

Morphological Characterization and Chemical Identification of TiO₂ Nanoparticles Doped with Ultrafine Metal Particles for Enhanced Photocatalytic Activity

Francesco Pellegrino^{1,2}, Valter Maurino² and Vasile-Dan Hodoroaba^{1*}

¹ Federal Institute for Materials Testing and Research (BAM), Division 6.1 Surface Analysis and Interfacial Chemistry, Berlin, Berlin, Germany

² Dipartimento di Chimica and Centro Interdipartimentale NIS, Università di Torino, Italy.

* Corresponding author: Dan.Hodoroaba@bam.de

In the next decades, the conversion of solar energy into electricity and solar fuels will be of crucial importance for a green and sustainable future [1]. The economic recovery after the pandemic will necessarily have to start by changing old paradigms with an energy transition towards renewable and clean sources. Considerable amounts of money will be invested for the energy transition, in particular to promote the production, distribution and use of hydrogen as an energy carrier. However, many challenges still remain to produce and exploit it in an efficient way, in particular the so-called “green hydrogen” [2].

In this context, water splitting using semiconductor photo-catalysts has been considered a sustainable method to produce clean hydrogen (H₂) fuel [3]. Nevertheless, H₂ photo-production efficiency remains still low, although extensive research effort has been carried out in these years about the mechanisms of the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER) [4]. In this respect, TiO₂ is a key photoactive material, usually employed with a co-catalyst deposited onto the surface to enhance charge carriers' separation and catalyze surface charge transfer reactions [5].

Irradiated slurries of metal-loaded TiO₂ can evolve H₂ through photoreforming of organic compounds [6]. Under irradiation, the Fermi level for electrons in TiO₂ becomes sufficiently negative to trigger H₂ evolution on catalytically active metal islands deposited on the surface. Therefore, the deposition of a co-catalyst on the TiO₂ surface represents a way to enhance the activity of the photocatalyst through a modification of its surface and redox properties [1]. A second approach, instead, studies the use of bare nanoparticles for understanding the peculiar reactivity of the unaffected TiO₂ facets [5]. Several works have deeply investigated the effect of different cocatalysts and of their amount as well as the role of exposed surface and morphology of TiO₂ nanoparticles in both the HER and the wastewater remediation. In this context, electron microscopy (coupled with chemical analysis) is fundamental for studying and understanding the effect of the nanoparticles morphology on the functional properties of shape controlled TiO₂ crystals. Moreover, a correct measurement approach of the electron microscopy analysis and the sample preparation are crucial for understanding the metal-semiconductor interaction during the photo-deposition. This interaction is crucial for the photocatalytic behavior of these materials.

The high-resolution capabilities of an SEM are well-suited for the accurate imaging of the TiO₂ nanoparticles of different shapes (bipyramidal, platelets or elongated), see Fig. 1 left [7]. For the visualization of the localisation of the ultrafine metal nanoparticles, a better Z sensitivity is given by the Everhart-Thornley detector, see Fig. 1 right, which as expected goes on the costs of a poorer morphological sensitivity. One can conclude that most of the Ag nanoparticles are found mostly at the edges (101 facets) of the TiO₂ nanoplatelets.

The nature of the bright spots of max 10 nm size has been identified by EDS as being Ag nanoparticles, see Fig. 2, taken in the point ID mode. Other types of metal-semiconductor combinations, TiO₂ shapes and dopant metal concentrations will be discussed.

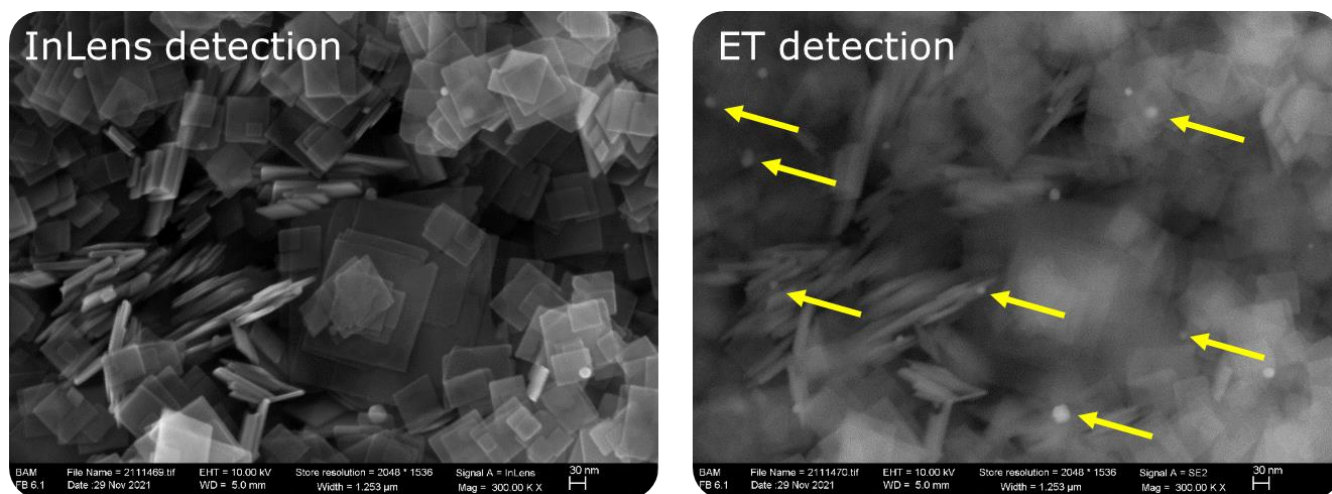


Figure 1. SEM micrographs of TiO₂ nanoplatelets doped with Ag ultrafine nanoparticles: left) SE InLens detection, right) with the Everhart-Thornley (ET) detector. Note the higher surface sensitivity and thus superior topography contrast with the SE InLens and the better Z contrast with the ET detector.

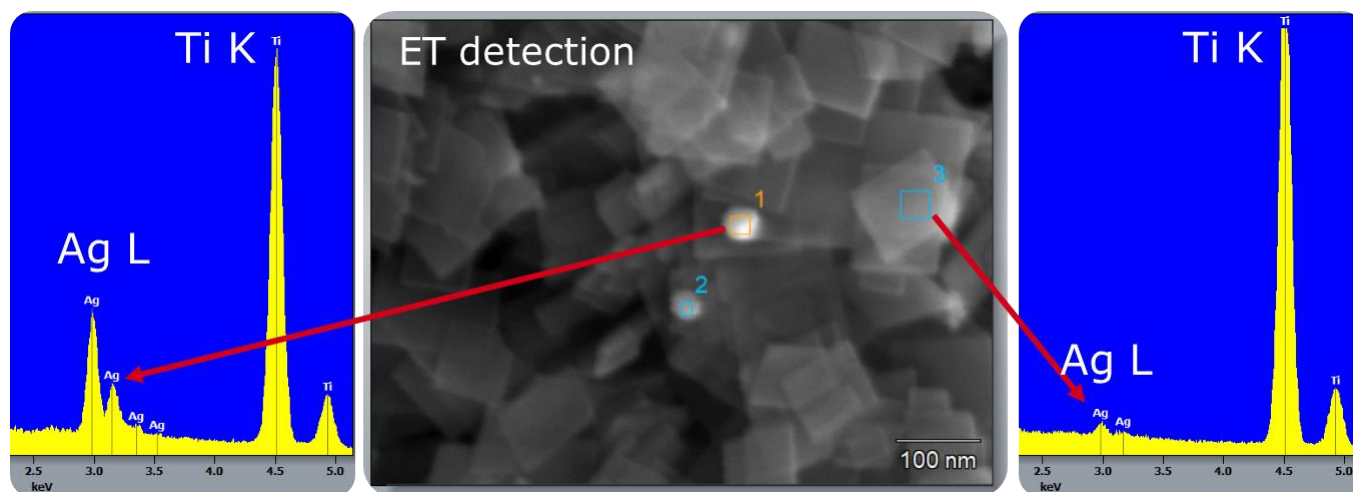


Figure 2. EDS point ID analysis of the metal-semiconductor nanoparticles from Figure 1. Note the clear presence of Ag in the marked location area '1' and minimal presence of Ag on a metal-free TiO₂ particle (area '3'), due to the slight co-excitation and fluorescence of the Ag ultrafine nanoparticles at sub- μ m distances.

References:

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