

The Influence of the Au Nanoparticles Dimension on the Photocatalytic Performances of TiO₂–Au Porous Composites

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The influence of Au nanoparticles dimension on the photocatalytic performances of the TiO₂ aerogels–Au composites was evaluated. Structural and morphological peculiarities of the TiO₂ aerogel, unloaded and loaded with 5 and 22 nm Au nanoparticles, were studied by transmission electron microscopy technique, X-ray diffraction and N₂-sorption measurements. UV-Vis diffuse reflectance measurements were performed to determine the band gap energies. The photocatalytic activity was evaluated by monitoring the salicylic acid photodegradation. It was found that the Au nanoparticles promote the anatase phase crystallization and produce the decrease of the specific surface area and band gap energy values. The porous composite with the smallest Au nanoparticles dimension exhibits the best photocatalytic performances.

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1. Introduction

TiO₂ based aerogels combine the properties of titania, i.e. high photosensitivity, nontoxic nature, and chemical stability [1], with those of aerogels materials, i.e. extremely low densities (up to 95% of their volume is air), very high specific surface areas (often > 600 m²/g), high pores connectivity, low refractive indexes (< 1.1), and low thermal loss coefficients (< 0.5 W/(m² K)) [2]. Such porous materials are attractive for various applications like organic pollutants oxidation, solar energy conversion, pigments, electronic device, etc. [3].

The photocatalytic activity of TiO₂ is drastically influenced by several structural and morphological particularities such as its crystalline structure and particle size, specific surface area, band gap, the number of electron–hole pairs that participate in the formation of active radicals, etc. [4]. Anatase TiO₂ crystalline structure shows greater photocatalytic activity than rutile and brookite TiO₂ [5]. However, TiO₂ meets two severe drawbacks. One major limitation is the quick recombination of charge carriers and the second one is that titania requires UV irradiation ($\lambda < 380$ nm, for anatase) for effective photocatalysis, thereby drastically limiting its practical application [6]. To solve these problems, a rapid transfer of one of the charge carriers (electrons, e⁻, or holes, h⁺) is required to

prevent the e⁻–h⁺ pair recombination, and an extended visible light absorption. This is usually required to enhance the overall photocatalytic efficiency [7].

The loading of noble metal nanoparticles was demonstrated to be an effective solution to enhance the photocatalytic activities of nanoscaled TiO₂ [8]. This study reports about the influence of the Au nanoparticles dimension on the morpho-structural characteristics and photocatalytic performances of the TiO₂ aerogel–Au nanoparticles composites by employing various complementary investigation techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), N₂-sorption measurements and UV-Vis diffuse reflectance spectroscopy.

2. Experimental

2.1. Samples preparation

The ≈ 22 nm Au nanoparticles were prepared by the following procedure: 100 ml of 10⁻³ M chloroauric acid (HAuCl₄) solution was brought to a boil under vigorous stirring. Six and a half milliliters of 38.8 mM sodium citrate was added to the solution all at once under vigorous stirring. Stirring and boiling was continued for 15 min after the burgundy color was observed. The

≈ 5 nm Au nanoparticles were obtained as follows: 42 ml of 2×10^{-2} M sodium borohydride was added to a 350 ml solution containing 0.5×10^{-3} M HAuCl₄. The reaction takes place in a bath of ice under vigorous stirring.

TiO₂ gels were prepared by the one-step sol-gel procedure using Ti₄(OCH₃)₁₆, HNO₃, C₂H₅OH and H₂O with the 1/0.08/21/3.675 molar ratios. The gels were aged for three weeks, immersed in Au colloidal solutions for three days (≈ 22 nm Au nanoparticles) and one day (≈ 5 nm Au nanoparticles), respectively, and then dried under supercritical conditions with liquid CO₂. The porous composites containing Au nanoparticles with dimensions of around 5 and 22 nm are further denoted as TA1 and TA2, respectively.

2.2. Sample measurements

A JEOL JEM 1010 TEM operating at an accelerating voltage of 100 kV and equipped with a MegaViewIII CCD camera was employed to obtain the images. X-ray diffractograms were recorded with BRUKER D8 Advance powder diffractometer and Cu K _{α} radiation ($\lambda = 1.540598$ Å). The morphological parameters of the samples were determined by means of N₂-sorption measurements by using a Sorptomatic 1990 equipment. Diffuse reflectance spectra of the composites were recorded with a JASCO spectrophotometer (800–200 nm). The band gap energy values were calculated after applying the Kubelka–Munk transformation.

The photocatalytic activity was established from the degradation rate of salicylic acid by monitoring its absorption band (295 nm) with an UV-Vis spectrophotometer. A medium pressure Hg HBO OSRAM lamp (500 W) was used. The working temperature was of 22 °C and the pH of the solution was 5.3. The photodecomposition reaction follows pseudo-first order kinetics and the apparent rate constant was calculated by plotting $\ln(C_0/C)$ vs. time (the slope of the plot given by the linear fit).

3. Results and discussion

Selected TEM images of the samples TA1 and TA2 are illustrated in Fig. 1. TEM pictures show a relative good dispersion of the Au colloidal nanoparticles inside the aerogel matrix and evidence the presence of the gold nanoparticles aggregates.

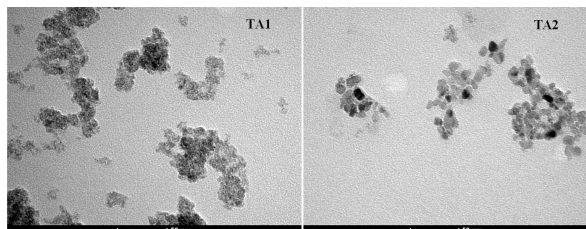


Fig. 1. Selected TEM images obtained for porous TiO₂-Au nanocomposites as indicated.

According to the XRD patterns (see Fig. 2) all samples are largely amorphous. However, the diffractograms of the gold containing samples display well defined characteristics associated with the presence of anatase TiO₂ crystalline phase. This result shows the influence of the Au nanoparticles on the TiO₂ nanostructures under supercritical drying conditions. Moreover, the pattern associated with the TiO₂ anatase structure is more defined for the sample containing 5 nm Au nanoparticles in size in comparison with that of the composite whose dispersed phase is made up from gold particles of 22 nm. The mean size of the TiO₂ crystallites has been calculated by using the Scherrer equation for all reflection lines in the range 20°–70°(2 θ) and was found to be close to 9 nm.

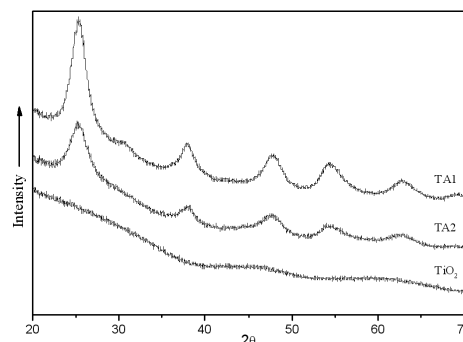


Fig. 2. X-ray diffractograms of porous TiO₂ and TiO₂-Au nanocomposites as indicated.

The adsorption/desorption isotherms are presented in Fig. 3 and show characteristics of the type IV adsorption isotherm. This type of isotherm denotes the existence of a mesoporous structure. The TiO₂ aerogel sample exhibits a H1 type of hysteresis loop, typical for large pore ordered mesoporous structures, while the samples TA1 and TA2 show characteristics associated with H2 type, typical of porous structures with a bottle-neck like geometry or with pores blocked with particles. A detailed view of the TA1 and TA2 hysteresis indicates the fact that the composite containing ≈ 5 nm Au nanoparticles possesses the lowest pores connectivity, according to the Seaton model [9].

TABLE

BET surface areas, band gap energies, photodegradation rates and apparent rate constants per surface unit.

Sample name	S_{BET} [m ² g ⁻¹]	E_{g} [eV]	k_{app} [min ⁻¹] × 10 ⁻³	$k_{\text{app}}/S_{\text{BET}}$ [g min ⁻¹ m ⁻²] × 10 ⁻⁶
TiO ₂	593	3	5.75	9.6
TA1	317	2.86	8.32	26
TA2	446	2.88	7.68	17.2

The band gap values were determined for the TiO₂ aerogel, unloaded and loaded with Au nanoparticles, after applying the Kubelka–Munk transformation (see

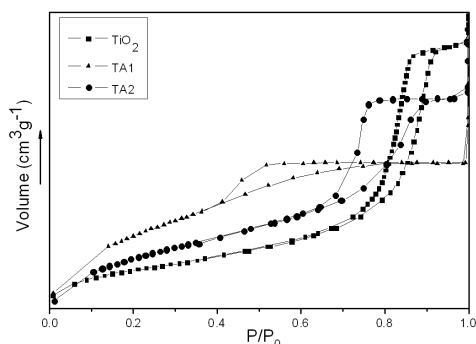


Fig. 3. N_2 adsorption/desorption isotherms of porous TiO_2 and TiO_2 -Au nanocomposites as indicated.

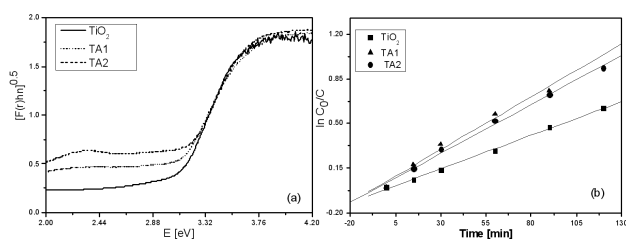


Fig. 4. Kubelka-Munk transformations of UV-Vis diffuse reflection data (a) and photocatalytic activity (b) for the porous TiO_2 and TiO_2 -Au nanocomposite samples as indicated.

Fig. 4a). The salicylic acid photodegradation rate constants were derived for all investigated samples and are illustrated in Fig. 4b. All these data together with the per surface unit photodegradation rates are given in Table. The data in Table reveal that by loading Au nanoparticles on the porous TiO_2 nanostructures one obtains a decrease of the specific surface area and band gap energy values, accompanied by an increase of the both overall and per surface unit salicylic acid photodegradation rates. A close analysis reveals that the decrease of Au nanoparticles dimension improves the photocatalytic activity, as indicated by the apparent rate constants per surface unit data in Fig. 4b.

4. Conclusions

The influence of the Au nanoparticles dimension on the photocatalytic performances of the porous TiO_2 -Au

composites was assessed by investigating the TiO_2 aerogel, unloaded and loaded with 5 and 22 nm Au nanoparticles. It was evidenced that the Au nanoparticles presence leads to the occurrence of the anatase TiO_2 crystalline phase and determines the decrease of the specific surface area and band gap energy value. The porous composite with the smallest gold nanoparticle dimension was found to exhibit the best photocatalytic properties.

Acknowledgments

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