

Growth of Ag Nanoparticles on TiO₂ Thin Films Prepared by Laser Ablation for Visible-light Water Splitting

Mariana Klementová¹, Radek Fajgar², Lancok Adriana¹, Ladislav Fekete¹ and Snejana Bakardjieva³

¹FZU – Institute of Physics of the Czech Academy of Sciences, Prague, Hlavni mesto Praha, Czech Republic, ²Institute of Chemical Process Fundamentals of the CAS, Prague, Hlavni mesto Praha, Czech Republic, ³Institute of Inorganic Chemistry of the Czech Academy of Sciences, Husinec-Řež, Stredocesky kraj, Czech Republic

Water splitting using semiconductor photocatalysts has been viewed as a potential process for large-scale production of hydrogen from renewable resources. Here we present preparation and characterization of efficient water splitting system based on TiO₂ thin film covered with nanostructured Ag.

The samples were prepared by ArF laser ablation (193 nm, 100mJ/pulse) of TiO₂ and elemental silver targets. The ablation of the TiO₂, sintered at 1000°C was carried out in a turbomolecular vacuum (10⁻³ Pa) using a focused laser beam (9 min, 10Hz) to prepare a thin layer. The prepared layer was then covered by nanoparticles, prepared by laser ablation of Ag target at 4 Pa. The deposits were grown on quartz, Cu, glass, FTO and NaCl substrates. The samples were heat treated (500°C, 1 hr under air) to crystallize TiO₂ layer and to form Ag nanoparticles on the surface. Both samples, as-prepared and annealed, were studied by S/TEM/EDX (Tecnai TF20/EDAX), AFM, EDS, UV-Vis, and Photoelectron (Kratos ESCA 3400 with Mg Ka line) spectroscopies. The photocatalytic activity towards water splitting was tested by cyclic voltammetry (Keithley Model 2450).

The as-prepared deposits are greyish and have extremely high adhesion to all substrates. After annealing, the deposit changes the color and samples become pink with metallic luster. For the TEM, the samples were prepared on NaCl substrates to facilitate the sample preparation which was simply done by dissolving the substrate and placing the layered sample on a grid. The two samples have a distinct morphology (Fig. 1). The as-prepared sample is composed of amorphous TiO₂ decorated with cubic Ag particles with irregular shapes with the size in the range 10-100 nm. In contrast, the annealed sample is composed of crystalline TiO₂ (anatase) thin film decorated with sphere Au nanoparticles with the size in the range 20-40 nm homogeneously distributed on the TiO₂ surface. The particles often exhibit twinning on (111). The thickness of the supporting TiO₂ layer was measured by AFM. It is 40 nm for the as-prepared sample and 47nm for the aanealed sample.

UV-Vis spectrum of the sample was measured on the quartz substrate by transmission technique in the range 190 – 1100 nm (Fig. 2a). The material shows high absorption under 330 nm (TiO₂) and a very broad bump above 350 nm (Ag). The deposit was then annealed to 200-600°C and X-ray diffraction was measured. Formation of Ag nanoparticles was observed at temperatures 400-500°C, but increased temperature had no effect on crystallization. The UV spectrum shows strong absorption peak centered at 300 nm dominating the spectrum. Broad absorption changes to intense plasmonic Ag peak centered at 730 nm.

Bulk stoichiometry measured by EDS revealed atomic ratio [Ti]/[Ag] = 12.6. The XP spectrum shows prevailing Ag in the superficial layer of the as-prepared sample as proved by calculation of the elemental composition based on Ti 2p and Ag 3d regions (Fig. 2b). The atomic ratio is [Ti]/[Ag] = 0.22 for the as

prepared sample. Silver in the sample is present in the elemental form, but corresponding Ag 3d bands are broadened due to nanosize effect. The annealed sample shows higher [Ti]/[Ag] atomic ratio (1.20) due to coalescence of Ag and formation of bigger particles at 500°C. The bands are narrower, but additional shoulder proves two chemical states of silver. Deconvolution of the Ag 3d5/2 band revealed presence of elemental Ag with binding energy 368.0 eV and silver oxide (BE = 367.1 eV).

Photoelectrochemical measurements were conducted with deposits on FTO glass substrates. The cyclic voltammetry was studied between bias potentials -1.2 and +1.2 V with Pt counter electrode, Ag/AgCl reference electrode in 0.5M H₂SO₄ as an electrolyte. Under irradiation by visible light (100W), hydrogen generation on Pt and oxygen on working electrodes were proved by mass spectrometry technique. Much higher photochemical activity of the annealed sample was observed. (Fig. 2c) [1].

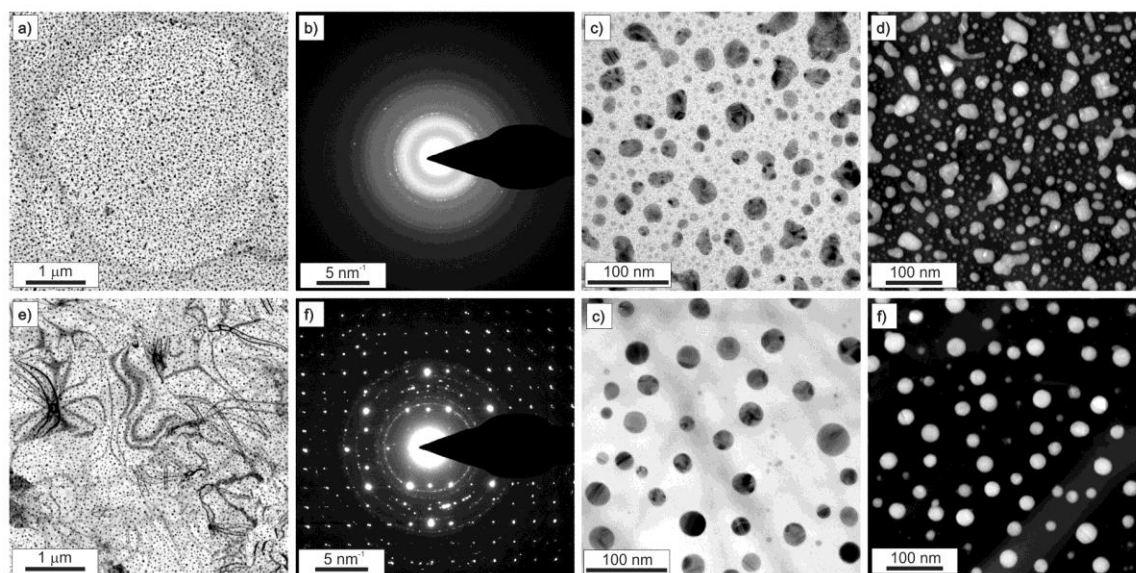


Figure 1. TEM and STEM observations of as-prepared (top-row) and annealed samples (bottom row).

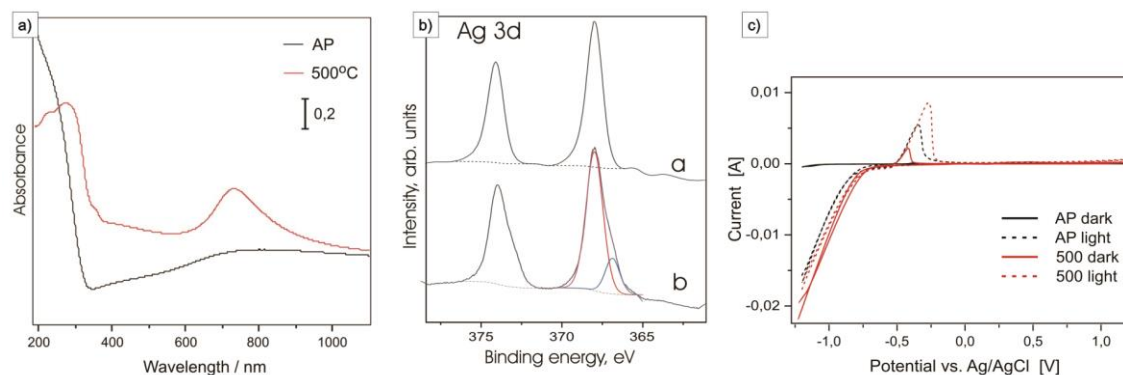


Figure 2. (a) UV-Vis spectra of the as-prepared (black) and annealed samples (red), (b) XPS spectra of the as-prepared (a) and annealed samples (b), (c) cyclic voltammetry curves of the as-prepared (black) and annealed samples (red).

References

[1] The authors acknowledge funding from the Czech Science Foundation (Project GACR 18-15613S).