Topical Symposia
Room On Demand - Session TS4
Photocatalytic and Superhydrophilic Surfaces

TS4-1 Bixbyite-based Ta-N-O film: A Promising Candidate for Water Splitting?, ***Jiri Capek (jcapek@kfy.zcu.cz)***, *S. Batkova, S. Haviar, M. Matas, J. Houska,* University of West Bohemia, Czech Republic; *F. Dvorak,* University of Pardubice, Czech Republic

The Ta–O–N materials are an interesting group of materials that may provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). However, it is still a big challenge to prepare highly crystalline Ta–O–N materials in a form of a thin film mainly due to their very high crystallization temperature (800–900 °C).

In our research we utilize the advantages of high-power impulse magnetron sputtering in combination with film post-annealing in a vacuum furnace to prepare single-phase Ta–O–N thin films. Recently, during our work[1] dealing with monoclinic TaON films, fine-tuning of the elemental composition of the films led to a successful preparation of bixbyite-based Ta_2N_2O films. To the best of our knowledge, this material has not been yet reported. In this work, we present the way of preparation of the films and we investigate their properties with respect to the water splitting application. The optical band gap width of this material is 2.0 eV, allowing absorption of visible light up to 620 nm and the band gap is also well aligned with respect to the water splitting redox potentials (based on the ultraviolet photoelectron spectroscopy data). Furthermore, in this work we present and discuss results of carried out ab-initio calculations providing a closer insight into the band structure of this material. Finally, we also present preliminary results of the activity of these films based on electrochemical measurements.

[1] J. Čapek, Š. Batková et al., *Effect of annealing on structure and properties of Ta-O-N films*

prepared by high power impulse magnetron sputtering, Ceram. Int. 45 (2019) 9454.

TS4-2 Double Perovskite $LaFe_{1-x}Ni_xO_3$ Coating Urchin-like Golden Nanoparticles to Enhance Water Splitting Reaction, ***Hsiang-Wei Tsai (flylittlewei@gmail.com)***, *Y. Su,* National Cheng Kung University (NCKU), Taiwan

$LaFe_{1-x}Ni_xO_3$ (LFNO) has attracted considerable attention. Ni^{3+} is in the low spin state (t^6_{2g}, e^1_g) and the conduction band is formed by the hybridization of Ni^{3+} e_g orbitals and O^{2-}2p orbitals. Since the t_{2g} band is full and e_g electrons form the delocalized $\sigma*$band, it has no localized moments and exhibits Pauli para-magnetism above 50K. In this research, I used the 0.00 mol, 0.01 mole, 0.03 mole, 0.05 mole, and 0.07 mol Ni concentrations to dope into the $LaFeO_3$. As a fundamental understanding, the bonding strength between surface TM (transition-metal) 3d and O 2p states is considered to be the major factor that determines the intrinsic OER activity. The bonding strength between catalyst and adsorbate is predicted by the $E-E_f$ parameter (relative to the E_f), where the larger $E-E_f$ value, the greater the bonding strength because the larger $E-E_f$ indicates a low energy 3d state of TMs and would produce higher hybridization between the TM 3d and O 2p states due to the shortened energy distance. The d-band center close to the E_f can enable strong bonding between adsorbed oxygenated species and surface TMs, which promotes electron transfer and thus boost OER activity.

Furthermore, another my attempt is to improve the localized surface plasmon resonances with sea-urchin-like Au nanoparticles fabricated. Au–Ag alloy Nus (Nano urchin structure) are novel metal nanoparticles that have been employed as a SERS active substrate. Moreover, an individual Au–Ag alloy Nus exhibit a high density of nanotips, which could dramatically increase its surface area and bring more active sites, further enhancing its catalytic properties. The photocatalytic water-splitting into H_2 and O_2 is a direct solar-to-chemical energy conversion technology and has become a research hotspot globally. Photocatalytic H_2 production usually goes through a route that photoexcited electrons reduce the protons in solution to hydrogen atom chemisorbed on the catalyst surface and then desorbed into H_2. Finally, $LaFe_{1-x}Ni_xO_3$ is combined with sea-urchin like Au nanoparticles to be as the hetero-junctional photocathode. Due to LSPR, porous structures, and mixed secondary-phase, the water-splitting process is augmented under visible-light irradiation.

TS4-3 Effect of Tungsten-Substitution on the Structure and Photocatalytic Properties of Anatase TiO_2 Thin Films Deposited on Polymer by PECVD, ***William Ravisy (william.ravisy@cnrs-imn.fr)***, Université de Nantes, France; *B. Dey, S. Bulou, P. Choquet,* Luxembourg Institute of Science and Technology, Luxembourg; *N. Gautier,* Université de Nantes, France , France; *A. Goullet,* Université de Nantes, CNRS, France; *M. Richard-Plouet, A. Granier,* Université de Nantes, France

Whereas most coating techniques require a high-temperature step in order to crystallize TiO_2 as the anatase phase, it has been shown that crystallized TiO_2 could be deposited at $T \leq 130°C$ with a Plasma-Enhanced Chemical Vapour Deposition (PECVD) process, without further thermal treatment and thus allowing the use of thermally sensitive substrates.[1] These films exhibit a potentially high surface area, due to a columnar morphology, with anatase crystallization, which are two necessary features for efficient photocatalysis. However, photocatalytic activity is still limited by the value of TiO_2 band gap in the UV domain, allowing absorption of only 10% of the solar spectrum and hence restricting its efficiency as photocatalyst.

Among other possibilities to enhance properties of the TiO_2 thin films, substituting Ti with an alliovalent cation such as tungsten is expected to increase oxygen vacancies and shift the band gap energy toward higher wavelengths and ultimately to induce absorption in the visible range.[2][3]

In this work, W-substituted TiO_2 thin films have been deposited on Si and polymer substrates by Low-Pressure Low-Temperature PECVD. Titanium Tetraisopropoxide (TTiP) and Tungsten(V) Ethoxide were injected in a 400W radiofrequency inductively coupled oxygen plasma. W concentration was tuned by varying the flowrate of tungsten ethoxide carrier gas (O_2) or container temperature. All the 250nm-thick films were characterized by Raman and X-Ray Photoelectron Spectroscopy, X-Ray Diffraction, SEM and TEM to investigate their composition and nanostructure. The film growth was monitored by in situ spectroscopic ellipsometry. Photocatalytic activity was studied by measuring methylene blue decomposition in aqueous solution.

W concentrations were measured ranging from 1 to 14 at% and it was found that tungsten precursor was partly oxidized in the plasma phase from oxidation state V to VI. In the thin films, the columnar morphology is retained and anatase is still found although in quantities diminishing with W concentration. Moreover, preferential orientation of anatase growth is also impacted by the substitution with W cations. Finally, it was found that photocatalytic activity was significantly improved by tungsten substitution, especially at low amounts (<10%at).

[1] Li et al.*Appl Surf Sci***2019**, *491*, 116–122

[2] Kubacka et al. *Catal. Today***2009**, *143* (3), 286–292

[3] Ratova et al. *Coatings***2013**, *3* (4), 194–207

TS4-4 Photocatalytic Activity of a ZnO/Bi_2O_3 Thin Film Heterojunction, ***Sandra E. Rodil (srodil@unam.mx)***, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico; *A. Hernandez-Gordillo, M. Bizarro,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México; *J. Medina,* Instituto de Ciencias Aplicadas y Tecnologias, Universidad Nacional Autonoma de Mexico

Zinc oxide (ZnO) has been known as an outstanding photocatalyst in water treatment with an important performance in the degradation and mineralization of several organic pollutants with the use of UV radiation. Unfortunately, UV radiation only represents a small part of the solar light spectrum. A possible method to extend the functionality of ZnO into the visible light is the formation heterostructures with another semiconductor material. An adequate candidate is bismuth oxide (Bi_2O_3) which has appeared recently as a photocatalytic material with the advantage of working in the visible range. In this work, bilayers of ZnO/Bi_2O_3 were produced combining spray pyrolysis and magnetron sputtering techniques aiming to produce a visible-light active photocatalyst for the degradation of organic compounds. Firstly, ZnO thin film was sprayed on glass substrates and subsequently Bi_2O_3 dots were sputtered on this surface. The structural, morphological and optical properties were studied and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis spectroscopy as well as the chemical composition by X-ray photoelectron spectroscopy (XPS). The photocatalytic response was evaluated following the degradation of indigo carmine (IC) under UV and visible light. The results show that the photocatalytic activity under white light irradiation of the ZnO film was improved with the coupling of the Bi_2O_3 dots, attaining a superior mineralization degree compared with ZnO and Bi_2O_3 films separately. It was found that depending on the irradiation source, the production of hydroxyl or superoxide radicals is affected which promotes different degradation mechanisms of the IC molecule.

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