Silver-doped titania nanoparticles: synthesis and characterization

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Abstract

The titanium dioxide nanoparticles (TiO_2-NP) doped with silver ions (Ag^+) were produced using a solution of silver nitrate and titanium isopropoxide.
Electron microscopy and XRD were used to confirm that the Ag^+ did not alter the crystalline structure of the TiO_2-NP. Moreover, UV–Vis spectroscopy analysis showed a remarkable photochromic behaviour. TiO_2-NP doped with Ag^+ could blacken when lightened with UV light and then whiten under visible light, quickly.

Keywords: Titania nanoparticles; Silver ions doping; UV-Vis; TEM; XRD; Photocromism

1. INTRODUCTION

Nanomaterials show interesting optical properties due to their ability to convert efficiently light energy into physical and chemical one [1]. Especially, the optical properties of metallic nanoparticles allowed the development of devices based on Surface Plasmon Resonance (SPR). For instance, the nanostructured materials which are photosensitive could be manipulated to assemble photochromic nanosystems. Photochromism is the term generally used to describe the reversible transformation of a chemical species between two configurations. Tipically, this event is due to the absorption of a suitable source of energy, such as visible or UV radiation [2].
The literature reports numerous photochromic systems [3–5] but there are limited study on metal doped TiO_2 nanoparticles ones. Photochromism can be observed in TiO_2 nanoparticles, when their surface is decorated with small noble metal nanoparticles [6,7], such as silver ones. In these systems, the UV radiation promotes the TiO_2 valence electrons to the conduction band which are able to reduce metal ions to metal nanoparticles [8].
This work reports a method to synthesize TiO_2 nanoparticles doped with different Ag^+ concentration. UV-Vis spectroscopy, morphological (TEM) and structural (XRD) methods attested that the obtained nanoparticles were both Ag^+ doped and in the anatase crystalline form. The photochromic behaviour of the nanoparticles were also analysed by spectrophotometer.

2. EXPERIMENTAL

2.1. Synthesis of Ag^+ doped TiO_2-NP powders

In a typical synthesis 5 mL of titanium (IV) isopropoxide was added to 10 mL of ethanol. Then, a proper amount of $AgNO_3$ previously solubilized in ethanol was added. After adding 50 mL of distilled water, the solution was stirred at 80 °C for 30 min, followed by an overnight thermal treatment (60 °C) until drying. The dry mixture was calcined [9] at 400 °C for 2 hours. The generation of TiO_2 nanoparticles in the anatase form was obtained by monitoring the pH in the solution. Thus, once the nanoparticles were formed, they precipitated on the bottom of the solution. Three samples with different amount of Ag^+ were produced: **a)** 2.1 ± 0.3; **b)** 4.8 ± 0.2 and **c)** 6.8 ± 0.3 mg/g. Silver concentration was identified by AAS (Varian Spectra AA-600) for each sample. The reported value is the average among three measurement performed for each sample. As error, was considered the mean absolute deviation.

2.2. Instruments

The optical properties of the different Ag^+ doped TiO_2 samples were analysed by diffuse reflectance spectroscopy performed with a Varian Cary5 spectrophotometer. All the samples were treated in the same way in order to study their photochromic behaviour. The staining process was analysed by exposing the different samples to UV light (Philips PL-S 9 W, NL). Afterwards, the bleaching analysis was obtained by exposing the same samples to a halogen lamp (Lexman EXN38D 12 W). A different reflectance spectrum was recorded for each sample.

Structural and morphological analyses were performed by transmission electron microscopy (TEM). The Ag^+ doped TiO_2 powders were suspended in ethyl alcohol and single drops of each sample were casted onto different standard carbon supported 600-mesh copper grids. A transmission electron microscope Hitachi 7700, operating at 100 kV, was used to record TEM images.

XRD studies were executed by using a diffractometer Rigaku model Mini Flex with Cu-K_α radiation (λ = 0.154 nm) for each sample. The measurements were conducted with 30 kV of accelerating voltage, 15 mA of current, scan angle in 2θ from 10° to 80°, with step size of 0.01° and scan speed of $0.05° \cdot s^{-1}$.

3. RESULTS

3.1 Morphological and structural analyses

Figure 1a shows typical TEM bright-field of TiO_2 nanoparticles. No images pointed out the presence of silver nanoparticles. An enlargement of a selected area in Figure 1a is shown in Figure 1b. As evident, the nanoparticles have a crystalline structure and this was confirmed by XRD analysis showed in Figure 1c. Moreover, XRD spectra indicated that all TiO_2 samples were in anatase form and this structure was not altered by increasing the concentration of silver ions. Finally, Figure 1d shows the Williamson-Hall plot of each sample. As evident, by increasing the silver concentration there was only a small reduction in the average diameter of the nanoparticles from 20 to 18 nm.

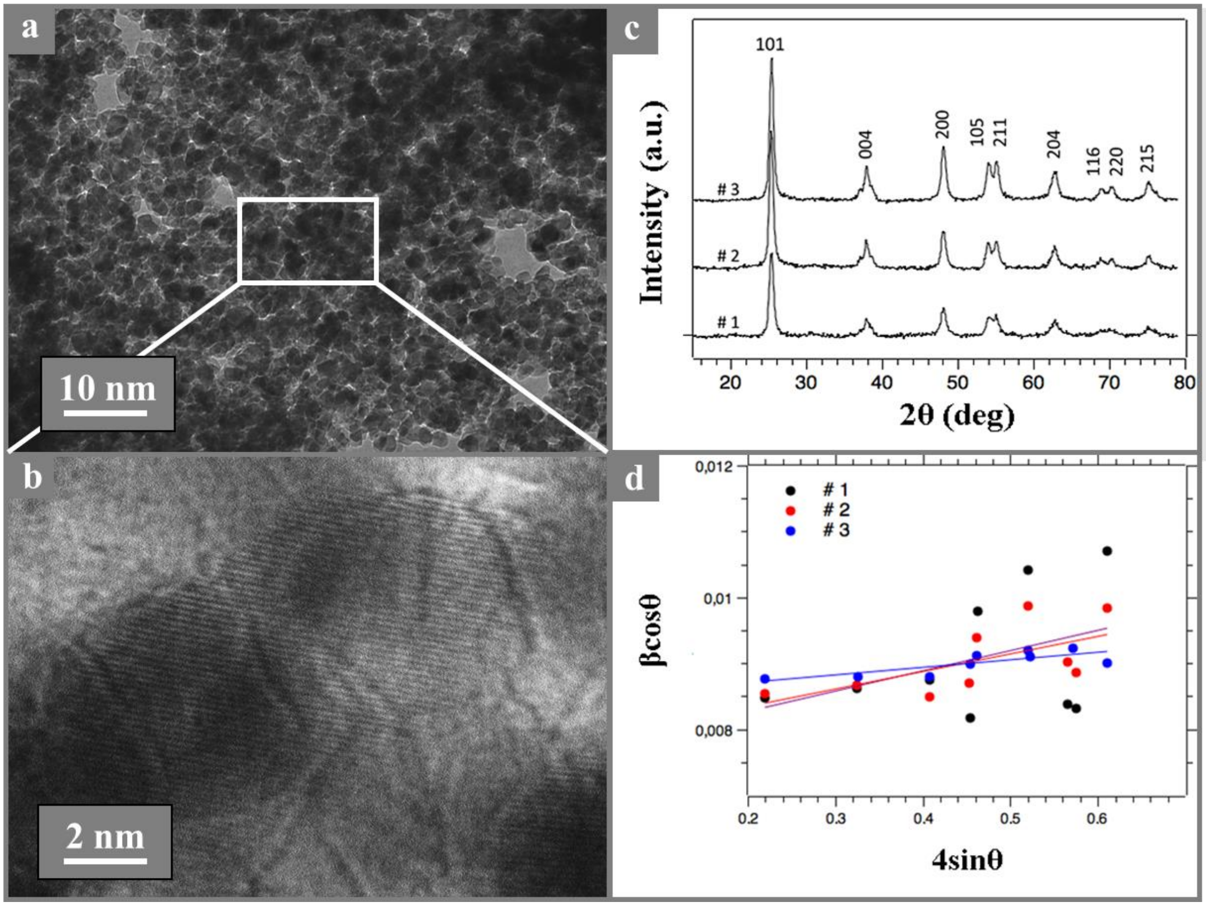

Figure 1: a) TEM bright-field of TiO_2 nanoparticles **b)** Enlargement of a selected area in Figure 1a **c)** XRD analysis of each sample **d)** Williamson-Hall plot of each sample.

3.2 Photochromic analysis

Figure 2 shows diffuse reflectance spectra (AS) following exposure to UV irradiation from all analysed samples (a; b; c). As evident, all examined samples undergo a decrease in diffuse reflectance after UV irradiation. The largest abatement was in sample b. This photocromic behaviour was also confirmed in the scheme reported in Figure 2 on the left. As shown, the TiO_2 nanopowder doped with Ag^+ darken under UV radiation and return to the initial condition under visible radiation.

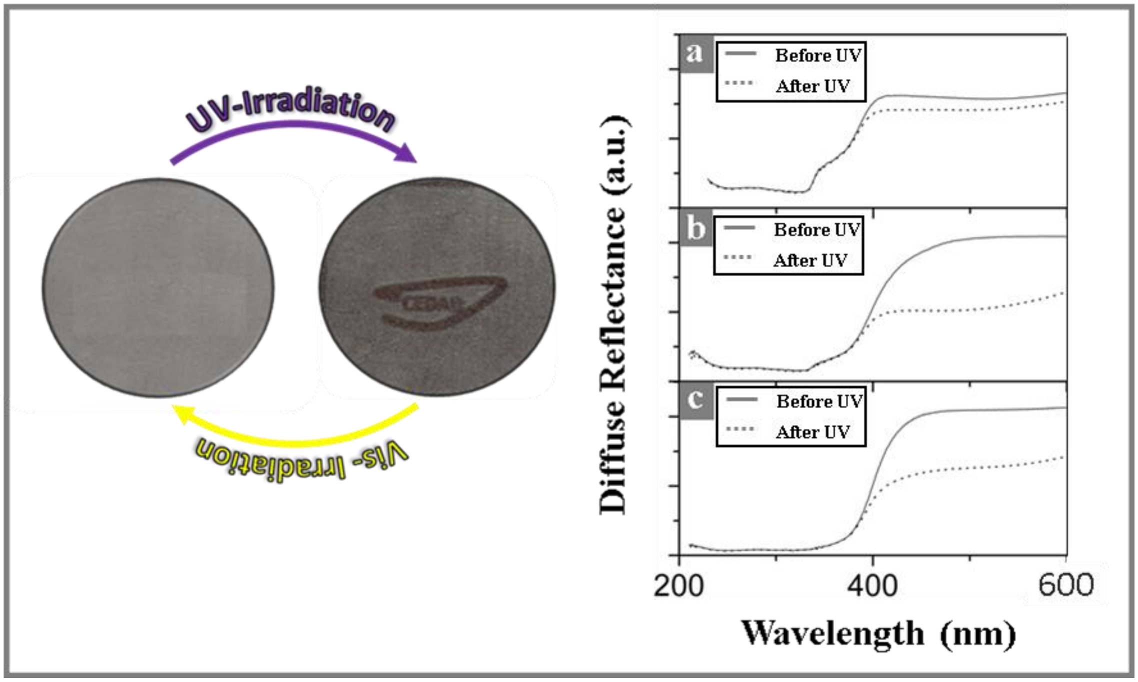

Figure 2: Photocromic behaviour scheme (on the left and diffuse reflectance spectra (AS) following exposure to UV irradiation for each sample (on the right)

Several Ag-TiO_2 systems are described as hetero-systems of silver nanoparticles-titania nanoparticles in literature. For these structures, all authors are in agreement to hypotheses that the darkening is due to reduction of Ag^+ to metallic Ag nanoparticles under UV irradiation, while bleaching is due to the photo-oxidation of silver nanoparticles via visible irradiation [10].

Our system is very different from those quoted in literature. According to literature data, in order to clarify the role of Ag ions we supposed that under UV irradiation Ag^+ ions can be reduced to Ag^0. In particular, irradiation of the Ag^+-doped titania nanopowder with UV-light could generate anion vacancy centres [11]. It is reasonable to suppose that the majority of holes formed by optical irradiation could be captured by Ag^+ reducing it to Ag^0.

The exposition to visible light determines the recovering process or bleaching of the photochromic absorption. This is then caused by release of electrons from the Ag^0 anion vacancy centres to valence band.

4. CONCLUSION

The synthesis procedure for inserting Ag ions into TiO_2 anatase structure was developed and allowed to obtain Ag-doped TiO_2 nanoparticles. XRD analysis confirmed that the increase in silver concentration did not modify the anatase structure of the TiO_2 nanoparticles. Moreover, the nanoparticles showed very interesting photochromic properties: they darken and whiten under UV light and visible light, respectively, in a very fast way. The optical properties of the materials have been studied through diffuse reflectance measurements.

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