



Understanding promotion of photocatalytic activity of TiO₂ by Au nanoparticles



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ABSTRACT

Au nanoparticles prepared by deposition–precipitation were evaluated in promoting photocatalytic activity of TiO₂ (P25) in the oxidation of methylcyclohexane. At 375 nm and in particular at 425 nm, Au was found to significantly enhance the rate induced by P25. Illumination of Au-promoted P25 at 525 nm did not result in any measureable activity. To validate whether the enhancement at 425 nm is purely catalytic, or if plasmonic effects are relevant, we compared the rates of Au/TiO₂ with Pt-promoted TiO₂ at 375 and 425 nm. At 375 nm, Pt nanoparticles induced larger catalytic effects than Au nanoparticles, whereas the rate enhancement induced by Pt was much lower than of Au at 425 nm. We assign the thus demonstrated Au based plasmonic phenomena at 425 nm to the so-called plasmon resonance energy transfer, rather than to hot electron transfer, given the absence of activity at 525 nm.

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1. Introduction

TiO₂ is by far the most studied metal oxide photocatalyst, and many ways of manipulating the bulk and surface composition have been reported in the literature to enhance the activity [1–5]. Modifications are generally aimed at improving light absorption over a large range of (visible) wavelengths, as well as promoting electron–hole separation and transfer efficiency by e.g. annealing and addition of metal-, and/or metal oxide nanoparticles [6,7]. Recently, intriguing studies have been reported on an additional method to promote activity of (doped) TiO₂, i.e. the use of plasmon absorption properties of metal nanoparticles of typically Ag or Au [8–10]. Enhanced activity by incorporation of plasmonic particles in photocatalytically active layers has been reported for various reactions, including (gas phase) oxidation reactions of organic molecules [11] and (liquid phase) water splitting [12–14]. Two phenomena have been proposed in explaining the rate enhancement by plasmonic (nano) particles. (i) Photo-excitation of Au nanoparticles leads to a quasi electron–hole pair, of which the electron can be transferred to the conduction band of TiO₂ and subsequently to a reactant (in this case oxygen), and the hole induces oxidation reactions on Au adsorbed species [15–19], and (ii) plasmon excitation by absorption of a photon corresponding to the plasmon absorption

band, results in an energy field (plasmon resonance energy) which positively influences TiO₂ excitation by absorption of a second photon, of larger energy than the band gap (in the case of TiO₂). This phenomenon is predominantly observed if overlap exists between plasmon and band-gap absorption [9,20–23].

In this study, we address the possible plasmonic effect of Au nanoparticles prepared by deposition–precipitation on the photocatalytic activity of TiO₂ in a liquid phase hydrocarbon oxidation reaction, i.e. the conversion of methylcyclohexane to methylcyclohexanone. Photocatalytic activity of Au/P25 was evaluated by *in situ* ATR-FTIR spectroscopy. We will demonstrate that of the wavelengths investigated (375, 425 and 525 nm, and combinations thereof), Au nanoparticles are only effective in promoting rates at 375 and 425 nm. Furthermore, by comparing the promotion in rate induced by Au nanoparticles and Pt nanoparticles at these two wavelengths, we demonstrate that besides a catalytic effect, a plasmonic enhancement induced by Au is apparent, which is most likely associated with plasmon resonance energy transfer, rather than electron transfer.

2. Experimental section

2.1. Catalysts and chemicals

P25 was obtained from Evonik, while HAuCl₄ and Methylcyclohexane (MCH) were purchased from Sigma–Aldrich. P25, HAuCl₄

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and MCH were used as received without further purification. The Pt promoted P25 catalyst was prepared by atomic layer deposition and kindly provided by the Delft University of Technology. Details of the methodology of atomic layer deposition and the morphology and characteristics of the Pt catalyst can be found in [24]. The loading of Pt was the same as in Au the catalyst, i.e. 0.2 wt%, while the average particle size was smaller, in the order of 5–6 nm.

2.2. Preparation of the Au/P25 catalyst

Gold was deposited on the P25 surface at 0.2 wt% loading by deposition–precipitation. In this procedure, 0.3 g of TiO₂ P25 was added to an aqueous solution of HAuCl₄ (0.1 M) previously adjusted to pH 9 by drop-wise addition of NaOH (0.1 M). The slurry was maintained at room temperature, and vigorously stirred overnight. Subsequently, the sample was filtered, washed with deionized water to remove chlorides, and then dried at 80 °C for 4 h in a furnace (static air). Finally, the obtained purple powder was calcined at 450 °C (heating rate 10 K/min) in static air for 5 h. To exclude the influence of preparative conditions on the behavior of P25 in the photocatalytic reaction [25], all preparative steps were performed for P25 in the absence of the Au solution (0.1 M HCl was used instead), and this sample is denoted as calcined P25 throughout the manuscript. To allow ATR analysis of methylcyclohexane oxidation, the catalysts were suspended in water at a concentration of 3 g/L. These suspensions were treated for 30 min in a 35 kHz Elmasonic ultrasonic bath; 2 mL of the resulting mixture was spread on a ZnSe crystal, followed by drying in vacuum overnight.

2.3. Material characterization

The crystal structure of the material was determined by powder X-ray diffraction (XRD), using a Philips PW2050 diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm). Measurements were recorded in steps of 0.005° with a count time of 1 s in the 2θ range of 20° and 80°. Raman spectroscopy was performed at room temperature using a Raman spectrometer (Bruker Senterra) with a green laser 532 nm (2 mW). Spectra were acquired at a resolution of ~ 15 cm⁻¹, and 10 scans were accumulated for each spectrum. The BET area was measured by nitrogen adsorption at liquid nitrogen temperature in a Micrometrics ASAP 2400 apparatus. Before analysis, the samples were degassed for 24 h at 300 °C in vacuum. Diffuse reflectance UV–vis spectra (DRS) of the powders were recorded at ambient pressure and temperature on a Thermo Scientific Evolution 600 spectrophotometer, equipped with a diffuse reflectance accessory of Harrick, using BaSO₄ as reference. Spectra were recorded in the wavelength range of 350–800 nm. TEM imaging was carried out using a Philips CM300ST-FEG microscope

equipped with a Kevex EDX detector. Samples for TEM were prepared by deposition of a dispersion in ethanol onto a carbon coated TEM grid.

2.4. Photo-oxidation of methylcyclohexane

The photocatalytic activity was determined using an attenuated total reflectance–Fourier transform infrared (ATR–FTIR) setup (Bruker Vertex 70 spectrometer, equipped with a Harrick Scientific ATR accessory). The ZnSe crystal coated with the catalyst formulation was inserted in the sampling compartment of the spectrometer. 20 mL of MCH was saturated with O₂ by bubbling dry air at 8 mL/min for 30 min. Subsequently, O₂ saturated MCH was added to the catalyst layer, and the composition enclosed by a top plate containing a quartz window. Prior to the photocatalytic oxidation experiments, adsorption of MCH on the catalyst coating was monitored for 100 min. Then, a spectrum of adsorbed MCH on the coating was collected, and used as background spectrum for photocatalysis experiments. To study the effect of multiple wavelengths on photocatalytic activity, an assembly of 7 LEDs was used as light source. We used two different LED arrays. Both have 3 LEDs emitting at 525 nm, one alternating with four 375 nm LEDs, and another alternating with four 425 nm LEDs. The LEDs of different wavelengths could be switched on and off independently. The light intensity of the LEDs was fine-tuned to be equal at 1.5 mW/cm². A scheme of the ATR–FTIR setup is shown in the Supporting Information (Fig. S1). Upon illumination, each spectrum was recorded at fixed time intervals (typically 1 min) from 4000 to 700 cm⁻¹ by collecting 64 scans with a resolution of 1.5 cm⁻¹.

3. Results

3.1. Characterization

Fig. 1 shows TEM images of the Au/TiO₂ sample prepared by the deposition–precipitation method (DP). Based on these images and energy-dispersive X-ray (EDX) analysis, Au nanoparticles are clearly identified ranging in size between 10 and 20 nm. Further, these results indicate that the deposition precipitation method did not induce changes in TiO₂ morphology, of which the mean primary particle size is estimated to be around 15 nm. The Au particle size obtained in this study is a bit larger than usually reported. This is likely because of the sensitivity of the Au particle size on synthesis procedure, such as Au source, stirring rate, pH, calcination temperature and ramp rate of calcination. XRD and Raman analysis confirm the absence of dramatic changes in crystallinity and size of P25 TiO₂, potentially induced by the solutions used for Au deposition, and/or calcination (Figs. S2 and S3). The lower intensities of the Raman features of P25 after Au deposition are likely the result

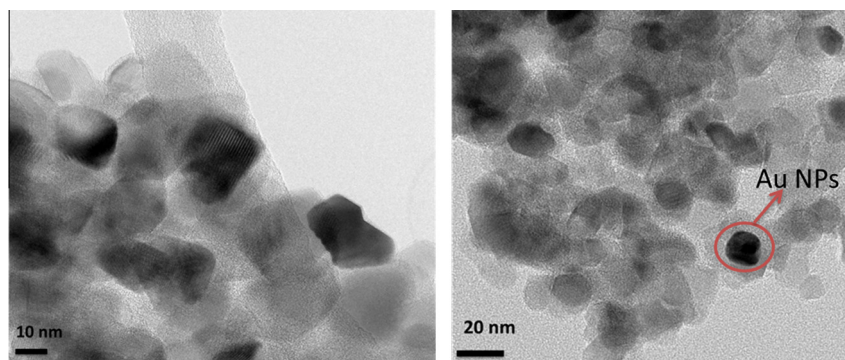


Fig. 1. Transmission electron microscopy (TEM) images of Au/p25 (0.2%).

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