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Shape tailored Pd nanoparticles' effect on the photocatalytic activity of commercial TiO_2

Sz. Fodor[a,b,c,1], G. Kovács[a,b,d,1], K. Hernádi[b], V. Danciu[e], L. Baia[a,d,*], Zs. Pap[a,b,c,*]

[a] *Institute for Interdisciplinary Research on Bio-Nano-Sciences, Babeş-Bolyai University, Treboniu Laurian 42, RO-400271, Cluj-Napoca, Romania*
[b] *Department of Applied and Environmental Chemistry, University of Szeged, Rerrich tér 1, HU-6720, Szeged, Hungary*
[c] *Institute of Environmental Science and Technology, University of Szeged, Tisza Lajos krt. 103, HU-6720, Szeged, Hungary*
[d] *Faculty of Physics, Babeş-Bolyai University, M. Kogălniceanu 1, RO-400084, Cluj-Napoca, Romania*
[e] *Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Arany János 11, RO-400028, Cluj-Napoca, Romania*

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ABSTRACT

Shape-controlled synthesis of noble metal nanoparticles and their impact on the photocatalytic activity of semiconductor oxides is continuously gaining more and more attention. Hence, commercial titania-based TiO_2-Pd nanocomposites were synthetized and characterized, using spherical and cubical Pd nanoparticles. The obtained photocatalysts were analyzed using optical (DRS) as well as morphological and structural (XRD, HR-TEM) methods in order to understand their properties. The effects of the Pd nanoparticles' shape on different commercial titania-based catalysts were highlighted in terms of photocatalytic efficiencies toward model organic pollutants (phenol and oxalic acid), evolution of reaction intermediates (hydroquinone, pyrocatechol and resorcinol) and photocatalytic H_2 production. It was found that both geometries (spherical, cubic) can enhance the activity of the base photocatalyst, although each Pd morphology modified the ratio of the primary degradation intermediates. Moreover, the photocatalytic hydrogen production of the spherical nanoparticles proved to be more efficient as the cubic ones. The observed activity differences were attributed to a possible change in the electron-transfer process, induced by the different Pd morphologies.

1. Introduction

The heterogeneous photocatalysis based water treatment methods have recently shown great promise [1–3]. By the irradiation with light/energy of an aqueous photocatalyst suspension, electron-hole pairs are generated and involved in a succession of redox processes. Large number of semiconductor-photocatalysts have been already reported; from the most studied titanium dioxide [4,5] to other materials with potential photocatalytic properties, like tungsten trioxide [6,7], zinc oxide [8], tin dioxide [9] and copper (II) oxide [10]. Titanium dioxide is the most frequently used semiconductor photocatalyst because of its several beneficial properties: physical and chemical stability, non-toxicity, safety, low cost, and resistance to photocorrosion.

In order to maximize the lifetime of the photogenerated charges, various approaches can be considered: deposition of noble metals [11], doping with transition metals/noble metals [12], creating composites with other semiconductors [13] and using of carbon nanomaterials [14]. It is already known that the first above mentioned approach can enhance the photocatalytic activity because the recombination of the electron-hole pairs is lowered as a result of the transfer of photogenerated electrons from the semiconductor oxide to the noble metal nanoparticle. Recently, the studies involving noble metal nanoparticles' application in photocatalysis have been focused not just on the nanoparticle content and the size of deposited noble-metal [15], but also on their shape [16]. The geometry of the nanoparticles can be controlled in a reproducible way by controlling the temperature [17] or by using different shape controlling agents [18]. Nevertheless, the geometry of the nanoparticles can have an important effect on the photocatalytic efficiency and hydrogen production of the catalyst [19]. The "classical" noble metals (Au, Ag and Pt) are more-or-less well

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[*] Corresponding authors at: Institute for Interdisciplinary Research on Bio-Nano-Sciences, Babeş-Bolyai University, Treboniu Laurian 42, RO–400271, Cluj-Napoca, Romania.
E-mail addresses: lucian.baia@phys.ubbcluj.ro (L. Baia), pzsolt@chem.u-szeged.hu, pap.zsolt@phys.ubbcluj.ro (Zs. Pap).
[1] 1st authors.

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studied, but palladium has recently gained much interest including in organic chemistry as (co)catalyst [20,21], in adsorbent materials [22] and in graphene-based composites, used as biosensing material [23] or in photocatalysis [24].

The other aspect that cannot be omitted when we are "pursuing" to obtain highly active photocatalysts is the intermediates' concentration profile during the photodegradation process. It is well known that phenol and phenolic compounds are one of the most pollutant class of organic materials. Their photodegradation can be quasi-successful, but often the reaction-intermediates occurring the process are not followed. This aspect can be really important, if we are planning a photocatalytic system for "real life", because some of these phenol intermediates (hydroquinone, pyrocatechol and resorcinol) are in category 1 or 2 carcinogenic risk and toxicity (according to Regulation (EC) No 1272/2008 [EU-GHS-CLP]), some of them having even lower LD_{50} values (hydroquinone – 320 mg kg^{-1}, pyrocatechol – 301 mg kg^{-1} and 260 mg kg^{-1} for resorcinol) than the phenol itself (317 mg kg^{-1}) [25,26].

Taking into account the above mentioned aspects the authors aimed to uncover the effect of the Pd nanoparticles' shape on the photocatalytic efficiency of commercial titanias and on the ratio of different primary degradation intermediates.

2. Experimental section

2.1. Synthesis of palladium nanoparticles

2.1.1. Materials

$PdCl_2$ (Merck, 59 % Pd), HCl (Nordic Invest, 99 %,), L-Ascorbic acid (Sigma-Aldrich, 99 %), cetyltrimethylammonium bromide – CTAB, trisodium citrate (ACS reagent grade, 99 %), $NaBH_4$ (purum, 96%), ethanol (99.8 % reagent grade) and acetone (99.9 %) were purchased and used without further purification.

Three reference photocatalysts were purchased and applied as received: Aldrich anatase (AA) and Aldrich rutile (AR) from Sigma–Aldrich, while Evonik Aeroxide P25 (P25) from Evonik Industries.

2.1.2. Preparation of H_2PdCl_4 precursor solution

To obtain the palladium precursor solution, 0.1773 g $PdCl_2$ was dissolved in 10 mL of 0.2 M HCl solution and it was further diluted with distilled water until 100 mL total volume was achieved. With this method 10 mM H_2PdCl_4 solution was prepared. The amount of the water was 50 mL when 20 mM H_2PdCl_4 solution was prepared.

2.1.3. Preparation of Pd cubic nanoparticles

To obtain the Pd nanocubes 0.5 mL of 10 mM H_2PdCl_4 precursor solution was added to 9.42 mL 12.5 mM of CTAB aqueous solution. This was further heated to 65 °C or 95 °C under stirring. After 5 min, 80 μL of freshly prepared 100 mM ascorbic acid aqueous solution was added, and the reaction was allowed to proceed for 20 min. The Pd nanoparticles were separated by centrifugation (16000 rpm, 5 min) and washed twice with acetone. Then the cubic Pd particles were redispersed in ethanol and stored at 25 °C for future use. The samples containing these nanoparticles were marked with: *Pd (c).*

2.1.4. Preparation of Pd spherical nanoparticles

43 mL of ultrapure water was measured into a vessel, followed by the addition of 6.3 mL 5 mM solution of trisodium citrate. After 30 min, 0.625 mL 20 mM H_2PdCl_4 solution was added and the mixture was stirred at room temperature for another 30 min. The last step in this synthesis was the reduction procedure by the addition of 1 mL 0.15 M $NaBH_4$. The reaction mixture was stirred for 1 h to eliminate the by-products and the unreacted $NaBH_4$. The obtained palladium nanoparticles were collected, washed and redispersed as in case of the Pd nanocubes. The samples containing these nanoparticles were marked with: *Pd (s).*

2.2. Synthesis of the nanocomposites

In a reaction vessel commercial titania was suspended in 400 mL ultrapure water and sonicated for 15 min. After this the necessary quantity of Pd suspension was added to the dispersion (the ratio was calculated to be 1 wt% Pd in the composites) under vigorous stirring. Then 5 min of ultrasonic homogenization was applied followed by 60 min of intensive stirring. The resulted suspension was dried at 80 °C for 24 h. The resulted powders were washed with ultrapure water three times (4400 rpm, 10 min) and dried again at 80 °C for 24 h. To be certain that all the nanoparticles were deposited, the supernatant (after centrifugation) of the composite suspensions were analyzed spectrophotometrically. No sign of either nanoparticles or the Pd precursor was found. In order to verify that all the Pd was reduced to 0 oxidation state, spectrophotometric means[1] (disappearance of the H_2PdCl_4 brownish color) and XPS[1] (detection of Pd^{2+} and Pd^0) was applied, and it was found that in each case the reduction process was complete. The samples were named as follows: the abbreviation of the base photocatalyst + abbreviation of the different type of Pd nanoparticles (e.g. AA-Pd(s)).

2.3. Methods and instrumentation

2.3.1. Characterization methods

X-ray diffraction (XRD) measurements were performed on a Shimadzu 6000 diffractometer using Cu Kα radiation (λ = 1.5406 Å) equipped with a graphite monochromator. The anatase-rutile phase ratio in TiO_2 was evaluated by the method used by Banfield [27], and the crystallites' average size was calculated using the Scherrer equation.

A JASCO-V650 spectrophotometer with an integration sphere (ILV-724) was used for measuring the *DRS (diffuse reflectance spectroscopy)* spectra of the samples (λ = 300–800 nm). To obtain the band-gap energy the reflectance data were converted to F(R) values according to the Kubelka–Munk theory. The band gap was obtained from the plot of $[F(R)\cdot E]^{1/2}$ versus energy of the exciting light (E).

TEM/HRTEM micrographs were obtained with a FEI Tecnai F20 field emission high-resolution transmission electron microscope operating at an accelerating voltage of 200 kV and equipped with an Eagle 4k CCD camera.

2.3.2. Evaluation of photocatalytic efficiencies

To measure the photocatalytic activities (both for phenol and oxalic acid degradation), a photoreactor system was used containing 6 × 6 W fluorescent lamps ($\lambda_{\text{emission.max}} \approx 365$ nm). A Pyrex glass reactor (100 mL, irradiated in a hexagonal display, irradiation distance from each lamp = 8 cm) thermostated at 25 °C was applied, while the suspension (1 g L^{-1}) was continuously purged with air in order to keep the dissolved oxygen concentration constant. Prior to the degradation experiment, the dark adsorption/desorption equilibrium was achieved in 10 min (the dark adsorption in each case was <5 %). The duration of the measurements were 2 h, and the samples were taken in every 10 min in the first hour, and in every 20 min in the second hour. The concentration of the chosen organic substrate (phenol – 0.5 mM and oxalic acid – 5 mM) and the phenol's primary degradation intermediates were followed using an *Agilent 1100 series HPLC* system (instrumental and intermediate detection details can be found in references [28,29]). The error of

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[1] Not shown in the present manuscript.

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