

Using Ice Crystals to Template Nanocavities on the Surface of Au Modified 2D TiO₂ Nanosheets: Visible Light Driven Water Splitting

Maria Caplovicova¹, Jakub Mares², Jakub Tolasz², Eva Koci², Snejana Bakardjieva^{2*}, Radek Fajgar³, Vera Jandova³

¹. Centre for Nanodiagnostics, STUBA, Vazovova 5, 811 07 Bratislava, Slovak Republic.

². Institute of Inorganic Chemistry of the Czech Academy of Sciences, 250 69 Rez, Czech Republic.

³. Institute of Chemical Process and Fundamentals of the Czech Academy of Sciences, Rozvojova 2/135, 165 02 Prague, Czech Republic.

* Corresponding author: snejana@iic.cas.cz

The production of hydrogen from water splitting by using sunlight has been accepted to be an environmentally friendly and inexpensive approach to solve the problems with emerging environmental related contaminants. The key to realize this process is to find an efficient and robust photocatalyst. Recently, two dimensional (2D) TiO₂ photocatalysts have attracted significant attention for photocatalytic water splitting in order of their complex properties including appropriate band structure, ultrahigh specific surface area and high number of active surface sites [1]. Additionally, TiO₂ is a low cost nontoxic material with high chemical stability. However, the application of TiO₂ for water splitting is limited by its wide band gap leading to the recombination of electrons and holes in the long travel distance to the surface of photocatalysts. An alternative to deal with these problems is to modify the TiO₂ by doping (for extension of adsorption wavelength into the VIS region), metal loading (for an efficient electron-hole separation) and introducing dense nanocavities in 2DTiO₂ nanomaterials [2].

Here we describe the advantages offered by cryo – lyophilisation technique as a smart and non-standard concept for making hollow (*nanocavity patterning*) 2D TiO₂ nanosheets decorated with Au nanoparticles (NPs) [3]. Hierarchical morphologies of nanocavities start to appear after annealing of lyophilized precursor at temperature higher than 500 °C [4]. The Au₂DTiO₂ *grate-like* structure supports integration of plasmonic (PL)/photonic (PC) surface effect and coupling to external VIS light is achieved *via* the synergistic interaction between Au (NPs) and hollowed 2D TiO₂ nanosheets. Our experimental results providing a promising approach to increasing [Au₂DTiO₂] activity for high electron utilization in hydrogen production from water splitting.

Figure 1 (a-b) displays BF and Z-contrast HAADF images of [Au₂DTiO₂]/800 sample annealed at 800 °C. A set of well-defined diffraction rings are observed in SAED pattern (Fig. 1c), which is in good agreement with the anatase. The lattice spacing $d_{(101)} = 0.354$ nm is close to TiO₂ (PDF 21-1272). Additionally, diffraction spots of Au were detected (PDF 04-0784). Fig. 1d shows dense regular polyhedral nanocavities inside the 2D TiO₂ nanosheets with size ranging from 5 to 78 nm in both, length and width, and depth of about 8 nm (Fig.1 c-d) [4]. The Au NPs with the size around 2-5 nm were anchored along the hollow patterned surface of the [Au₂DTiO₂]/800. We can suggest that cryogenic process is a hexagonal ice template process. The formation of crystalline hexagonal ice causes the Au₂TiO precursor to be expelled to the boundaries between adjacent ice crystals. Template removal by sublimation and annealing yields a nanocavited structure that is a replica of the original ice crystals (Fig. 1e-f). Detailed STEM observations revealed that Au NPs with a narrow size of 3 nm were embedded in the cavities of [Au₂DTiO₂]/800 and NPs interfaces (Fig. 2d).

Photoelectrochemical (PEC) study of the sample fixed on FTO glass substrates was performed. The cyclic voltammetry was measured between bias potentials -0.5 and $+0.5$ eV (Pt counter electrode, Ag/AgCl reference electrode in $0.5\text{M H}_2\text{SO}_4$). Under irradiation by visible light source, hydrogen generation on Pt and oxygen on working electrodes were observed (Fig. 2e).

References:

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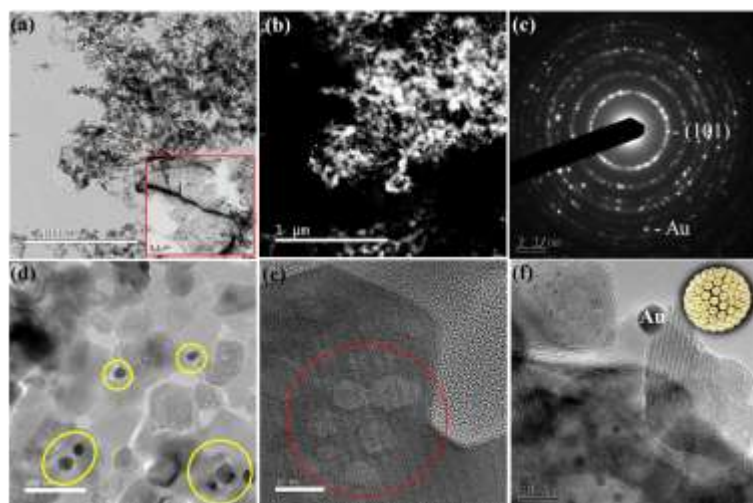


Figure 1. STEM observation of $[\text{Au}_2\text{D TiO}_2]/800$ (a) low MAG BF (b) HAADF images (c) SAED pattern (d-f) high MAG confirming nanocavities and homogeneously distributed Au NPs.

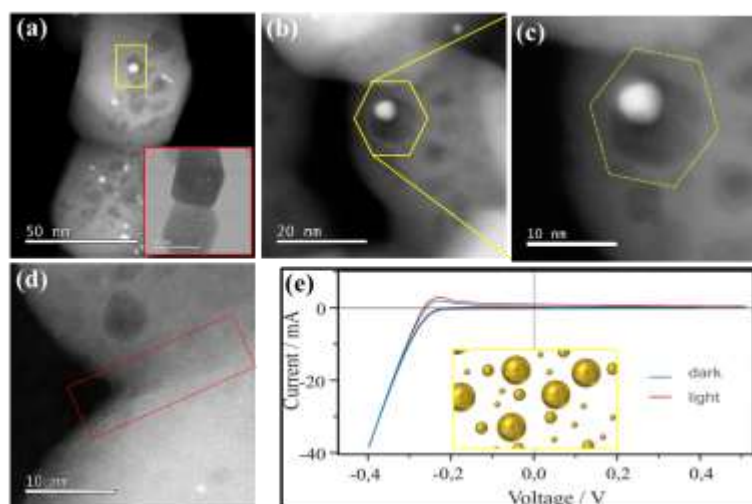


Figure 2. Z-contrast HAADF observation of $[\text{Au}_2\text{D TiO}_2]/800$ (a-c) Au NPs with a narrow size of 3 nm uniformly anchored in the cavities (e) PEC water splitting in VIS region.