal through the nitrogen atom of its amine moiety, and not through the aromatic ring as commonly believed.

PC+AS+BI+EM+NS+PB+SS-TuP4 Wettability Behaviour of Synthesized Carbon Nanospheres and its Application as a Photocatalyst, *Sonal Singhal, A.K. Shukla*, IIT Delhi, India

Superhydrophobic and superhydrophilic surfaces have been widely investigated due to their diverse range of applications such as self-cleaning, microfluidic application in biotechnology, corrosion, Anti-reflecting coatings and microelectronic mechanical system etc. Here, a facile chemical vapour deposition method is reported for the synthesis of carbon nanospheres (CNSs). Henceforth, the morphology of as-synthesized sample is characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD), Raman spectroscopy and FTIR spectroscopy are used to determine the phase purity, chemical composition and presence of chemical bonds on the surface of synthesized CNSs. TEM and SEM results reveal the presence of CNSs with a diameter ranging from 50 nm to 400 nm. Raman spectroscopy confirms the presence of disordered carbon and low graphitization, which are also confirmed by TEM and XRD results. Optical properties of as-synthesized CNSs is investigated by UV-Vis spectroscopy and photoluminescence. Wettability behaviour of as-synthesized carbon nanospheres is investigated by contact angle measurements. CNSs shows a water contact angle of 152°, which confirms the fabrication of superhydrophobic carbon nanosphere surface. After the proper explanation of wettability behaviour, it also discusses the application of as-synthesized CNSs as a photocatalyst. As it is well known, catalyst enhances the chemical reaction rate without changing its properties. Therefore, various kind of catalysts has been developed for the purpose to enhance the catalysis for environmental applications. Among different materials, carbon-based materials are widely used as a catalyst support due to their excellent properties. Considering these facts, the degradation of an organic pollutant under UV light is discussed here using CNSs.

Tuesday Evening Poster Sessions, October 23, 2018

PC+AS+BI+EM+NS+PB+SS-TuP5 Thermally Driven Solid-solid Li⁺ Transfer into Nanostructured TiO₂, *Tiffany Kaspar, T. Varga*, Pacific Northwest National Laboratory; *D.A. Shapira*, Advanced Light Source, Lawrence Berkeley National Laboratory; *A. Martinez, Y. Shin, K.S. Han, M.-S. Lee, S. Thevuthasan, V. Murugesan*, Pacific Northwest National Laboratory

Due to their good chemical stability, strong oxidation capability, and desirable lithium electrochemical activity, nanostructured titanium dioxide (TiO₂) anode materials have received considerable attention recently. Decreasing the particle size to 10-20 nm can increase the electrochemical capacity to 200-300 mAhg⁻¹. Furthermore, nanostructured TiO₂ anodes are non-toxic and would be suitable for cost effective mass production. Among the rutile, anatase, and brookite polymorphs of TiO₂, anatase nanoparticles have shown the best Li ion insertion properties and maximum reduction, indicating increased Li ion intercalation into the material. Here, we have synthesized 10-20 nm anatase TiO₂ nanoparticles and contacted them with solid Li- bis(trifluoromethanesulfonyl)imide (LiTFSI) as a function of temperature to understand the chemical and structural effects associated with thermally driven solid-solid Li⁺ transfer to, and intercalation in, TiO₂ nanoparticles. We have used a combination of x-ray photoelectron spectroscopy (XPS), Ti L-edge scanning transmission x-ray microscopy (STXM), Raman spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy to gain a fundamental understanding of the structural evolution of TiO₂ nanoparticles during Li⁺ intercalation. Our results indicate that thermally driven solid-solid Li⁺ transfer to TiO₂ has occurred, and altered the TiO₂ structure at the edges of the agglomerated nanoparticles.

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