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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.

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 allotropic 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 it's 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 photoactivity 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), $HAuCl_4.3H_2O$ (98%, Aldrich), H_2PtCl_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.

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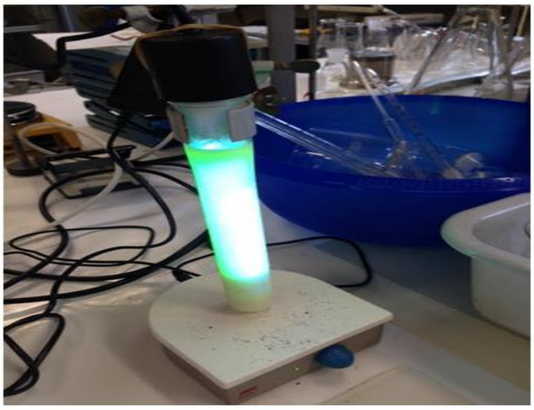

Fig. 1. Photo impregnation unit including UV lamp 15 watts.

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.

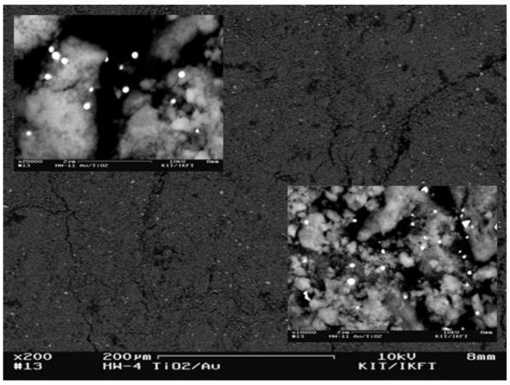

Fig. 2. Scanning Electron Microscope (SEM) micrographs for Au-impregnated anatase TiO_2 with different magnifications.

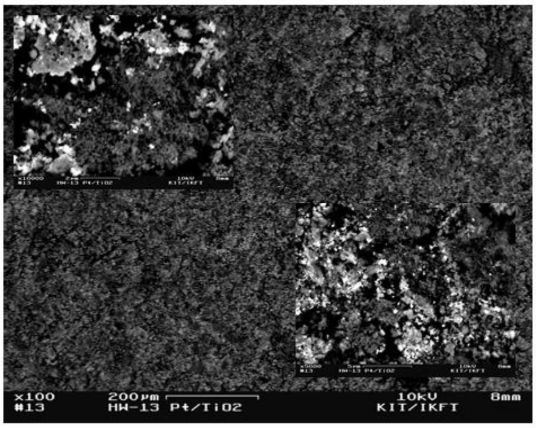

Fig. 3. Scanning Electron Microscope (SEM) micrographs for Pt-impregnated anatase TiO_2 with different magnifications

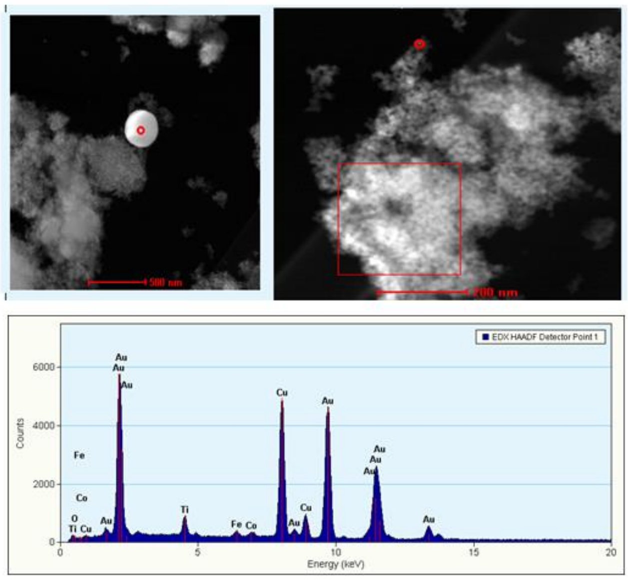

Fig 4. Transmission Electron Microscope (TEM) micrograph for Au-impregnated nano TiO_2 powder and EDX composition.

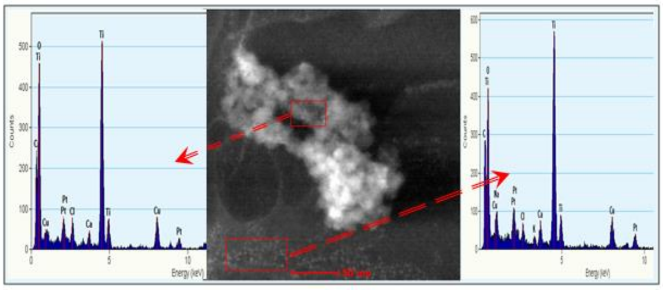

Fig. 5. Transmission Electron Microscope (TEM) micrograph for Pt-impregnated nano TiO_2 powder and EDX composition.

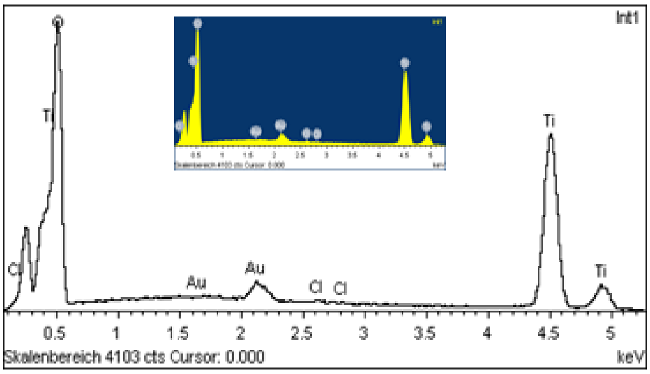

Fig. 6. Energy Dispersive X-ray Spectroscope (EDXS) image of Au-impregnated nano TiO_2 powder.

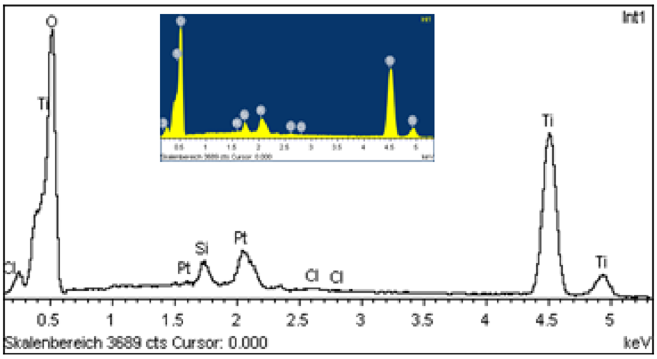

Fig. 7. Energy Dispersive X-ray Spectroscope (EDXS) image of Pt-impregnated nano TiO_2 powder.

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).

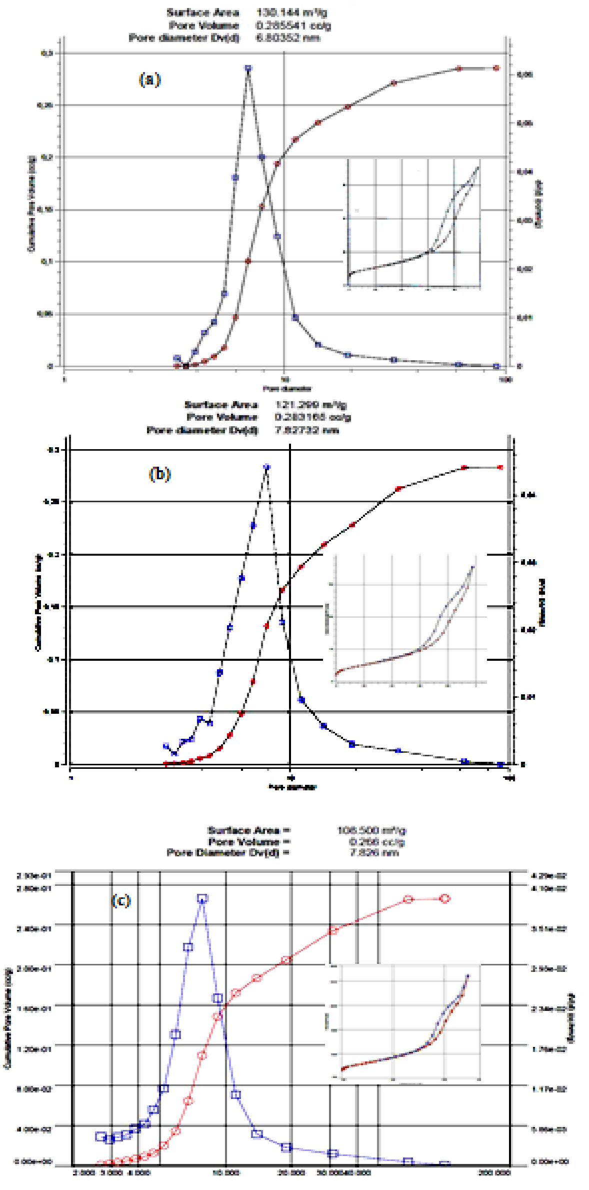

Fig. 8. Pore size measurements for ;(a) Synthesized nano anatase TiO_2; (b) Au-impregnated nano anatase TiO_2; (c) Pt-impregnated nano anatase TiO_2; insets represent adsorption-desorption isotherms.

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 0^0 to 120^0 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.

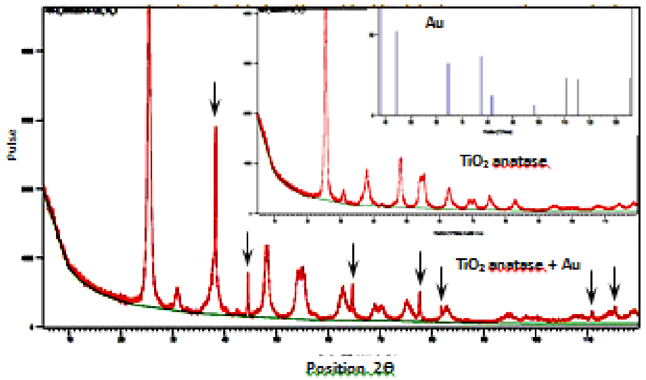

Fig. 9. X-ray Diffraction Spectroscope (XRD) patterns of impregnated anatase TiO_2; arrows present gold positions.

The average crystalline sizes for Au-TiO_2 and Pt-TiO_2 powders were computed by Sherrer's equation using the XRD line broadening method [11]. The crystal size C.S. = 0.9 λ /(Bcosθ) where λ represents the wavelength of X-ray, B the FWHM and the θ diffraction angle. By using the experimental data, an average crystalline size of 15.3, 14.2 and 12.4 nm were derived for TiO_2, Au-TiO_2 and Pt-TiO_2 .

The crystalline size relates reciprocally with the peak width in which by increasing the peak width the size of nano TiO_2 decreases [12]. Consequently, Figs. 9 and 10 confirm this phenomenon in which the synthesized nano TiO_2 band shows less broadening than that of the impregnated TiO_2 bands.

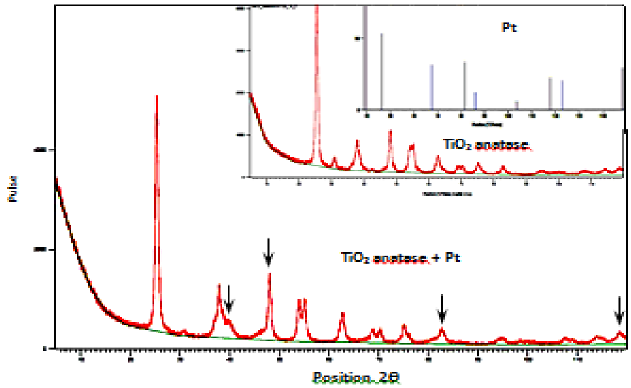

Fig. 10. X-ray Diffraction Spectroscope (XRD) patterns of impregnated anatase TiO_2; arrows present platinum positions.

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-TiO_2 (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.

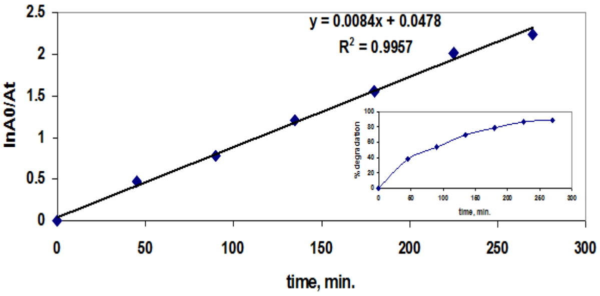

Fig. 11. Kinetics of photocatalyalytic decolourization of Orange G dye at optimum experimental conditions. Inset represents degradation percent versus photodecolourizing time.

4. Conclusions

Nano Au-TiO_2 and Pt-TiO_2 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-TiO_2 photocatlyst resulted in an excellent photo decolourization of the model dye pollutant, Orange G.

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