THE EFFECT OF DOPING AND LASER IRRADIATION ON THE PHOTOCATALYTIC WATER SPLITTING OVER TiO_2 NANOPARTICLES

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Designing New Heterogeneous Catalysts
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INTRODUCTION

- Photocatalysis with TiO_2 was applied successfully to several processes, including hydrogen production and decomposition of organic pollutants in air or in water[1].
- Recently, photocatalytic water splitting has attracted large attention because of its great potential for low-cost and clean hydrogen production[2].
- Loading of noble metals on TiO_2, doping with another oxide or modification by irradiation are some strategies for decreasing the band-gap of TiO_2 and enhancing its photoactivity[3].
- Here we report the effect of doping with CeO_2 or CuO and of laser modification in affecting the activity of TiO_2 towards the water splitting under UV or Vis irradiation.
- The role of different phases of TiO_2 and the presence of metal nanoparticles (Au or Ag), was also evaluated.

EXPERIMENTAL

- TiO_2 (Degussa P25)-Mixed Oxides catalysts (TiO_2-CeO_2 and TiO_2-CuO) were prepared by wet impregnation. The slurry was stirred for 4 h, dried at 120°C and calcined at 350°C for 4 h in air. The deposition-precipitation with KOH was used for synthesizing Au and Ag (1 wt.%)/support catalysts using $HAuCl_4$ and $AgNO_3$ as precursors.
- Laser modified TiO_2 P25 sample was obtained starting by a colloidal solution of TiO_2 in water subjected to a laser irradiation with a fluence of 300 mJ/cm^2, under continuous stirring. The second harmonic (532 nm) radiation of a Nd:YAG pulsed laser system was used.
- Photocatalytic tests were carried out in a Pyrex reactor irradiated by a UV or Vis lamp. An inverted water-filled burette in a water-filled vessel was used to monitor the evolved H_2. Catalyst was placed inside the photoreactor, with 100 mL of deionized water under stirring. The suspension was purged with a nitrogen flow for 30 min before irradiation in order to remove dissolved air.

RESULTS

- Photoactivity data (Fig. 1A) pointed out that the use of different TiO_2 phases and the presence of Au or Ag nanoparticles only slightly affect the performance.
- The doping with CeO_2 and, at higher extent, CuO (Fig. 1B) has a moderately positive effect in the H_2 production rate.
- The photoactivity strongly increases by laser modification: up to three times under UV irradiation (Figs. 1A-B) and two times under VIS irradiation (Fig.1C).
- The morphology and the structure of laser modified TiO_2 P25 was characterized by SEM and TEM (Figs. 2-3).
- The SEM imagine (Fig. 2) show two different groups of spherical particles that present a bimodal distribution centered at 25 and 200 nm.
- TEM analysis suggests the existence of amorphous phase due to the presence of defined contour and to the absence of internal order of the spherical particles (Fig. 3A).
- Another effect of laser irradiation is shown in Fig. 3B: after the laser process, crystals are more indented respect to the initial well-defined squared shape of the commercial product, as the crystals were evolving towards a nanorod structures. It is also evident an increasing of the porosity of TiO_2 nanoparticles that can be ascribed to the high pressure condition of the laser irradiation process.
- The major presence of Ti^{3+} defects in the TiO_2 laser modified sample in comparison to bare TiO_2 was detected by XPS measurements (Tab. 1) and was related to the blue color of laser-treated sample .

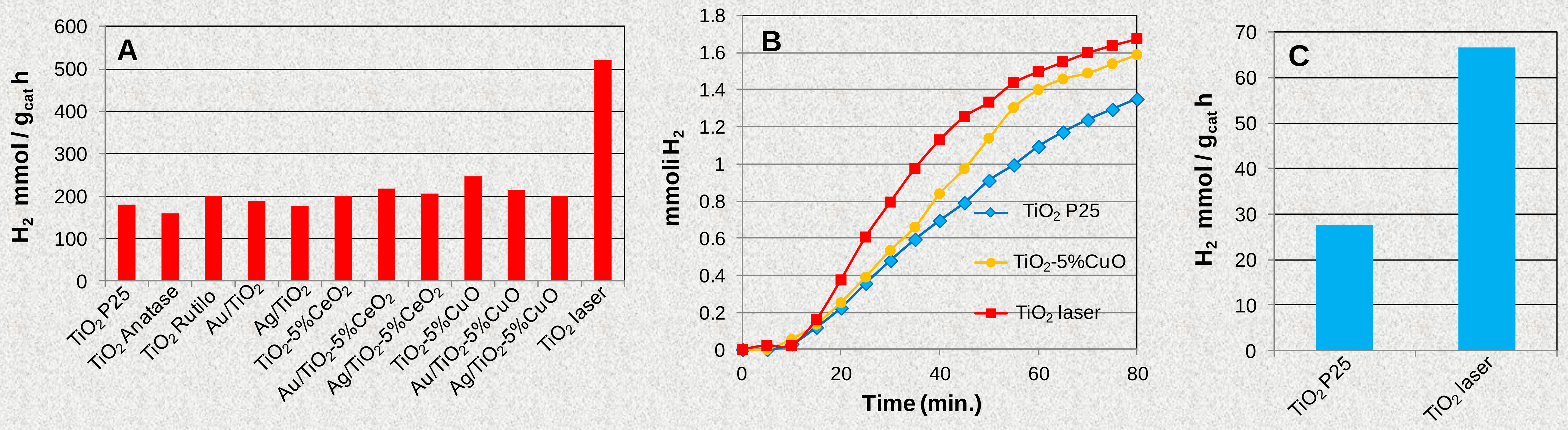

Fig. 1. *Photocatalytic H_2 production: (**A**) Comparison under UV irradiation; (**B**) H_2 generation rate under UV irradiation over best catalysts; (**C**) Comparison under Vis irradation.*

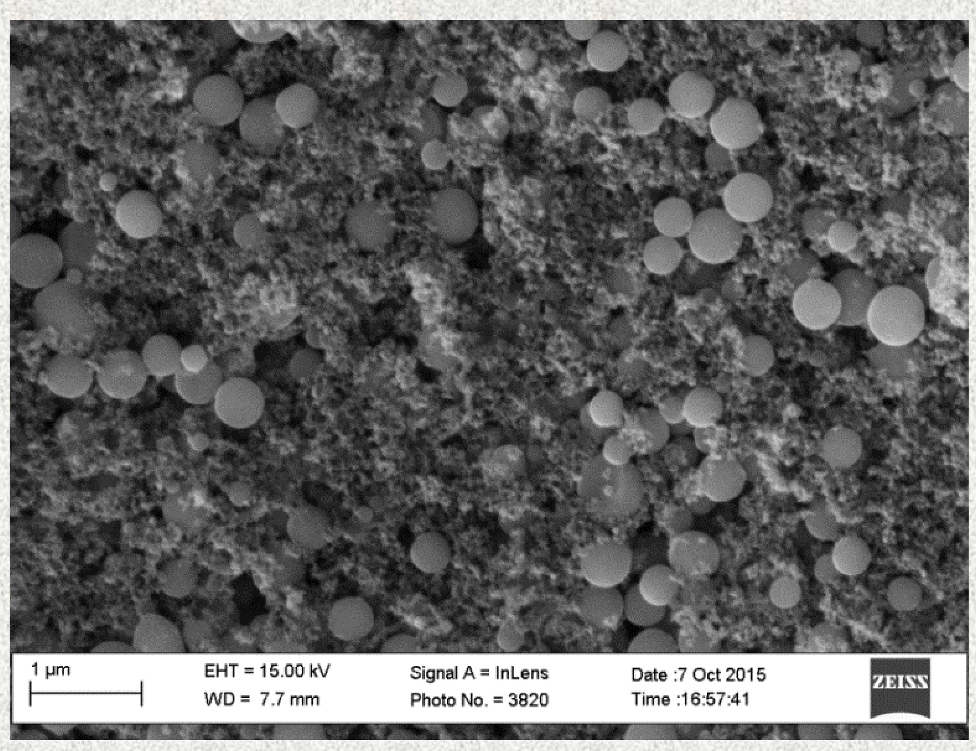

Fig. 2 *SEM Image of TiO_2 laser modified sample.*

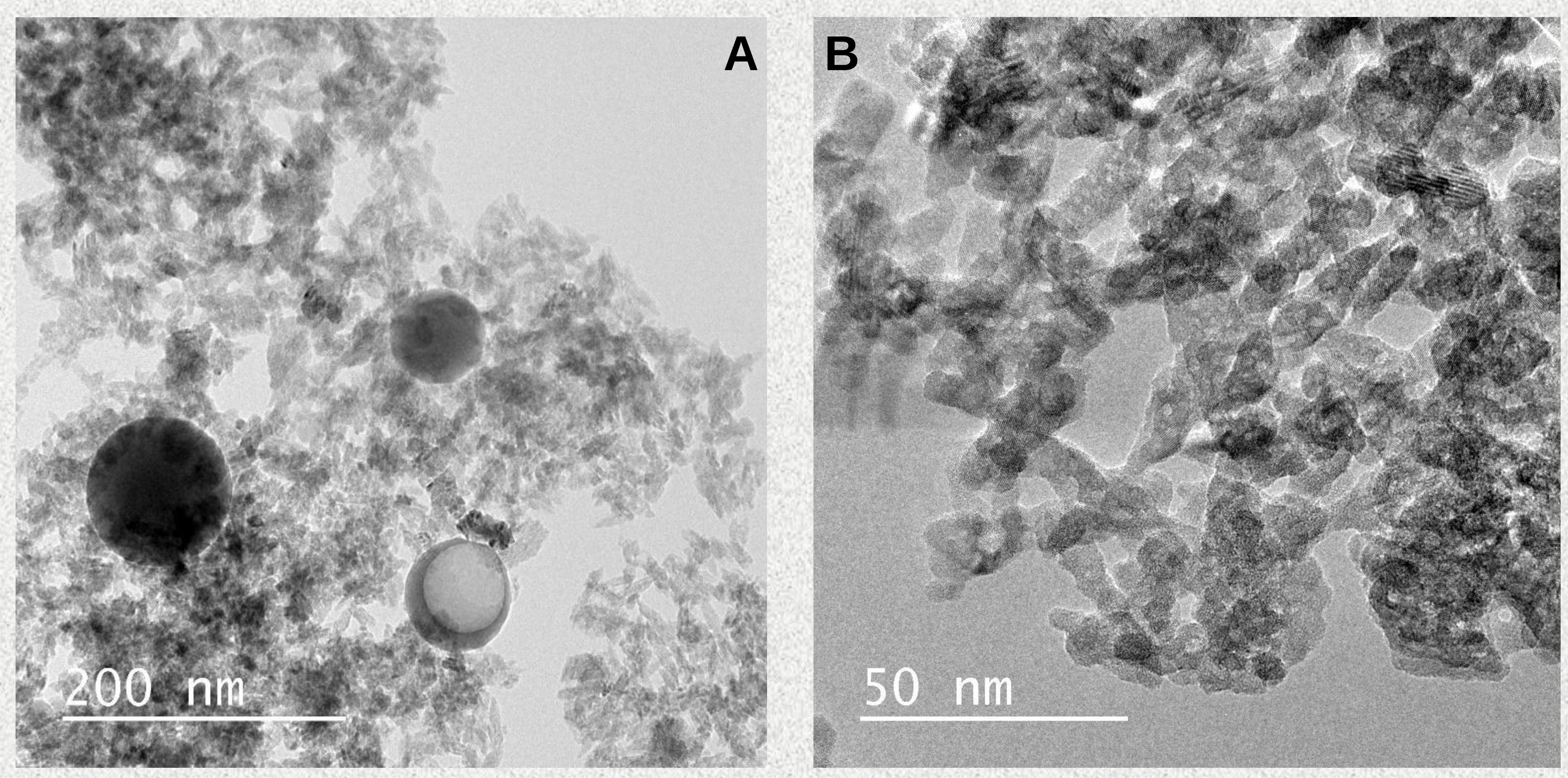

Fig. 3. *TEM images of TiO_2 laser modified sample: (**A**) Amorphous phase, (**B**) Formation of nanorods.*

Tab. 1 *XPS analysis of TiO_2 and TiO_2 laser sample.*

Catalysts	State	Species	Binding Energy (eV)	Atomic (%)
TiO_2 P25	Ti $2p_{3/2}$	Ti^{2+}	455.7	0.8
		Ti^{3+}	457.3	6.0
		Ti^{4+}	458.2	93.2
TiO_2 laser	Ti $2p_{3/2}$	Ti^{2+}	455.7	1.3
		Ti^{3+}	457.1	8.6
		Ti^{4+}	458.3	90.1

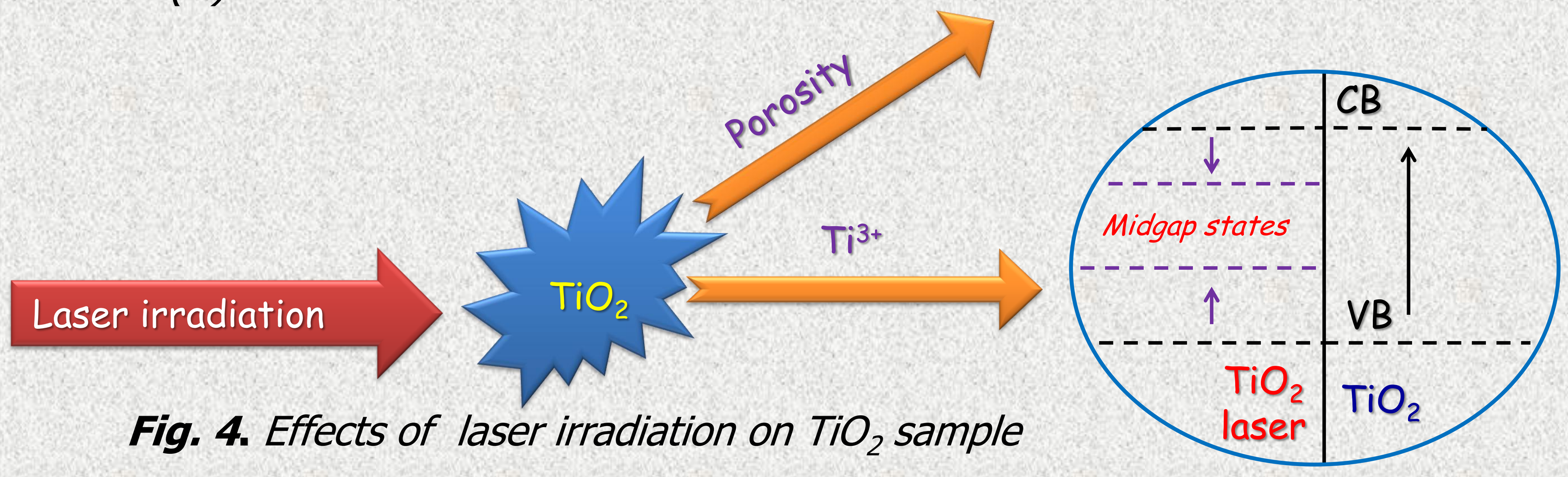

Fig. 4. *Effects of laser irradiation on TiO_2 sample*

CONCLUSIONS

- ✓ The TiO_2 laser modified sample is the most active system both under UV and Vis irradiation.
- ✓ The doping with metal NPs or another oxide does not change significantly the surface structure and the chemico-physical properties of TiO_2, whereas the laser treatment leads to deep modifications in the TiO_2 structure and morphology.
- ✓ Major effects of laser irradiation are the formation of Ti^{3+} defects and the improvement of porosity *(Fig.4).*
- ✓ The enhancement of photocatalytic performance is related to the presence of Ti^{3+} and disorder on the surface of TiO_2 nanorods with formation of midgap states between the VB and the CB of TiO_2[4].

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