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Plasmonic-Photonic Hybrids by Freeze-Casting: Ag decorated 1D and 2D TiO_2 Hollow Patterned Nanostructures for Green Photocatalysis

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Titania, in particular anatase TiO_2 has been extensively used in photoelectrochemistry (dye-sensitized TiO_2 electrodes for water splitting) and photocatalysis (TiO_2 based catalysts for degradation of emerging environmental substances). TiO_2 is the most studied photocatalyst because of its non-toxicity and chemical stability [1]. On the other hand, high recombination rate of the photogenarated electron-hole pairs restricts the photocatalytic activity of TiO_2 and novel strategies to design effective TiO_2 photocatalysts for enhanced light harvesting could be developed. Several reports have been announced to increase the lifetime of the generated electron-hole pairs by loading of noble, Ag metal nanoparticles (NPs) onto the TiO_2 surface, which can act as electron trapping centers.

In this work we demonstrated the capability of the ice-templating phenomenon, reported also as the ice-segregation-induced self-assembly (ISISA) process, for synthesis of Ag modified TiO_2 materials with highly sophisticated structures – $1DTiO_2$ microrods (MRs) and $2DTiO_2$ nanosheets - hierarchical materials demonstrating different levels of spatial organization. $1DTiO_2$ MRs and $2DTiO_2$ NSHTs with dense polyhedral stacked 3D nanovoids were prepared by using simple freeze-casting (a cryo-lyophilization) procedure [2, 3]. Hierarchical morphologies of nanocavities start to appear at temperature higher than 800 °C and are strongly influenced by polymorph TiO_2 evolution competing reactions.

The morphology of Ag modified $1DTiO_2$ sample annealed at 800 °C is shown in Fig. 1a-c. Photoelectrochemical measurements were conducted with deposited of as obtained sample on FTO glass substrates. The layer was then dried and fixed to the electrode surface by heating (500^oC, 1hr). The cyclic voltammetry was studied between bias potentials -0.5 and +0.5 eV with Pt counter electrode, Ag/AgCl reference electrode in 0.5M H_2SO_4 as an electrolyte. $2cm^2$ of the electrode surface with 0,66 mg of the deposited sample was irradiated by Vis light (100W). Efficient hydrogen generation on Pt and oxygen on working electrodes were observed (Fig. 1d). The best catalysts exhibited enhanced photocatalitic activity under UV light in decomposition of 4 chlorophenol was Ag modified 2D TiO_2 sample annealed at 800°C ($Ag\_2DTiO_2/800$). The photocatalitic activity of $Ag\_2DTiO_2/800$ sample, with nanocavities is much higher than that of TiO_2 without nanocavities. The extra ordinary photoactivity could be explained by evenly distributed nanocavities inside perfectly crystalized $2DTiO_2$ nanocrystals with homogeneously dispersed metallic Ag on their surface. Figure 2 revealed microstructure of $Ag\_2DTiO_2/800$.

References:

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[2] F Mamon et al. submitted to IUPAC Pure Appl Chem., 2018.
[3] S Bakardjieva et al. submitted to Appl Surface Sci., 2018.
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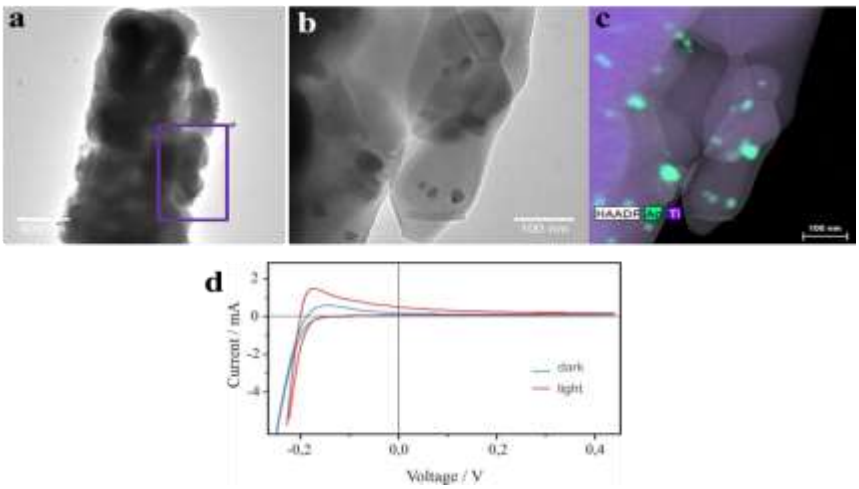

Figure 1. Ag modified 1DTiO$_2$ MRs obtained at 800°C (a-c) morphology by BF and HAADF detectors (d) voltammetry curve.

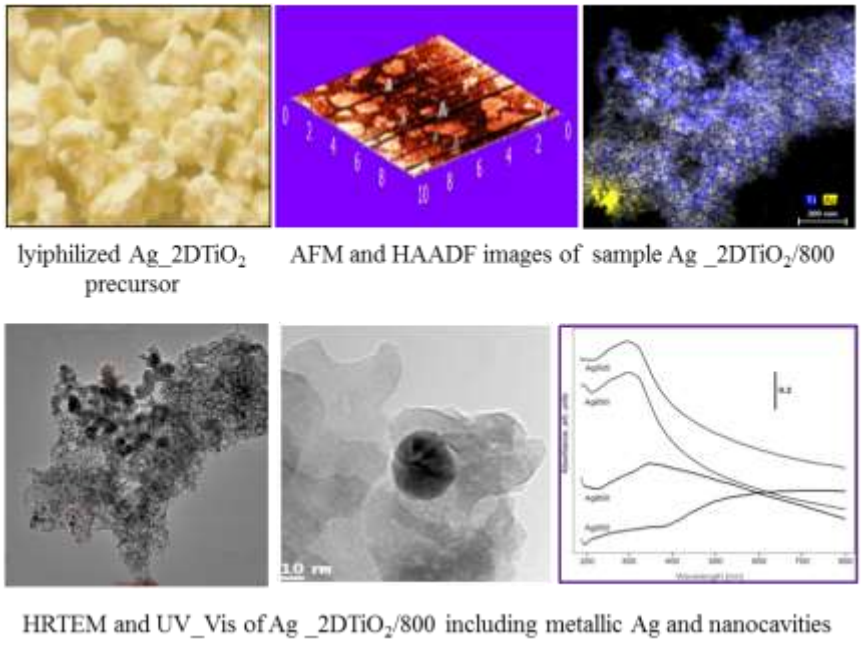

Figure 2. Digital image, AFM and HAADF observations (top row), TEM images and UV/Vis spectra of Ag modified 2D TiO$_2$ nanosheets obtained at 800°C (bottom row).

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