

# Tuesday Afternoon, October 21, 2008

## Advanced Surface Engineering

Room: 204 - Session SE-TuA

### Photocatalytic Coatings

**Moderator:** P.H. Mayrhofer, Montanuniversität Leoben, Austria

2:40pm **SE-TuA4 Wettability Controlled Surface of Photocatalytic Coatings : Application for Dynamic hydrophobicity, T. Watanabe, N. Yoshida**, The University of Tokyo, Japan **INVITED**

Highly hydrophobic coating attracts much attention for long time as antifouling surface because it provides low energy surface whose interaction with contamination is smaller. Especially hydrophobic coating with photocatalytic oxidation capability is expected to become an ideal antifouling surface. According to Young, Dupre and Girifalco-Good equations, substances that can be highly hydrophobic are restricted to polymer material. Therefore it is usually hard to obtain highly hydrophobic thin film with TiO<sub>2</sub> photocatalyst because polymer material is oxidized by photocatalysis. Moreover TiO<sub>2</sub> photocatalyst itself is hydrophilicized by photo illumination. Due to such reasons, there are not many reports of hydrophobic coating with photocatalyst. However the situation can be dramatically changed when the concept of dynamic hydrophobicity is introduced. Parameter of dynamic hydrophobicity such like sliding speed or sliding angle does not depend on not only thermodynamic stable parameters but it strongly depends on surface microstructure. In fact, we have been investigating the dynamic hydrophobicity on self-assembled monolayer surfaces and found that the dynamic hydrophobicity is strongly affected by the surface roughness of only a few nanometers. Therefore if we focus on dynamic hydrophobicity, the inorganic substances can become potential candidates for having higher hydrophobicity by controlling surface roughness. Inorganic materials are hardly oxidized by TiO<sub>2</sub> photocatalysis, and this is a great advantage. Of course even though a high flat surface is obtained, a water droplet cannot form on the surface and the liquid does not slide off as a droplet. Therefore, we have to choose an inorganic material with the lowest possible hydrophilicity. Although most of the inorganic materials exhibit a higher surface energy as compared to organic materials, it was reported that HfO<sub>2</sub> is less hydrophilic. Therefore, we have prepared HfO<sub>2</sub> combined with a TiO<sub>2</sub> composite film and examined the water sliding angle of the surface. The result shows that the surface processed by the optimized preparation procedure shows a water contact angle of around 70° and a sliding angle of 30° are observed. This surface also shows high photocatalytic decomposability against IPA. Also very recently, we have obtained TiO<sub>2</sub> with highly dynamic hydrophobic surface by physical deposition process. It shows sliding angle of 17° and at the same time show fairly well photocatalytic activity.

4:00pm **SE-TuA8 The Role of Carbon in Anatase as Visible Light Photocatalyst, Y.J. Chen, G.Y. Jhan, M.S. Wong**, National Dong Hwa University, Taiwan

Titania is known as the favorable material as photocatalyst. However, the wide bandgap of titania limits its efficient utilization of solar light with most photon energies below the bandgap of titania. In this paper, we report that titania powders synthesized by low-pressure flat-flame metalorganic chemical vapor deposition shows high photocatalytic efficiency under visible light illumination. Using acetylene and oxygen as fuel and oxidizer for the flame, the titanium isopropoxide was decomposed and oxidized, and the nanoparticles of titania were formed. The phase of titania powder can be manipulated by carrier gas flow rate such that the higher the carrier gas flow, the higher the rutile content. From the methylene blue decomposition study we found that the powder with almost pure anatase phase synthesized under slightly oxygen deficient environment possesses best photocatalytic efficiency under illumination of visible light. The reaction rate constant is even higher than that of ST-01 titania powder, which is commercially available for photocatalytic applications. The visible light absorption is resort to the presence of carbon since no other chemical bonds not associated with carbon are chromophores. It also suggest that carbon species are associated with catalytic site on anatase surface so that carriers generated by photon absorption by the carbon species can transfer quickly onto catalytic sites and perform the subsequent catalytic reactions. Evidence will be provided to show that the carbon species does evolve with annealing, and the presence of carbon species is in coincident with the presence of visible light absorption.

4:20pm **SE-TuA9 Nb-doped TiO<sub>2</sub> Thin Films for Solar Energy Conversion, P.A. DeSario, K.A. Gray, M.E. Graham**, Northwestern University

A deeper understanding of synthesis, structure and function is needed to improve the design of materials tailored to solar energy conversion and storage. This study highlights the efficacy of reactive sputtering as a means to fabricate cation-doped TiO<sub>2</sub> films having controlled properties tailored to the generation of energy rich fuels such as CH<sub>4</sub> or CH<sub>3</sub>OH by photoreduction of CO<sub>2</sub>. It is our hypothesis that cation substitution in the TiO<sub>2</sub> lattice is an effective way to shift the photoresponse of the material further into the visible light region without deleteriously modifying its photochemical properties. Unbalanced reactive dc magnetron sputtering (UBMS) with partial pressure control of oxygen was utilized to synthesize a series of pure and mixed phase TiO<sub>2</sub> films. Films were doped with Nb to evaluate the effect of cation doping on optical, chemical and physical properties. Nb doping was achieved by altering a pure Ti target in a pieced manner by adding slugs of dopant material at regular intervals. The films were interrogated structurally and functionally using SEM, EDS, XPS, XRD and UV-vis spectroscopy. The ability of these materials to selectively and efficiently reduce CO<sub>2</sub> to energy rich fuels was evaluated in a gas phase reactor coupled with a GC/FID. While earlier work established the relationships between sputtering process parameters and the film structure, including phase identity and distribution in pure TiO<sub>2</sub>, this work is focused on how the addition of Nb cations in the range of 0-20%Nb change the film growth and phase formation relative to the pure material. The work also tries to characterize the cation valence and location in the TiO<sub>2</sub> lattice, but this is still under investigation. The parametric response of film structure still suggests that in the mixed phase system, greater energy input favors the formation of rutile and lower energy favors anatase, but the Nb additions shift the regions of phase stability compared to the pure TiO<sub>2</sub> case. The shift in optical absorption to the visible wavelength range as a function of Nb concentration and anatase-rutile phase distribution is also presented.

<sup>1</sup> L. Chen, et al., Fabricating Highly Active Mixed Phase TiO<sub>2</sub> Photocatalysts by Reactive DC Magnetron Sputter Deposition. *Thin Solid Films*, 2006. 515(3): p. 1176-1181.

4:40pm **SE-TuA10 Effect of Phase, Crystallinity and Carbon Content on Photocatalysis of Carbon-Doped Titania Films, P.W. Chou, Y.S. Wang, M.S. Wong**, National Dong Hwa University, Taiwan

Amorphous pure and carbon-doped titania films were prepared by reactive sputtering of titanium metal target and co-sputtering of Ti and carbon targets, respectively, in Ar and oxygen plasma. The as-deposited films were subsequently annealed in vacuum and in air. The influence of annealing atmosphere and temperature on the composition, phase and crystallinity of the films was systematically studied to understand their effects on photocatalytic activity. Both the pure and the carbon-doped films annealed in air transformed into anatase phase at 300°C and retained pure anatase phase even at 800°C; while those annealed in vacuum transformed into rutile/anatase mixed phase at 300°C and into pure rutile at 600°C. Carbon incorporation and oxygen deficient environment seem to favor phase transformation of amorphous titania to rutile at low temperatures in post-annealing.

5:00pm **SE-TuA11 Rules for Efficient Titania Coatings. Applications to Water, Air and Material Cleaning, J.-M. Herrmann, CNRS-Université de Lyon, France** **INVITED**

Photocatalysis concerns Fine, Green and Environmental Chemistry. Titania coatings must follow the rules of photocatalysis with the influence of 5 basic parameters governing the activity (mass of catalyst, wavelength, concentrations or partial pressure of reactants, temperature and radiant flux). Besides mild selective oxidations obtained by generating active neutral atomic O\* species in the absence of water, photocatalysis can detoxify inorganics in water by oxidizing them in their harmless upper oxidized state. Similarly, organic pollutants are totally oxidized in CO<sub>2</sub>. Complex molecules (pesticides, dyes, herbicides, insecticides) are totally destroyed as well as bacteriae (E.Coli, streptococcus faecalis) in water without re-growth. Air pollutants (VOC's, odors) can also be destroyed by cracking OH° radicals produced by UV-irradiated titania-coated supports. The applications concern domestic anti-odor refrigerators, electronics with a "molecular" purity of the ambient working atmosphere, the destruction of odors emitted by water treatment plants and solid waste landfills. Eventually, Virus H5N2, a model virus close to H5N1, responsible for the aviar flu, was totally destroyed in a contaminated air flux of 40 m<sup>3</sup>/h with a 99.93% efficiency in a single pass. Photocatalytic self-cleaning technology consists in depositing sub-micronic thin layers of titania at the surface of glass, metals, concrete, etc, whose photocatalytic activities are calibrated by test-reactions. In the real world, dirty materials, such as glasses, to be "self-

cleaned” are soiled by greasy and sticky deposits, which, in addition, induce a strong adherence of ambient dusts. The mechanism of self-cleaning glasses was elucidated by the mineralization of palmitic acid ( $n\text{-C}_{15}\text{H}_{31}\text{COOH}$ ), present in the human sebum and in the natural varnish of plants. It disappeared by successive “photo-Kolbe” reactions with photo-produced holes  $h^+$ . The linear hydrophobic aliphatic chains are progressively “peeled off,” carbon atom after carbon atom, via successive photo-Kolbe reactions. Palmitic acid degradation would require 16 of them. Fortunately, the overall self-cleaning glass process can be strongly accelerated by by-passing many intermediates via the release of several VOC’s in the atmosphere, quite innocuous for the environment. The efficiency of titania demands two requirements: (i) a good crystallinity (anatase phase) and (ii) a high (cationic) purity.

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