

# Photocatalytic hydrogen evolution of transition metal sulfides deposited on TiO<sub>2</sub>: a structure-activity relationship of bifunctional catalysts

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## Abstract:

Nine transition metal sulfides deposited on titanium dioxide were tested for the photocatalytic dehydrogenation of isopropanol. Activities were compared based on photon yields and on the apparent activation energy for dihydrogen production. A structure-activity relationship of the bifunctional catalysts is discussed. Capacity to activate hydrogen, catalyst morphology and electrochemical behavior play a role in the activity. Another key parameter is the band alignment between the two semiconductors. Well-positioned valence bands and conduction bands enhanced the charge carrier separation.

**Keywords:** Photocatalysis, Transition Metal Sulfides, Photoelectron Spectroscopy.

## 1. Introduction

Since a few years, photocatalysis topics have moved from pollutants degradation to production of clean and renewable energy. Thus, dihydrogen (H<sub>2</sub>) can be obtained by photocatalytic water splitting or dehydrogenation of alcohol from biomass.

Titanium dioxide (TiO<sub>2</sub>) is a well-known photocatalyst. Deposition of semiconductor or metal co-catalysts on its surface enhances its efficiency. At the interface, a band alignment occurs and strongly influences electron transfer process. To this day, platinum supported on TiO<sub>2</sub> is one of the most efficient couple for HER. Because of platinum cost, alternatives are investigated. Transition metal sulfides (TMS) are potential candidates due to their ability to activate H<sub>2</sub> molecule as well as their semiconducting properties. Screenings of several TMS deposited on other semiconductors were already reported without clear understanding of the synergetic effects observed.<sup>1,2</sup>

## 2. Experimental

Nine different TMS were deposited on commercial anatase (CristalACTiV™ PC500): CoS<sub>x</sub>, NiS<sub>2</sub>, CuS, MoS<sub>x</sub>, RuS<sub>2</sub>, Ag<sub>2</sub>S, PtS<sub>x</sub>, FeS<sub>2</sub> and HgS following a soft route method already reported by Girel et al.<sup>3</sup> Photocatalyst loading was measured around 1.3 mol% by ICP-OES.

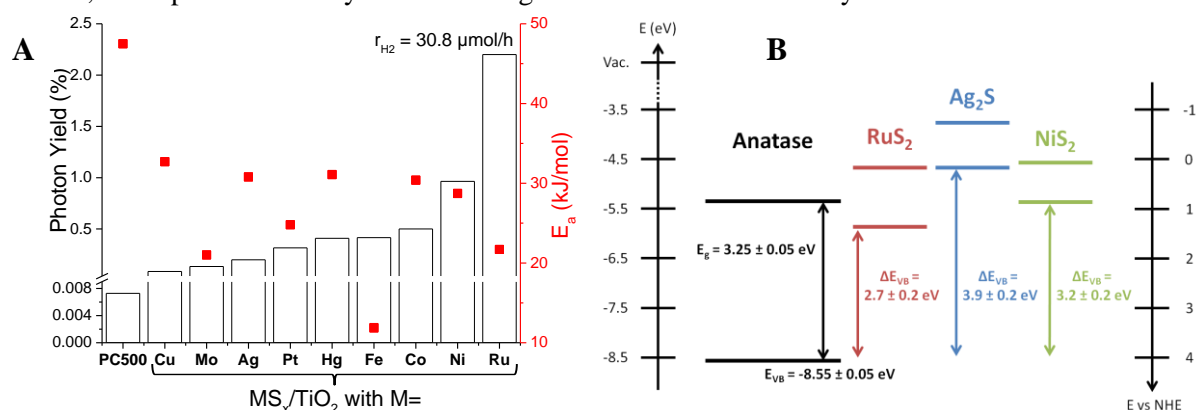
Photocatalytic HER performance was measured, at 10, 20, 35 and 45°C, in a double-wall batch reactor (50ml) loaded with 5 g/L of photocatalyst in an aqueous solution of isopropanol (50/50 %<sub>vol</sub>). A 125 W high-pressure mercury lamp is used as an incident light. Intensity of photons available for TiO<sub>2</sub> absorption is measured at 1400 μmol/h. Photon yield (PY) is calculated as the ratio between the hydrogen production rate and the photons intensity. Water recirculation in the double-wall controls photoreactor temperature.

For electrochemical measurements, samples are prepared using method described by Girel et al.<sup>3</sup> Apart from the electrolyte which is a 0.05 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. TEM analysis coupled with EDS was performed on a JEOL 2010 microscope. For XPS, a Kratos Axis Ultra DLD spectrometer is used with monochromatized Al K $\alpha$  radiation (1.486.6 eV). UPS measurements were made with a negative bias voltage applied to the samples with He I discharge (h $\nu$ =21.2 eV).

UV-vis absorption is done with a Fiber-optic Spectrometer (AvaSpec-2048 Avantes). Powders were diluted in BaSO<sub>4</sub>. A halogen deuterium lamp illuminates the sample. Optical fibers collect and transfer the diffuse light to a CCD detector. Kubelka-Munk function is calculated from the spectra and the band gap is determined at the intercept of the linear part of the curve with the x-axis.

### 3. Results and discussion

Figure 1. A shows the photocatalytic activity of the nine  $MS_x/TiO_2$  photocatalysts and their apparent activation energy ( $E_a$ ). For all of them, the PY is higher and  $E_a$  is lower than for  $TiO_2$  alone. Depending on the TMS, those parameters vary in a wide range. Reasons of this co-catalytic effect are discussed.



**Figure 1. A:** Photon yield determined at 20°C (black bar chart) and apparent activation energy (red square) for  $MS_x/TiO_2$ . Values for the support only are also given. **B:** Electronic structure for anatase phase and three of the nine co-catalysts:  $RuS_2$  (red),  $NiS_2$  (green) and  $Ag_2S$  (blue). Valence band are studied by UPS for  $TiO_2$  and by XPS for the  $MS_x/TiO_2$ .  $E_g$  are measured by UV-vis absorption.

Hydrogenation of organic compounds by TMS, reported in the literature, estimates the metal sulfides's ability to activate hydrogen. Photocatalytic activity is independent to this property. For instance,  $HgS$  is not claimed as good as  $MoS_2$  in hydrogenation reactions but it is a better photocatalyst ( $PY_{HgS/TiO_2} = 3 PY_{MoS_2/TiO_2} = 57 PY_{TiO_2}$ ). TEM analyses show that small and well-dispersed TMS particles are suited to separate efficiently charge carriers and thus, to be more active. Electrochemical measurements also reveal that best co-catalysts have a good conductivity but again, it is a necessary condition not a sufficient one.

More efforts were made to study the electronic band alignment of  $MS_x/TiO_2$  architecture. Two preparation methods for studying powder photocatalyst by UP Spectroscopy are reported. It permits to investigate real material and to take into account potential defects. UPS measurements of  $TiO_2$  deposited on an ITO substrate or on a silver foil give an absolute measurement of  $TiO_2$  valence band maximum. XP spectra of  $MS_x/TiO_2$  (M=Ru, Ag, Ni) powders combined with Kraut method gives the highest occupied state for each co-catalyst relatively to the one of the anatase.<sup>4</sup>

UV-vis absorption measurements provide more details about the electronic structure of  $MS_x/TiO_2$  and especially their optical band gap. Band alignment for  $RuS_2/TiO_2$ ,  $Ag_2S/TiO_2$  and  $NiS_2/TiO_2$  were thus determined with accuracy (Figure 1. B). Instead of  $Ag_2S$ , conduction and valence bands of  $NiS_2$  and  $RuS_2$  are well-positioned. Photogenerated carriers can migrate from one semiconductor to the other. Those TMS enhance charge carrier separation and increase photocatalytic efficiency (See Figure 1. A).

### 4. Conclusions

$MS_x/TiO_2$  are promising photocatalysts for alcohol dehydrogenation. Among the nine TMS reported in the present work, all of them have a co-catalytic effect on the  $TiO_2$ . Activity of the photocatalyst depends of the TMS phase because of their intrinsic properties. Co-catalytic particles must be small, well-dispersed, with a good electrochemical behavior. Relative position of the TMS electronic bands will enhance charge carrier separation and thus, the photocatalytic efficiency. The aim is now to find the optimal electronic structure to improve the efficiency of  $MS_x/TiO_2$  photocatalysts.

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