Preparation and spectroscopic characterization of Au / Pt impregnated nano sized TiO$_2$ particles

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ABSTRACT

Precious metals doped anatase titanium dioxide nanoparticles are used in various applications including environmental photocatalysis and solar cells. In this work we present the synthesis of Au- doped and Pt-doped TiO$_2$ nanoparticles employing sol-gel methodology. The doping procedures based on reduction by UV photodeposition. The morphology, composition, particle size and specific surface area of these synthesized nanoparticles have been characterized using several instrumental techniques namely, Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDXS), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and N$_2$-adsorption Brunauer–Emmett–Teller (BET) methodology. Au impregnated (2%) nano anatase TiO$_2$ powder was examined in photo decolourization of Orange G as dye environmental pollutant under visible light illumination and optimum operational conditions.

Keywords

Titanium oxide,
Pt-doped,
Au-doped,
Anatase,
Characterization.

1. Introduction

Titania is the most widely used photocatalyst, but its limited activity under visible light irradiation has motivated the researchers for modified titania materials absorbing visible light [1]. Furthermore, TiO$_2$ is a very robust solid with excellent photochemical stability [2]. Therefore and also for its availability, affordability and lack of toxicity, TiO$_2$ is considered as the most stable and used photocatalytic material [3]. The anatase allotrope of TiO$_2$ semiconductor is reported to give the best combination of photoactivity and photostability because it is the most active allotrope form among the various available allotropes, rutile and brookite [4]. However, anatase is characterized by large band gap (E$_g$ = 3.2 eV) [5] and consequently low quantum yield which limit its practical applications. In order to circumvent this discrepancy, certain precious metals like Ag, Au and Pt which are deposited on a TiO$_2$ surface may enhance the photocatalytic efficiencies because they act as an electron trap promoting interfacial charge transfer processes. Accordingly, non metal [6] or metal [7] doping strategy has been adopted. Although, doping is an effective method to enhance visible light absorption, but Ag, Au and other noble metals are not being used for conventional "doping", in the sense that the Ag, Au occupy particular crystallographic sites of the TiO$_2$, or rather, inside the TiO$_2$. They are typically used to modify "impregnate" the surface of light absorbers in order to enhance the catalytic properties via plasmonic effect enhancement. Recent reports revealed that Au, Pt and Ag are optimal candidates among the impregnating species such as the transition metals [7]. Silva et al. [8] reported that under visible light irradiation, the presence of gold is beneficial because it introduces visible light photocactivity by irradiation at the surface plasmon band of gold, whereas, under UV irradiation conditions, gold acts as electron–hole recombination center and consequently the photocatalytic activity of Au/TiO$_2$ decreases. Also, Wang et al. [9] stated that in the metal impregnated photocatalysts, the noble metal nanoparticles act as a major component for harvesting visible light due to their surface plasmon resonance while the metal– semiconductor interface efficiently separates the photogenerated electrons and holes.

2- Experimental

2.1. Chemicals

All the chemicals which have been used were as high purity as available and used without further purification. Titanium Isopropoxide (98%, Acros Organics), Isopropanol (99.8%, Riedel Dehean), HAuCl$_3$.3H$_2$O (98%, Aldrich), H$_2$PtCl$_6$ (99% Sigma-Aldrich). Deionized nanofiltered water, DNFW (TDS = Zero) was used for all experiments.

2.2. Impregnation of TiO$_2$ nanoparticle catalyst

Titanium dioxide nanosized catalyst was initially synthesized by the sol-gel method by means of a gradual addition of a solution of titanium isopropoxide (15 ml isopropanol + 15 ml titanium isopropoxide) onto 200 ml of DW at pH = 5 with a rate of addition of 2 ml / min. The mixture was kept, after completion of addition, under continuous vigorous mixing at room temperature until the completion of hydrolysis (2 hours).The resulting transparent colloidal solution was left aging for 24 hours then filtered, dried at 90°C for three hours and finally was calcined at 400°C for 4 hours. Grounding into fine powder, if needed, overcomes the agglomeration. One gram of the prepared nano TiO$_2$ powder was added into 200 ml of Au and / or Pt solution at certain weight content. The solution was illuminated with UV radiation by means of 15 watts UV lamp (Fig. 1) for 24 hours under room temperature and vigorous stirring. The resulting solid-liquid mixture was filtered using 0.45 micron cellulose membrane filter. The filtered solid was afterwards dried at 90°C for three hours.

3- Results and Discussion

3.1 Surface morphology and composition aspects

Leo 982 Scanning Electron Microscope (SEM) was employed for the surface morphology study of the mesoporous Au-TiO$_2$ and Pt-TiO$_2$ powders.
Fig. 1. Photo impregnation unit including UV lamp 15 watts.

Figures 2 and 3 exhibit smooth and homogeneous surfaces for gold and platinum impregnated TiO$_2$, respectively. The insets show the precious metals distribution onto the photocatalyst surface at two different magnifications. The surfaces have also been explored by Philips Scanning Transmission Electron Microscope (TEM) coupled with TECNAI device for nanoscale analysis. Figures 4 and 5 reveal the excellent dispersion of irregular spherically shaped Au and Pt metals over TiO$_2$ particles which are more explicitly presented, in terms of metal atoms content, in the accompanied EDX templates. Moreover, the overall surfaces for both Au-TiO$_2$ (Fig. 6) and Pt-TiO$_2$ (Fig. 7) have been scanned and explored employing Leo 982 Energy Dispersive X-ray Spectrometer (EDXS). These figures (6 and 7) show obviously the abundance of the precious (Au and Pt) metals encompassed into the prepared nano TiO$_2$ powders.
3.2 Porosity and surface area analysis
Brunauer.Emmett.Teller (BET) St 1 on NOVA touch 4LX nitrogen adsorption apparatus was employed for the measurement of both pore size and surface area of the Au and Pt impregnated anatase TiO$_2$ nanoparticles after the samples were vacuum degassed at 110 °C (2 °C/min) for 720 minutes. Figure 8 presents the measured pore sizes for the synthesized nano TiO$_2$ particles, Au-impregnated and Pt-impregnated powders. The maxima at pore sizes of 6.8, 7.8 and 7.8 nm are illustrated for TiO$_2$ nanoparticles, Au-TiO$_2$ and Pt-TiO$_2$ composites, respectively. These values of pore size indicate the mesoporosity of the neat and impregnated powders. Furthermore, the insets in Fig. 8 show adsorption-desorption isotherm plots which result in surface area of 130, 121 and 109 m$^2$/g for TiO$_2$, Au-TiO$_2$ and Pt-TiO$_2$ specimen, respectively. Also from Fig. 8, one could observe the impacts of precious metals impregnation on the pore size and surface area of the prepared nano powder. The pore sizes were increased, whereas surface areas have been decreased, particularly in presence of Pt. This could be ascribed to the greater size (5d shell) of Pt in comparison to Au (4d shell).

3.3 Phase and crystalline size features
Pananalytical (X’ Pert PRO) Philips diffractometer with Cu Kα radiation (0.15425 nm) in the range of 2θ from 0$^o$ to 120$^o$ was used for the X-ray Diffraction (XRD) spectroscope patterns of Au and Pt impregnated anatase TiO$_2$ powders. Diffraction signal assigned to the anatase (101) structure at 25.3$^o$ (25.4$^o$–25.6$^o$ in this work) is explicitly observed in TiO$_2$ [10]. From Fig. 9, the diffraction signals which are located at 38.2, 44.4, 64.6, 77.5, 81.7, 110.8 and 115.3 degrees are assigned for Au (111), Au (200), Au (220), Au (311), Au (222), Au (331) and Au (420) allotropes, respectively. Whereas, Fig. 10, presents diffraction signals located at 39.8, 46.3, 82.3 and 117.7 degrees which belong to Pt (111), Pt (200), Pt (311) and Pt (331) allotropes, respectively. Both Figs. 9 and 10 don't show any rutile phase (110) diffraction signals, which consequently concludes that appropriate conditions were employed for the sol gel impregnation methodology.

3.4 Photocatalytic degradation of Orange G
For the sake of application, the Au impregnated nano anatase TiO$_2$ powder was examined in photo decolourization
of Orange G as dye environmental pollutant under visible light illumination. Optimum operational conditions namely, photocatalysis medium initial pH = 3, nano Au-TiO₂ (2% Au) powder loading = 40 mg, visible light intensity (lamp of 500 watts) = 35 E-08 Ein / sec. L and dye concentration = 10 mg/L have been employed. Figure 11 shows a gradual Photo decolorization of the polluted dye solution over 4.5 hours of irradiation ending with > 90% photodegradation.

4. Conclusions

Nano Au-TiO₂ and Pt-TiO₂ powders were successfully prepared by the simple sol gel method. SEM and TEM images illustrated smooth surfaces with high dispersion of Au and Pt metal atoms. EDXS measurements revealed the content of the precious metal impregnated powders which were resulted from the impregnation process. BET measurements confirmed the mesoporosity of the impregnated photocatalyst powders with variation in surface area due to the inclusion of precious metal atoms. XRD patterns confirmed the existence of Au and Pt diffraction signals within the photocatalyst pattern. Finally, the evaluation of the synthesized nano Au-TiO₂ photocatalyst resulted in an excellent photo decolourization of the model dye pollutant, Orange G.

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References