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## Evaluation of the plasmonic effect of Au and Ag on Ti-based photocatalysts in the reduction of CO<sub>2</sub> to CH<sub>4</sub>

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### ABSTRACT

Crystalline TiO<sub>2</sub> (P25) and isolated titanate species in a ZSM-5 structure (TS-1) were modified with Au and Ag, respectively, and tested in the gas-phase photocatalytic CO<sub>2</sub> reduction under high purity conditions. The noble metal modification was performed by photodeposition. Light absorbance properties of the catalysts are examined with UV-vis spectroscopy before and after the activity test. In the gas-phase photocatalytic CO<sub>2</sub> reduction, it was observed that the catalysts with Ag nanostructures are more active than those with Au nanostructures. It is thus found that the energetic difference between the band gap energy of the semiconductor and the position of the plasmon is influencing the photocatalytic activity. Potentially, plasmon excitation due to visible light absorption results in plasmon resonance energy, which affects the excitation of the semiconductor positively. Therefore, an overlap between band gap energy of the semiconductor and metal plasmon is needed.

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### 1. Introduction

The scarcity of fossil fuels and the increasing atmospheric CO<sub>2</sub> level necessitate the development of new strategies for providing the humanity with renewable energy sources. Photocatalytic CO<sub>2</sub> reduction bears the possibility to synthesize basic chemicals such as CH<sub>4</sub> with the help of a semiconductor catalyst and (UV-) light. This artificial photosynthesis enables the formation of mobile energy sources while CO<sub>2</sub> is reduced [1]. A multiplicity of photocatalytic systems have been tried, but TiO<sub>2</sub> is still the most studied and promising material [2]. Unfortunately, the photocatalytic reduction of CO<sub>2</sub> with bare TiO<sub>2</sub> as the photocatalyst shows insufficient activity for an industrial application.

Various strategies for improving the activity of TiO<sub>2</sub> have been tried [3,4]. Most of the modifications try to achieve an increase in the visible light absorption properties, for instance (non-)metal ion doping [4,5]. Furthermore, suppression of the charge carrier recombination is another goal of photocatalyst modification [6]. Another approach is the use of plasmon-active particles, for instance Au and Ag [7–12]. In recent studies it has been shown that Au and Ag nanoparticles enhance the photocatalytic activity

of TiO<sub>2</sub> [8,13–20]. Tsukamoto et al. [15] modified rutile/anatase interfaces with Au nanoparticles for photocatalytic oxidation of organic molecules. They found visible light activity of their modified Au/TiO<sub>2</sub> materials [15]. Chen et al. [16] investigated Au/TiO<sub>2</sub> in the photocatalytic H<sub>2</sub>O splitting. They observed an enhanced formation of H<sub>2</sub> when TiO<sub>2</sub> was loaded with Au. The reason for the enhancement of photocatalytic activity could be the high “optical activity” [21], a term that the authors used to describe the excitation of plasmon resonance by light irradiation. Plasmon resonance can be described as a photon-induced resonant collective oscillation of valence electrons. Excitation takes place when the photon frequency matches the natural frequency of the oscillating surface electrons. The resonant photon wavelength is a function of the type of the employed metal nanoparticles [21] and the plasmon properties can be influenced by shape, size and the surrounding environment of the nanoparticle [21–24].

It is questionable how a plasmonic nanostructure can enhance the activity of a photocatalyst. Charge carrier transfers between the semiconductor and the plasmonic nanostructure is one potential explanation. On the one hand it has been argued that photo activated electrons in the plasmonic particles are transferred into the semiconductor [15,25,26]. On the other hand, it is assumed that photogenerated electrons in the semiconductor migrate to the plasmonic nanoparticle. The outcome of these processes are an efficient charge separation and therefore an improved lifetime of charge carriers which increases the photocatalytic

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activity [16,20,22,27]. In addition to electron transfer processes it is assumed that the intense plasmon resonance that is induced by an electromagnetic field of the plasmonic nanostructure can interact with the semiconductor, leading to an enhanced electron hole pair formation in the semiconductor [6,23,27]. In this sense it has been observed that the photocatalytic activity is predominantly improved in those cases where an overlap between the band-gap absorption and the plasmon resonance occurs [6,21]. A further explanation is an improved reaction rate due to the conversion of light energy into thermal energy by the plasmonic nanostructure [28].

To study the influence of plasmonic nanostructures in photocatalytic CO<sub>2</sub> reduction, P25 and TS-1 were modified with photo-deposited Au or Ag nanoparticles in this study. The optical properties and their activity in the photocatalytic CO<sub>2</sub> reduction to methane were tested under conditions of the highest purity.

## 2. Experimental

### 2.1. Sample preparation

Sample modification was performed with the photodeposition technique. The photodeposition of Ag and Au onto P25 and TS-1 was carried out in a semi-batch reactor. A 700 W Hg immersion lamp, installed in the center of the reactor, was used as irradiation source. During photodeposition the concentration of CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub> in the exhaust gas were detected by a non-dispersive IR photometer, a paramagnetic and a thermal conductivity detector (XStream, Emerson Process Management) [29]. 350 mg of P25 or TS-1, respectively, was dispersed in 550 mL distilled H<sub>2</sub>O and 50 mL methanol. In the following the reactor was deaerated with pure N<sub>2</sub> for 45 min. Afterwards 3.5 mL of a 1.5 × 10<sup>-3</sup> molar HAuCl<sub>4</sub> solution, or 3.5 mL of a corresponding 1.5 × 10<sup>-3</sup> molar AgNO<sub>3</sub> solution were added to the suspension. Another purging process with pure N<sub>2</sub> followed, before the light source was started. The photo-deposition was performed at 30 °C for two hours. Afterwards the material was filtered and dried overnight.

### 2.2. UV-vis spectroscopy

UV-vis experiments were used to investigate light absorption properties of the samples. The measurements were performed with a LAMBDA 650 Spectrometer and a praying mantis diffuse reflection accessory. Diffuse reflection was measured in a range between 200 and 800 nm.

### 2.3. STEM and XRF

TEM analysis has been performed to determine the noble metal particle sizes. The measurements were performed with a Hitachi HD-2700 STEM. In this set-up a Cold FEG (200 kV) is used as the cathode and a EDAX Octane T Ultra W EDX-System is used as the detector. The deposited amount of noble metal was measured with XRF using a Niton XL3t from ThermoFisher at the 'Deutsches Bergbau Museum Bochum'.

### 2.4. High-purity gas-phase photoreactor

The photocatalytic CO<sub>2</sub> reduction experiments were carried out in a high-purity gas-phase photoreactor set-up. A detailed description of the set-up was given by Mei et al. [18]. In brief, the reactor is made from stainless steel components for ultra-high vacuum applications. All tube connections are realized by VCR fittings. For this reason, all sealing materials are grease-free. The sample is spread as a loose thin powder film inside a quartz petri dish (diameter ~3 cm) which is placed in the center of the reactor. Gas supply is realized by mass flow controllers, which introduces

the 1.5% CO<sub>2</sub>/He mixture to the reactor. H<sub>2</sub>O enrichment of the gas-phase is realized with a temperature-controlled metal-sealed stainless steel saturator. The irradiation is performed with a 200 W Hg/Xe lamp. A water-based filter is used for the removal of the IR radiation from the lamp spectrum. Product analysis is performed with a Shimadzu GC 14B and a Tracera GC 2010 plus, respectively. The GC 14B is equipped with a flame ionization (FID) and thermal conductivity (TCD) detector. This system allows gas phase analysis of C<sub>1</sub>–C<sub>5</sub> hydrocarbons in the low ppm range. It is possible to perform four gas chromatographic measurements during an experiment of six hours. The Tracera GC is equipped with a barrier discharge ionization detector (BID) and allows gas phase analysis in the 0.1 ppm range. This GC enables nine gas chromatographic measurements during an experiment of 6 h.

### 2.5. Sample pretreatment

Unless otherwise noted, 50 mg of each photocatalyst have been employed for each measurement. Before investigating a sample in the photocatalytic CO<sub>2</sub> reduction it is necessary to clean the sample from carbon-containing species, which originate from the sample synthesis and photodeposition for noble metal modification. These species could react to hydrocarbons under photocatalytic conditions and thus contribute to the product formation, which would then be overestimated. This cleaning step is performed in the high-purity gas-phase photoreactor. It is possible to perform the cleaning step in batch mode or in flow mode. The latter means that H<sub>2</sub>O enriched He (purity 99.9999%) is flushed through the reactor while the light source irradiates the sample. The flow mode cleaning is more efficient. Unfortunately, the flow conditions do not allow gas chromatographic measurement. Gas chromatographic analysis is only possible in the batch mode. Consequently, monitoring the cleaning progress requires a subsequent cleaning step in batch mode. Thereby, the reactor is filled with H<sub>2</sub>O enriched (~6000 ppm H<sub>2</sub>O) He until the pressure increased up to 1500 mbar. Then the irradiation is started for 6 h. It is possible to perform 9 gas chromatographic measurements in this period of time.

### 2.6. Photocatalytic CO<sub>2</sub> reduction

The CO<sub>2</sub> reduction experiment is performed in batch mode. The gas chromatographic analysis interval and the experimental conditions are similar to the batch cleaning procedure except that CO<sub>2</sub> is also added to reaction mixture and fed into the reactor. So the gas-phase of the reactor consists of 1.5% CO<sub>2</sub> and ~6000 ppm H<sub>2</sub>O as the reactants in ultrapure He (99.9999%).

## 3. Results and discussion

### 3.1. Hydrogen evolution during metal nanoparticle photodeposition

In Fig. 1 the effluent amounts of H<sub>2</sub> during photodeposition of Au and Ag on P25 and TS-1 are presented. It can be seen that there was H<sub>2</sub> evolution during photodeposition of Au on P25, after the light source has been started at 1000 s. For all other samples, there was no H<sub>2</sub> evolution observable. After 6000 s irradiation, the H<sub>2</sub> evolution of Au/P25 seems to be fairly stable.

First of all, it is implausible to attribute the lack of H<sub>2</sub> evolution to an unsuccessful photodeposition, because the UV-vis spectra clearly show the plasmon of Ag and Au on P25 and Au on TS-1 (Fig. 4).

In general, the metal cations of the precursor are the sacrificial agents for the photogenerated electrons. Formation of H<sub>2</sub> is possible when H<sup>+</sup> is reduced by photogenerated electrons. The choice of

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