



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod



Enhanced photo-degradation of bisphenol pollutants onto gold-modified photocatalysts

Bogdan Cojocaru^a, Veronica Andrei^a, Madalina Tudorache^a, Feng Lin^{b,c}, Chris Cadigan^b, Ryan Richards^{b,*}, Vasile I. Parvulescu^{a,*}

^a Department of Organic Chemistry, Biochemistry and Catalysis Faculty of Chemistry, University of Bucharest, Bdul Regina Elisabeta, 4-12, Bucharest 030016, Romania

^b Department of Chemistry and Geochemistry, Materials Science, Colorado School of Mines, Golden, CO 80401 USA

^c Department of Chemistry, Virginia Tech, Blacksburg, VA24061, USA

ARTICLE INFO

Article history:

Received 13 July 2016

Received in revised form 3 October 2016

Accepted 6 November 2016

Available online xxx

Keywords:

TiO₂ photocatalyst

Gold

Plasmon

Bisphenol A

ABSTRACT

Here we report a comparative study of Au supported on different types of TiO₂ in the photocatalytic degradation of BPA. The beneficial presence of a small amount of rutile was proven once again, the TiO₂ anatase showing a lower activity despite a higher surface area. Also, the role of gold plasmon was evidenced by the use of an inert silica support.

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1. Introduction

Bisphenol A (BPA) is an endocrine disruptor (ED), i.e. an exogenous substance that alters function(s) of the endocrine system and consequently causes adverse health effects in intact organism, or their progeny, or (sub)populations [1–4]. Other chemicals that are known EDs include diethylstilbestrol (the synthetic estrogen), dioxins, polychlorinated biphenols (PCBs), phthalates, methoxychlor, phenolic derivatives, linear alkylphenols, DDT and some other pesticides. All these chemicals are found in our daily lives (in many of the products we encounter or use regularly such as plastics, liners of metal food cans, detergents, flame-retardants, toys, cosmetics, and pesticides). In some cases, these chemicals imitate the estrogens in the body [5–7]. Exposure to these substances occurs throughout our lives from food, air, water, soil, and household products that can reach a developing fetus and additionally be passed on from a mother via breast milk [3,7]. Furthermore, since they can sometimes leach out of the plastics or other materials and migrate into the food, especially after heating or when the plastic is old or scratched, these compounds have aroused concerns as possible

cancer-causing agents. However, the human health risks that may be associated with these low-level yet constant exposures are still largely unknown and highly controversial. Since the turn of the century, manufacture and use of synthetic chemicals has rapidly increased. Many of the environmental estrogens, which are man-made chemicals, are persistent and ubiquitous, leading to a higher risk of environmental pollution.

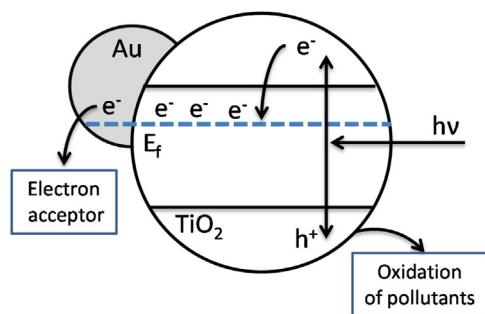
Bisphenol A (BPA) is a synthetic resin widely used in food packaging, dental sealants and polycarbonate plastic products, which range from CDs and eyeglass lenses to tableware and food and beverage containers, including baby bottles [8]. This compound has now been found to disrupt important effects of estrogens in the developing brain, according to a report from Medical Research News, 2 December 2005 [9]. While high doses cause little effect, analysis of cellular and molecular markers of estrogens signaling revealed that near-maximal effects of BPA on rat brain neurons not only occurred at surprisingly low doses of 0.23 parts per trillion, but they also happened in a matter of minutes. From the literature, it's clear that these low concentrations are in line with human fetal exposures, and at levels one might even see in the water supply. This “low-dose” effect of BPA is troubling since its maximal effects occur at the level typical of human exposure. This means that the harmful effects of BPA could easily be missed using standard approaches for determining the risks of chemical exposure. The scientific research in the field of EDs involves mainly the study

* Corresponding authors.

E-mail addresses: r-richard@mines.edu (R. Richards), vasile.parvulescu@chimie.unibuc.ro (V.I. Parvulescu).

<http://dx.doi.org/10.1016/j.cattod.2016.11.009>

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Scheme 1. Interfacial charge transfer in Au-TiO₂ NPs with Fermi level equilibration.

on endocrine disruptors' toxicology as well as the development of analytical methods for detection and quantification of EDs contaminants at low concentration levels [10–12]. Currently, a new aspect of the EDs issues is considered such as the environmental cleanup of ED hazard compounds. A brief search on the literature shows the scientific interest on EDs remediation, especially catalytic remediation (e.g. photo-remediation) that is continuously growing.

Among “classical” routes to degrade BPA, the photocatalytic route is gaining much interest as a green method requiring a cheap (practically free) energy source and limited only by the light absorbing capacity of the catalysts. Besides the reference TiO₂ [13], “improved” photocatalysts like Ti/TiO₂ [14], Pr,N-TiO₂ [15], H₃PW₁₂O₄₀/TiO₂ [16], Ag-TiO₂ [17], Pt-TiO₂ [18] or Photo-Fenton systems [19,20] showed a promising behavior for the removal of BPA.

Gold catalysis has attracted great interest in the past period [21]. In addition to the catalytic oxidative reactions, gold nanoparticles were found to promote the catalytic activity of TiO₂ [22–26]. It has also been observed that the visible light absorbed by gold nanoparticles due to the surface plasmon resonance is leading to the generation of photo-excited states of gold nanoparticles followed by the transfer of the electrons to the TiO₂ [27]. Thus, the surface plasmon resonance originating from the collective oscillations of the electrons on the surface of the gold nanoparticles was suggested to be the essential factor of the promoting effect. The enhanced interfacial charge transfer between TiO₂ and gold resulting from the accumulation of more electrons can be achieved by a negative shift in the Fermi level of the Au-TiO₂ composite [22–28]. Metal or metal ion doped semiconductor composites typically exhibit a shift in the Fermi level to more negative potentials. This improves the energetics of the composite system and enhances the efficiency of the interfacial charge-transfer process [22]. For the particular case of Au/TiO₂, previous reports already indicated the accumulation of more electrons in system [25] having as an ultimate effect an enhanced photo-catalytic activity (Scheme 1). The resonances of the surface plasmons are directly affected by the wavelength, particle size, shape, and local dielectric environment.

Starting from this state of the art, the aim of this study was to investigate the photo-activity of a series of catalysts containing gold deposited on titania in the decontamination of water solutions containing BPA and to elucidate the effect of the gold plasmon and of the nature of the support.

2. Experimental

2.1. Catalyst preparation

SBA-15 was synthesized according to the procedure developed in a previous work [29]. TiO₂ NA was obtained from NanoScale Corporation (NanoActive TiO₂) and used as received. TiO₂ was

synthesized by the quick hydrolysis of titanium butoxide (reagent grade, Sigma-Aldrich) by adding drops of DI water into a solution of titanium butoxide and butanol followed by centrifugation, drying and calcination at 500 °C for 6 h. Then SBA-15, TiO₂ NA and TiO₂ were used as the supports for the deposition of Au nanoparticles. To deposit Au nanoparticles, supports were dispersed in 200 mL of 6 mM trisodium citrate (premium quality level, Sigma-Aldrich) aqueous solution and stirred vigorously for 1 h. Then, 50 mL of 3 mMHAuCl₄ (99.9% metals basis, Aldrich) aqueous solution was added to the above suspension dropwise and the mixture was allowed to react overnight under vigorous magnetic stirring. Finally, the product was centrifuged and cleaned with DI water several times and dried at 100 °C for 24 h. Au/meso-TiO₂ was synthesized using a one-pot method. In detail, a designated amount of HAuCl₄ was dissolved in 40 mL of butanol and stirred at room temperature to complete dissolution, then 4 g of poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO₂₀PO₇₀EO₂₀, P123, MW = 5800, Aldrich) was added and stirred for 30 min. Titanium butoxide solution (20 g of titanium butoxide in 25 mL of butanol) was added dropwise to the above solution. Finally, the mixture was aged at 40 °C overnight, filtered, dried and calcined at 500 °C for 6 h. The deposition of Au onto Degussa P25 was carried out following the precipitation-deposition method. Thus, 1 g of TiO₂ Degussa P25 was added to the corresponding volume of an aqueous solution of HAuCl₄·3H₂O (0.2 M). The pH of the solution was stabilized at 8–9 by addition of a 0.2 M NaOH solution. The mixture was stirred at 80 °C for 12 h. After that, the suspension was filtered, washed with water till free of Cl⁻. Finally, the solid was dried at 80 °C for 48 h. Using this procedure samples with 0.1, 0.3, 0.7 and 1 wt% Au, respectively, were obtained.

2.2. Catalyst characterization

Textural characteristics of the investigated catalysts were determined from the adsorption-desorption isotherms of nitrogen at –196 °C using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. DR-UV-vis spectra were collected under ambient conditions with a Specord 250 (Analytic Jena) with an integrating sphere and MgO as reference. The registered spectra were transformed using the Kubelka-Munk F(R) function. The band gap energy was calculated from the dependence of $[F(R) \cdot hv]^2$ as a function of hv , where hv is the energy of the incident photons. Raman spectra were taken with a Horiba Jobin Yvon – Labram HR UV-vis-NIR (200–1600 nm) Raman Microscope Spectrometer, using a laser with the wavelength of 632 nm. Powder X-ray Diffraction patterns were collected at room temperature using a Shimadzu XRD-7000 with Cu K α monochromatic radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA) with a scanning rate of $0.1^\circ \text{ min}^{-1}$, in the 2θ range of 5–80. XPS spectra were recorded at room temperature using a SSX-100 spectrometer, Model 206 from Surface Science Instrument. The pressure in the analysis chamber during the analysis was 1.33 mPa. Monochromatized Al-K α radiation ($h\nu = 1486.6 \text{ eV}$) generated by bombarding the Al anode with an electron gun operated with a beam current of 12 mA and acceleration voltage of 10 kV has been used. The spectrometer energy scale was calibrated using the Au 4f_{7/2} peak centered at 83.98 eV. Charge correction was made with the C 1s signal of adventitious carbon (C–C or C–H bonds) located at 284.8 eV. The atomic surface compositions were calculated using the sensitivity factors provided with the ESCA 8.3 D software, applied to the surface below the corresponding fitted XPS signals. An estimated error of $\pm 0.1 \text{ eV}$ can be assumed for all measurements. Specimens for electron microscopy were prepared by suspending them in acetone and transferring to a copper grid coated with an amorphous carbon support. TEM images were recorded on a JEOL JEM ARM 200 F electron microscope operated

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