

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

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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 Au.

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

The prepared deposits are blue-gray and have extremely high adhesion to all substrates. 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 very distinct morphology (Fig. 1). The as-prepared sample displays a eutectic-like structure of Au nanoparticles forming worm-like aggregates composed of nanoparticles with the size from a few nanometers up to 20 nm. The TiO₂ thin film supporting the gold structures is amorphous. In contrast, the annealed sample is composed of crystalline TiO₂ (anatase) thin film decorated with Au nanoparticles with the size in the range 10-100 nm homogeneously distributed on the TiO₂ surface.

UV-Vis spectra of the as-prepared and annealed samples were measured on the quartz substrates by transmission technique in the range 190 – 1100 nm (Fig. 2a). The as-prepared material shows high absorption under 360 nm (TiO₂), moderate absorption between 360 and 550 nm (titanium suboxides) and a very broad bump above 600 nm (Au). After annealing, the deposit changes and a strong absorption peak centered at 270 nm is dominating the spectrum. Broad absorption changes to plasmonic Au peak centered at 660 nm. The absorption in the middle region does not change due to preservation of suboxides.

The XP spectra were measured using Mg K α line (1253,6 eV, resolution 0.8 eV). The spectrum in the Au 4f region shows high concentration of elemental Au (Au 4f7/2 at 83.9 eV, Fig. 2b) in the superficial layer, while Ar⁺ sputtered surface reveals presence of Au⁺ at an Au/TiO₂ interface. Ti 2p bands are weak in the as prepared sample (Fig. 2c), but intense in the Ar⁺ sputtered layer and annealed samples. A single Ti 2p3/2 contribution located at 458.9 eV proves Ti⁴⁺ in the as-prepared superficial layer, while lower

oxidation states are present in the deeper layers.

Photoelectrochemical measurements were conducted with deposits on FTO glass substrates. 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 H₂SO₄ as an electrolyte. Under irradiation by visible light (100W), hydrogen generation on Pt and oxygen on working electrodes were observed. Higher photochemical activity of the as-prepared sample at higher negative potential is visible (Fig. 2d).

References:

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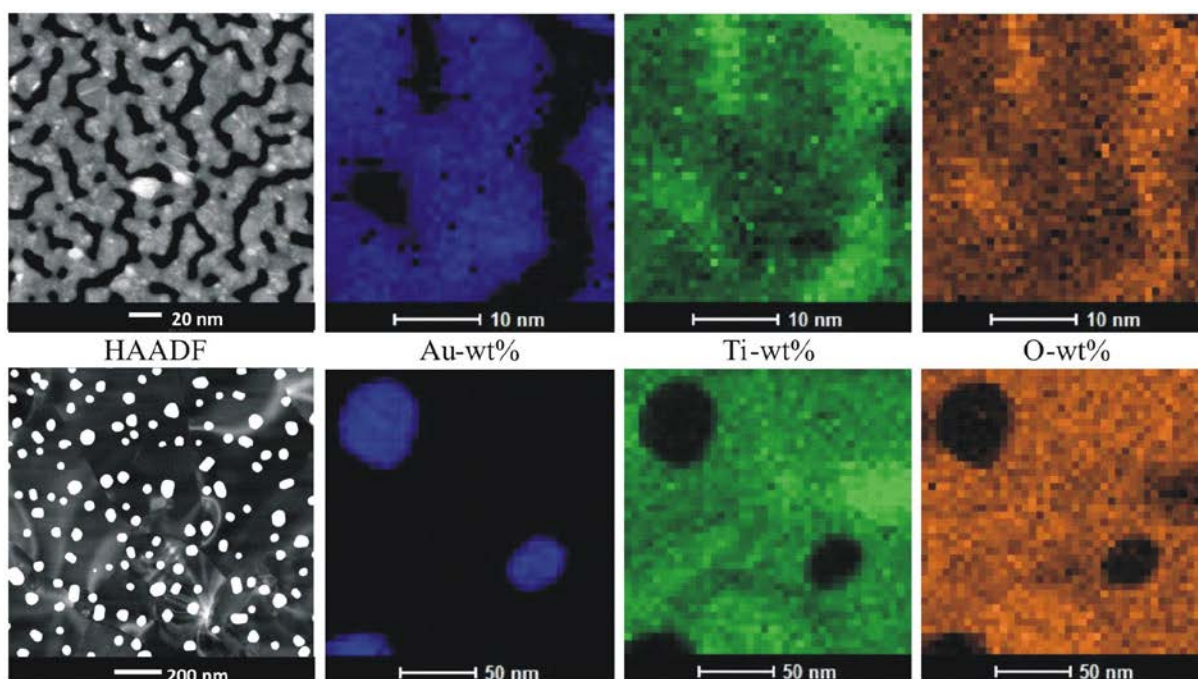


Figure 1. STEM and EDX observations of as-prepared (top row) and annealed samples (bottom row).

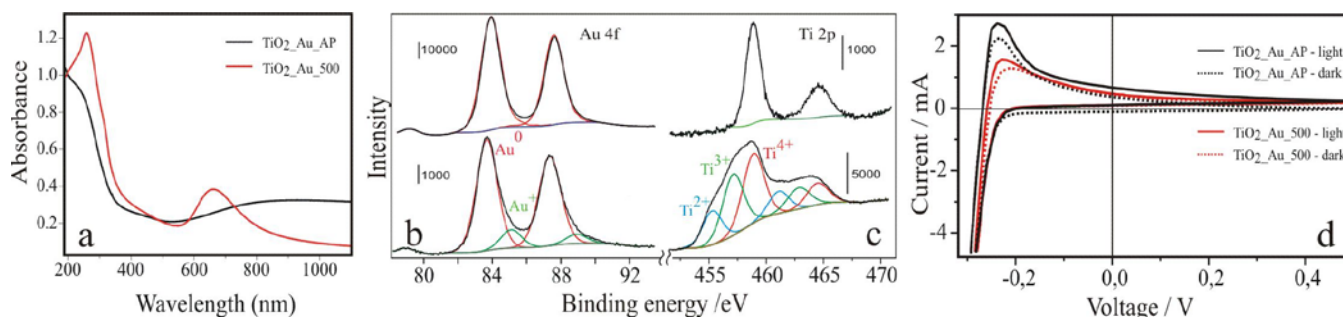


Figure 2. (a) UV-Vis spectra of the as prepared and annealed samples, XP spectra of the as-prepared sample in (b) Au 4f and (c) Ti 2p regions, (upper lines) and Ar⁺ sputtered sample (bottom lines) (d) cyclic voltammetry curves of the as-prepared and annealed samples.