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Effective photoreduction of a nitroaromatic environmental endocrine disruptor by Ag°NPs functionalized on nanocrystallineTiO$_2$.

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Unprecedented photoactivity of silver nanoparticles photodeposited on nanocrystalline TiO$_2$ for the efficient reduction of 4-nitrophenol at room temperature is reported. The use of Na$_2$SO$_3$, as a harmless scavenger agent for the reduction of a nitroaromatic endocrine disruptor yields a valuable 4-aminophenol reagent.

Nowadays, many organic pollutants have been targeted as endocrine disrupting chemicals (EDCs). Natural and synthetic hormones, plastics, detergents, pharmaceuticals, pesticides, and industrial chemicals affect the endocrine system of humans and wildlife[1]. Numerous individual biological processes including reproduction, brain function, and the immune system are disrupted by these pollutants.[2] Phenolic and nitroaromatic compounds, used in industrial and agricultural wastewaters, have exhibited both estrogenic and anti-androgenic activities on humans, animals and plants, even at very low concentrations.[3, 4] 4-nitrophenol (*4-NP*) is a highly harmful compound and has been quoted as a potential endocrine activity disruptor in immature male rats.[5] *4-NP* is present commonly in diesel exhaust and it is also found in industrial and hospital wastewaters since it is a precursor not only of pesticides, but also of certain pharmaceuticals, plasticizers and azo-dyes.[6-7] The permitted level of *4-NP* in water is, in general, 30 μg L^{-1} and its photolysis in aqueous solutions is a very slow and inefficient process.[7] Currently, the use of hydroxyl radicals (UV-C/H$_2$O$_2$) has been of interest in the degradation of *4-NP* because of the good photo-oxidation rates[8], nevertheless, nanometric sol-gel crystallites of TiO$_2$ catalysts are more efficient[8-9] than other crystalline TiO$_2$ catalysts. The use of metallic nanoparticles supported on these metal oxides has enhanced the oxidation or reduction of *4-NP*, but partial oxidation of *4-NP* and by-products still remain.[9, 11] Noble metals can carry out the reduction of *4-NP* to 4-aminophenol (*4-AP*), increasing the reduction rate and selectivity to the valuable *4-AP* by the

addition of reducing agents, which helps remarkably the reduction reaction. It is generally agreed that the use of the typical sodium borohydride (NaBH$_4$) or hydrazine (NH$_2$NH$_2$) as strong reducing agents can accelerate the *4-NP* reduction, but their toxic and dangerous nature compromise their role.[12-16] On the other hand, TiO$_2$ without noble metals can hardly reduce *4-NP* in the presence of these powerful reducing agents. If TiO$_2$ is modified with polyamine and UV-visible light irradiation is used, the reduction of *4-NP* is possible.[17] In this communication, it is demonstrated for the first time that the complete reduction of the endocrine-disruptor *4-NP* to *4-AP* is possible by using a soft reducing agent such as sodium sulfite (Na$_2$SO$_3$) as sacrificing agent at room temperature by means of a photocatalytic process with silver nanoparticles photo-functionalized on the surface of a nanocrystalline TiO$_2$.

The TiO$_2$ substrate was synthetized by a previously reported sol-gel technique.[9] In brief, titanium isopropoxide, n-butanol and an urea/butanol/water solution were added simultaneously dropwise to a 4-neck round bottom flask under continuous stirring. The reactant solution was aged for 72 h at 80°C. The solvents were removed with a vacuum evaporator at 80 ºC, dried overnight under vacuum at 100 ºC, and finally annealed at 450ºC for 4 h. Furthermore, practical UV functionalization with 1.5 wt% of Ag°NPs on sol-gel TiO$_2$ and commercial TiO$_2$-P25 surfaces was carried out using a silver nitrate ethanol solution. Either, the sol-gel TiO$_2$ or commercial TiO$_2$-P25 was added to the solution and the resultant slurry was irradiated with a UV-lamp (TecnoLite G15T8, 214 nm, 17 W) for 60 min. under vigorous stirring and finally dried overnight at 80ºC. The photocatalysts were labeled as Ag/TSG and Ag/TP25, respectively. To understand their behaviour in the photoreduction reaction and correlate it with the reducing properties of the materials, structural and optical characterizations were carried out by means of XRD, UV-Vis spectroscopy and TEM microscopy in HRTEM and STEM-HAADF modes. A possible photoreduction mechanism of the *4-NP* endocrine disruptor was proposed.

The diffuse reflectance UV-Vis spectra of all the samples (Fig. 1-a) show an absorption peak at 320 nm, which is characteristic of TiO_2 semiconductors.[18] The band-gap energy (Eg) value ranged from 3.05 to 3.28 eV. It has been reported that when the TiO_2 framework is functionalized with Ag°NPs by different methods, the Eg values are red-shifted, depending on the size and dispersion of particles. In this case, the Eg energies are practically unchanged due to the low silver loading (<2 wt%), however, the dispersion of the Ag°NPs can be estimated by considering the Surface Plasmon Resonance (SPR), which is correlated with the Ag°NPs size.[19] Thus, in the Ag/TP25 catalyst, the absorption band centered at 585 nm is attributed to the SPR of Ag°NPs due to closer Ag°NPs, but it is detected scarcely in the Ag/TSG catalyst. The sol-gel TiO_2 catalyst has a surface area of 116 m^2/g, while the commercial TiO_2-P25 presents normally an area of 56 m^2/g; therefore, two times more surface area with high dispersion of Ag°NPs is expected in the Ag/TSG catalyst. Fig. S1 (see Electronic Supplementary Information, ESI) shows the selected High-Angle Annular Dark-Field (HAADF) images for the sol-gel TiO_2 catalyst obtained in STEM mode in order to identify more clearly the size of the Ag°NPs. By contrast, in the Ag/TSG catalysts, it is more difficult to identify the Ag°NPs due to their high dispersion and very small size. The EDX analysis confirmed the presence of silver on the TiO_2 surface. The XRD patterns of both silver functionalized TiO_2 catalysts are shown in Figure 1-b, where anatase is the main TiO_2 crystalline phase. The peak corresponding to the anatase reflection (25.41 of 2 theta; JCPDF 070-6026) is slightly broad for the Ag/TSG catalyst, showing a smaller crystallite size. In both materials, the Ag°NPs are no observed due to the high dispersion and nanometric size $\leq$ 5 nm as it is observed in the HAADF images (see, ESI). Histograms of the average particle sizes in both samples are presented. For Ag/TSG, the average particle size is 3 nm, while for the Ag/TP25 catalyst the average particle size is 9 nm, which explains the presence of SPR of Ag°NPs on the P25 surface. Figure S3 shows the interplanar spacing for TiO_2, ~0.34 nm (101 plane of anatase, and for Ag°, ~0.21 nm (111 plane 15-3325) and a HAADF image that confirms the presence of AgNPs.
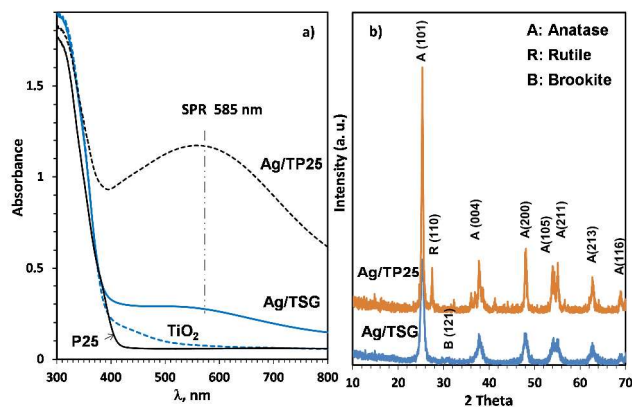

Fig. 1. UV–Vis diffuse reflectance spectra and XRD patterns of: (a) TSG, (b) Ag/TSG, (c) Ag/TP25 photocatalysts.

The photocatalytic reduction test was performed in a home-made, glass reactor system containing 200 mL of an aqueous solution with 7.5 ppm of 4 NP, 8 mM of Na_2SO_3 and 0.025-0.2 g/L of the photocatalyst loading, under previously established conditions.[20] The suspension was maintained under magnetic stirring (600 rpm) at room temperature and the system was irradiated with 254 nm UV light (UVP-Pen-ray, 4400 $\mu W/cm^2$). The determination of the concentration of the *4-NP* endocrine disruptor was made by UV-Vis spectroscopy using a Varian Cary 5000 spectrometer by following

the disappearance of the absorption band at 400 nm for the 4-NPhenolate (*4-NPate*) ions in alkaline media by the presence of Na_2SO_3. When the EDC *4-NPate* solution was irradiated with UV light in the presence of the TSG catalyst without noble metals, the absorption band at 400 nm, corresponding to the *4-NPate*, got reduced within 3h and a new absorption band appeared at 295 nm, characteristic of the *4-AP* formation, (Figure 2), suggesting that the EDC *4-NPate* was successfully photoreduced.[17, 20] A slight decrease in the *4-NPate* absorption band was detected for the photocatalytic reaction in the absence of any catalyst (photolysis), suggesting that a certain reduction degree of the EDC *4-NPate* took place.
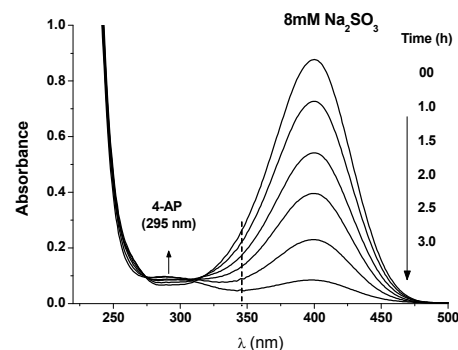

Fig. 2. UV-Vis spectra for the photoreduction of *4-NPate* with the TSG photocatalyst under UV light irradiation with 8 mM of Na_2SO_3.

A good linear correlation of the C/C_0 plot versus time for the *4-NPate* reductions at low photolysis conversion (<50%) for the TSG and Ag/TSG catalysts (Fig. 3-A) is the proof for a zero order rate kinetics, which indicates that the reduction rate is independent of the EDC *4-NPate* concentrations.[21] The *4-NPate* photoreduction with Ag/TSG was completed in ~1.5 h. The photoreduction rate in the absence of any photocatalyst (photolysis) was very low (k=0.15 M h^{-1}), but when the TSG catalyst was added, the photoreduction rate was increased as the photocatalyst load was also increased (Fig. 3-B), obtaining a rate constant value of 0.57 M h^{-1} (~4 times higher than the one obtained with photolysis) at 0.2 g/L of photocatalyst load. In the same way, when the TSG photocatalyst was functionalized with Ag°NPs (1.5 wt %), the photoreduction rate was also increased as the photocatalyst load was increased, obtaining a rate constant value of 2.7 M h^{-1} at 0.15 g/L of photocatalyst load, which is ~5 times higher than that for the TSG photocatalyst and ~18 times higher than that for photolysis.
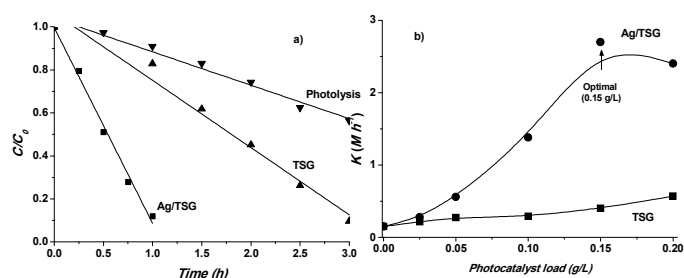

Fig. 3. A) Plot of C/C_0 versus time for the photoreduction of the *4-NPate*: a) without and b) with TSG catalyst. B) Apparent zero order rate constant for the photoreduction of *4-NPate* with TSG and Ag/TSG as a function of photocatalyst load.

By comparing the photocatalytic reduction rate of EDC *4-NPate*, using commercial TiO_2-P25 (TP25) as reference (Fig. 4), the photoreduction rate of the TSG photocatalyst (0.4 M h^{-1}) was slightly higher than that of TP25 (0.26 M h^{-1}). But, when TP25 was

functionalized with Ag°NPs, the photoreduction rate was increased 12 times until reaching 3.2 M h^{-1}, suggesting that the Ag°NPs deposited on TiO$_2$-P25 are the best. These results suggest that the Ag°NPs deposited on both TiO$_2$ surfaces enhanced remarkably the electron transfer process from the semiconducting surface to the acceptor reactant (EDC *4-NPate*), achieving a high photocatalytic reduction rate. In order to show the unprecedented photocativity of the Ag°NPs on TiO$_2$, an evaluation of substrates with Ag°NPs functionalization like Ag/ZnS(en)$_{0.5}$ hybrid and Ag-Al$_2$O$_3$ was carried out confirming the superior photoactivity of the Ag-TiO$_2$ nanocrystalline composite (see Figure S4 in ESI).
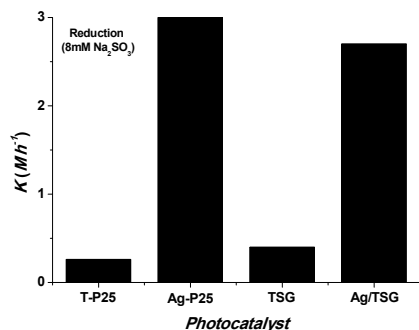

Fig. 4. Comparison of the pseudo zero order rate constant value for the photoreduction of the *4-NPate* over the TiO$_2$ photocatalyst and functionalized TiO$_2$ with Ag°NPs with 0.15 g/L of photocatalyst load.

The photocatalytic mechanism for the reduction of the endocrine-disruptor *4-NPate* by using TiO$_2$ without noble metal follows a similar-previously-reported mechanism,[9, 17] where the photogenerated holes on the TiO$_2$ surface react with the sulfite ions (SO_3^{2-}) causing their oxidation until the sulphate is formed, while the photogenerated electrons are transferred to the acceptor molecule *(4-NPate)* from the nitro group to form the *nitrophenolate* radical and, as consequence, to form *4-hydroxylaminophenol* and the transform it into *aminophenol*.[22] Considering that the redox potential for couples (*4-NP/4-AP*) and (SO_3^*/SO_3^{2-}) in aqueous solution is -0.76 V[23] and 0.63 V (NHE),[24] respectively, in the presence of SO_3^{2-} ions at pH=9.5, the position of the conduction band of the TiO$_2$ semiconductor should be favourably negative (<-0.8) V NHE). (Fig. 5). This electron transfer is fast when the Ag°NPs are deposited onto the TiO$_2$ surface because the Ag°NPs act as electron captors and help to transfer electrons from the semiconducting surface to the acceptor molecule through all the Ag°NPs. The electronic transfer contributes to the stability of the Ag°NPs during the UV irradiation.
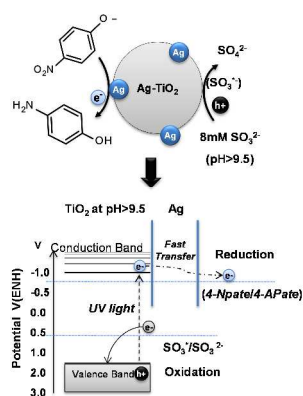

Fig. 5. Schematic representation of the photoreduction of *4-NP* in the presence of Na$_2$SO$_3$, with AgNPs-TiO$_2$ photocatalysts.

For recyclability studies the powdered systems need to be immobilised because recuperation from aqueous media implies the loss of the photocatalyst. Further studies will be developed in order to immobilize the material as a coat of foams as we reported previously for the inactivation of marine algae[25] and dye solar discoloration[26].

In summary, either sol-gel TiO$_2$ or commercial TiO$_2$-P25 were tested on the reduction of the endocrine-disruptor *4-NPate* to *4-AP* in the presence of Na$_2$SO$_3$ as a soft reducing agent by means of a photocatalytic process. The Ag°NPs photodeposited over sol-gel TiO$_2$ and P25 photocatalysts enhanced around 7 and 12 times the photocatalytic process, respectively. The Ag°NPs act not only as electron captors, but also as electron transfer agents that enhance the *4-AP* yield. Ag°NPs functionalized over Ag/ZnS(en)$_{0.5}$ hybrid or Al$_2$O$_3$ substrates did not enhance the *4-NPate* photoreduction confirming the unique activity of Ag/TiO$_2$ materials. For the first time, a practical functionalization of TiO$_2$ with 3-nm Ag°NPs has shown potential reduction photoactivity using Na$_2$SO$_3$ as a harmless reducing agent, yielding a valuable *4-Aminophenol* reagent for the analgesic industry. The possible applications of the UV-driven harmless photocatalyst system may be extended to the reduction of other nitro-aromatic compounds to amino-aromatics.

Notes and references

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