

GREEN SYNTHESIS AND CHARACTERIZATION OF TITANIUM (IV) OXIDE NANOPARTICLES: EFFECTS OF SOLUTION PH, TEMPERATURE AND METALLIC AG PARTICLES

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ABSTRACT

Abstract: A facile green route for the synthesis of TiO₂ nanoparticles using titanium(IV) isopropoxide precursor and aqueous extract of *Plumeria acuminata* leaves is reported. The effects of solution pH and calcination temperature on grain size and TiO₂ phase type were investigated. Additionally, different concentrations of Ag in the range of 0.05 M - 0.2 M were incorporated onto the lattice layer of TiO₂ via a wet-impregnation hydrothermal method to obtain Ag doped TiO₂. The synthesized nanomaterials were characterized by HRSEM, BET and XRD. The HRSEM micrograph revealed the presence of well dispersed and distinct aggregated spherical particles of TiO₂ and Ag-TiO₂. The XRD pattern demonstrated the formation of purely body-centred tetragonal TiO₂ anatase phase only at solution pH (3) and calcination temperature 400°C with an average size of 8.2 nm. The optimum concentration of Ag incorporated onto the TiO₂ lattice layer was 0.1 M and the doping effect of metallic Ag did not distort the TiO₂ phase however responsible for particle size reduction to 7.1 nm. The BET analysis showed that Ag doped TiO₂ nanoparticles exhibited higher surface area (85.97 m²/g) than the bare TiO₂ nanoparticles with surface area of 65.00 m²/g. The study revealed that Ag concentration, solution pH, the calcination temperature played an important role on the morphology and the phase type of as-prepared TiO₂ nanoparticles.

Keywords: Green Synthesis, TiO₂ nanoparticle, silver doping, characterization

INTRODUCTION

Titanium oxide (TiO₂) as one of the heterogeneous semiconductor metal oxides remains the most widely studied among researchers due to its photochemical and biological stability, non-toxicity, optical properties, high photocatalytic activity compared to ordinary bulk material [1]. TiO₂ nanoparticles can be prepared via different methods namely sonochemical, sol-gel, hydrothermal, solvothermal, anodization, electrospinning, catalytic chemical vapour deposition amongst others [2]. These methods have certain shortcomings such as high cost of chemicals/reagents, high energy requirement and also complex synthesis procedure [3]. Conversely, green synthesis involving the use of plant extracts has been identified as an alternative route to prepare nanoparticles due to its relative abundance, cost effectiveness and environmental friendliness [4]. Currently, researchers have employed different plant species for nanoparticles synthesis.

For instance, Thiyyagarajan *et al.*, [5] synthesized TiO₂ nanoparticles using Titanium Oxysulfate solution and extract of *Hibiscus* flower as titanium precursor and reducing agent respectively. In this study, synthesis of TiO₂ nanoparticles, using Titanium (IV) Isopropoxide as Titanium precursor and the aqueous extract of *Plumeria acuminata* where the influence of solution pH, calcination temperature and metallic Ag on the morphological characteristics and surface area were investigated.

MATERIALS AND METHODS

Materials

Chemicals such as Titanium (IV) Isopropoxide, Silver Nitrate, sodium hydroxide, and hydrochloric acid used in this study were of analytical grade with percentage purity of 99%. The chemicals were purchased from Sigma Aldrich and used as received without any further purification. The leaves of *Plumeria acuminata* were collected from different locations in Bosso, Area, Minna, Niger state. The collected *Plumeria acuminata* leaves were washed with water, cut into small pieces; air dried and grounded using a wooden mortar and pestle. The powdered sample was stored in an air tight container.

Green Synthesis of the TiO₂ and Ag doped TiO₂ Nanoparticles

About 50 cm³ of aqueous leaves extract of *Plumeria acuminata* was measured into a 250 mL beaker and 10 cm³ of 0.1 M Titanium (IV) Isopropoxide was added in drops under continuous stirring at 150 rpm on a magnetic stirrer for 2 hours. The pH of the mixture was adjusted to the desired value 3, 5, 7, 9 and 13 using 0.5 M NaOH or 0.5 M HCl. The TiO₂ nanoparticles formed were later separated from the mixture using Whatman (No.1) filter paper and washed repeatedly with distilled water to remove the residual by-products. The residue was later oven dried at 100°C overnight. In order to investigate the effect of calcination temperature on the nature of TiO₂ nanoparticles, 3.2 g of the obtained TiO₂ cakes was calcined in a muffle furnace at different temperature range of 200°C, 300°C, 400°C, 500°C, 600°C and 700°C for 2 hours. Silver doped TiO₂ nanoparticles was prepared by mixing 4 cm³ each of different concentrations of AgNO₃ (0.05, 0.1 and 0.2 M) with 2 g TiO₂ nanoparticles in separate beaker and then stirred at 150 rpm on a magnetic stirrer under direct sunlight for 2 hours each. The mixtures were left to age overnight and subsequently oven dried at 100°C and later calcined at 400°C for 2 hours.

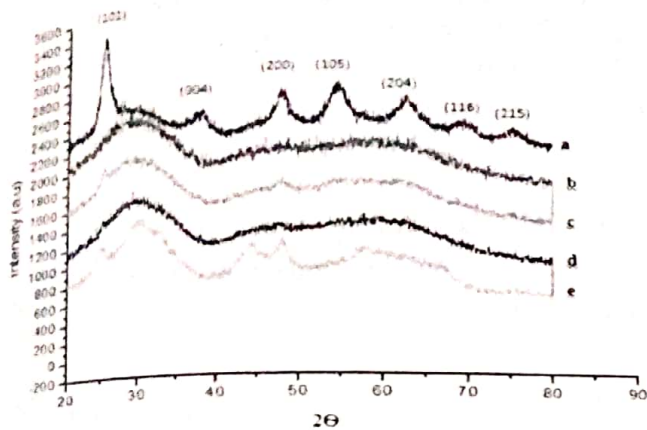
Characterization of the prepared TiO₂ and Ag doped TiO₂ nanoparticles

The synthesized TiO₂ nanoparticles were characterized using High Resolution Scanning Electron Microscope (HRSEM) Zeiss Auriga, X-ray Diffraction (XRD) Bruker D8 Cuka radiation, and Brunauer-Emmett-Teller (N₂ BET) technique

RESULTS AND DISCUSSION

XRD Analysis of TiO₂ prepared at different pH

The phase structure of the prepared TiO₂ nanoparticles at different pH was examined using X-ray diffraction technique. Figure 1 shows the XRD patterns of the synthesized TiO₂ nanoparticles at different pH values.



It can be noticed that there was no evidence of formation of define peaks that corresponds to anatase, rutile or brookite at pH 5, 7, 9 and 13. On the contrary at pH 3, sharp and intense peaks were observed at 2θ value of 25.39° , 38.52° , 47.89° , 54.51° , 62.30° , 68.85° , 75.19° which corresponds to the following crystal planes (101), (004), (200), (105), (204), (116), (215) of a body centred tetragonal anatase TiO_2 [5].

XRD Analysis of Prepared TiO_2 nanoparticles calcined at different temperatures

Figure 2 shows the XRD patterns of TiO_2 nanoparticles prepared at different calcination temperatures.

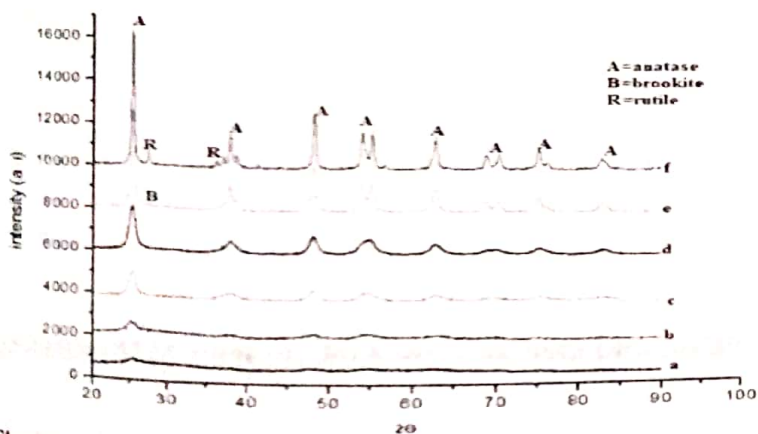


Figure 2. XRD spectrum showing TiO_2 nanoparticles at optimum pH of 3 calcined at (a) 200°C (b) 300°C (c) 400°C (d) 500°C (e) 600°C (f) 700°C

As shown in Figure 2, it was noticed that at 200°C , there was no evidence of formation of peaks while at 300°C , weak peaks began to form with no defined phase (anatase, rutile or brookite). At 400°C there were evidence of formation of sharp, intense and well defined diffraction peaks at 2θ value of 25.3° , 37.8° , 49.6° , 55.1° , 62.6° , 68.8° and 75.5° . These diffraction peaks correspond to the crystal planes (101), (004), (200), (211), (204) and (215). The diffraction peaks obtained at 400°C suggested the formation of pure body-centred tetragonal TiO_2 anatase polymorph. It should be mentioned that at this temperature no peaks corresponding to rutile or brookite were observed. In addition, between $500 - 700^\circ\text{C}$, the XRD spectrum revealed the formation of a mixed phase (anatase/brookite or anatase/rutile) diffraction peaks at 2θ value of 27.5° , 36.2° , 41.2° , 44.4° , 54.3° , 56.8° depicts the rutile peaks and while 25.5° , 25.6° and 30.9° correspond to brookite peaks. These diffraction peaks correspond to the following crystal planes (110), (101), (111), (210), (211) (220) of rutile and (210), (111) and (121) of brookite respectively [4]. With increase in calcination temperature to 700°C , the TiO_2 nanoparticles was observed to be more crystalline as evident in the

formation of sharp and intense diffraction peaks especially at (101). The diffraction peaks became more strong and sharp, thus suggesting the formation of larger crystal size and of course higher crystal degree. It was found that as the temperature increases (400°C - 700°C) the average crystallite size was found to increase from range 8.2-11 nm. This increase could be attributed to Oswald ripening process and destruction of hollow structure assisted by the elevated temperature, which is a diffusion process where the particles increases in size at the expense of small particles [3].

HRSEM analysis of undoped TiO₂ and Ag-doped TiO₂ nanocomposites

The morphological arrangement of the silver immobilized TiO₂ nanoparticles was examined using HRSEM and the micrographs obtained are shown in Figure 3.

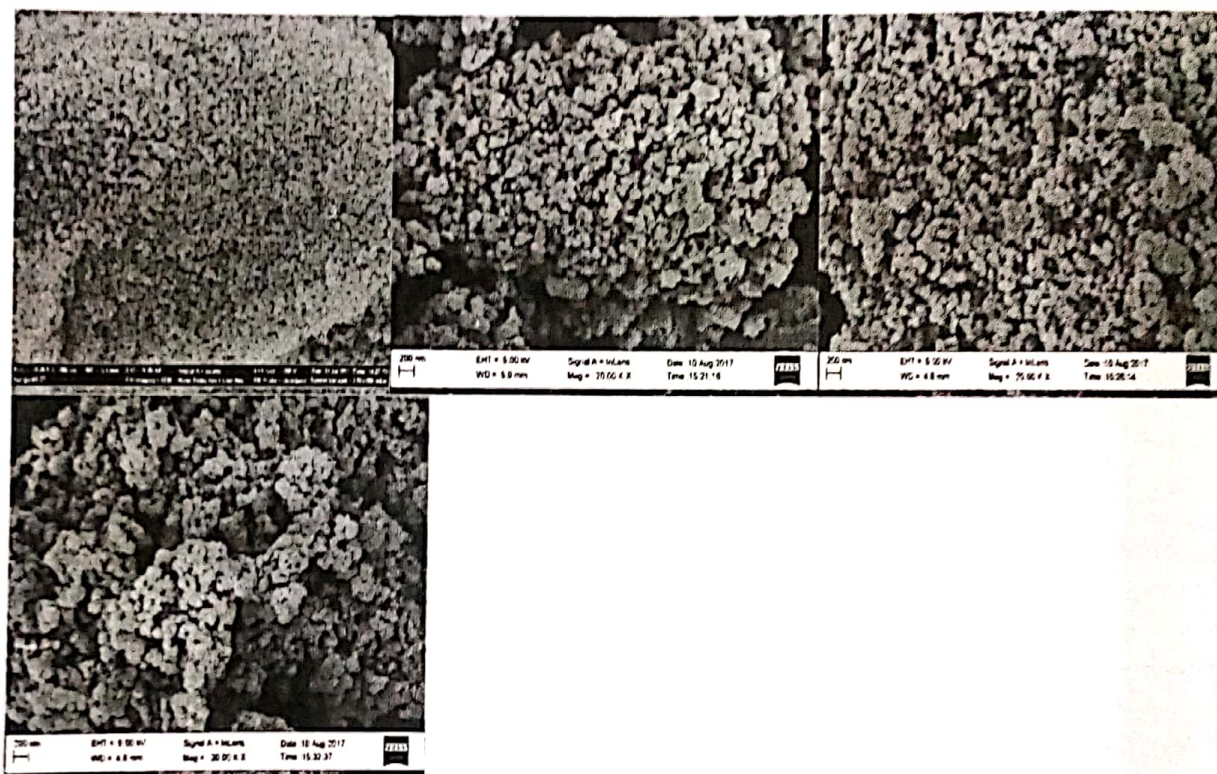


Figure 3: HRSEM micrographs showing (a) undoped TiO₂, (b) 0.05 M (c) 0.1 M (d) 0.2 M Ag-doped TiO₂ nanoparticles

It can be seen from Figure 3 (a) that the bare TiO₂ nanoparticles exhibited closely packed agglomerated crystals arrangement with no inter-particle gap or lattice stripe. On the contrary more space voids or channels were observed due to the incorporation of Ag onto the lattice layer of TiO₂. The creation of more space and channel is responsible for the slight increase in specific surface area of doped TiO₂, which improves its photocatalytic performance compared to undoped TiO₂ nanoparticles (see Table 1). It can be concluded that silver particles were readily dispersed and incorporated in Figure 3 (c) than Figure 3 (b) or (d). In addition, the doping effect of metallic Ag influences the morphological arrangement of the nanoparticles formed.

XRD Analysis of Undoped and Ag doped TiO₂ Nanocomposites

Figure 5 shows the XRD pattern of undoped and Ag doped TiO₂ nanoparticles

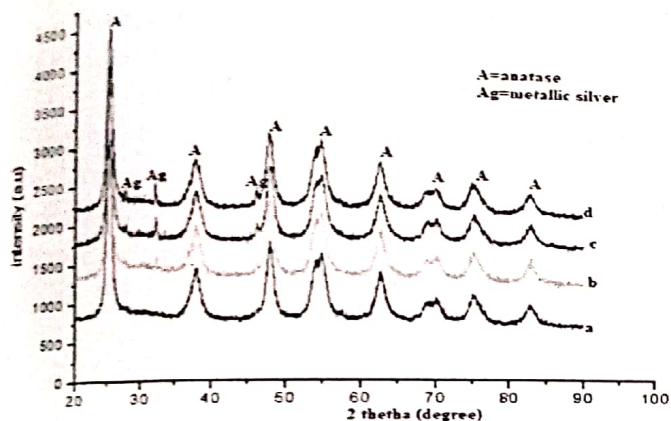


Figure 4. XRD patterns of (a) TiO₂ alone (b) 0.05 M (c) 0.1 M (d) 0.2 M Ag doped TiO₂

The XRD pattern in Figure 4 (a-e) illustrates the presence of strong, sharp, and relatively intense diffraction peaks at 2θ values of 25.4° , 37.7° , 48.23° , 54.8° , 62.78° , 68.8° , and 75.70° . These peaks aligned well to the crystal planes of (101), (004), (200), (211), (204), (220), and (215). The XRD patterns indicated the formation of pure anatase TiO₂ irrespective of the dopants (Ag). Also, very small peaks belonging to silver were observed at 2θ values of 32.2° and 45.6° . These diffraction peaks can be attributed to the crystal planes of metallic silver (111) and (200). It was found that the intensity of peaks increases, the particle size reduces despite increase in the concentration of metallic Ag [2].

BET Analysis of Undoped and Ag doped TiO₂ Nanoparticles

The surface area of each prepared catalyst is given in Table 1.

Table 1 Specific surface area and pore volume of prepared TiO₂ and Ag doped TiO₂

| Samples | BET surface area (m ² /g) | Pore volume (m ³ /g) |
|----------------------------------|--------------------------------------|---------------------------------|
| P 25 Commercial TiO ₂ | 56.000 | 0.640 |
| Prepared TiO ₂ | 65.000 | 0.198 |
| 0.05 M Ag-TiO ₂ | 76.123 | 0.136 |
| 0.1 M Ag - TiO ₂ | 80.267 | 0.109 |
| 0.2 M Ag-TiO ₂ | 85.975 | 0.040 |

It was found that the surface area of the synthesized TiO₂ nanoparticles in this study is higher than that of commercial TiO₂ nanoparticles. This increment is attributable to the capping and stabilization effect provided by the plant extract, which prevented particles aggregation compared to commercial TiO₂ nanoparticles prepared via chemical route. Also, the surface area of the silver doped nanoparticles increases with Ag concentration. The narrow pore volume distribution observed for all the synthesized materials suggests that the catalysts exhibited pore channels of a typical mesoporous material [5]. The more the number of atoms residing on the surface of the nanoparticles, the higher the adsorption ability towards organic pollutants.

CONCLUSION

The morphological characteristics of pure anatase phase of TiO₂ nanoparticles prepared through green synthesis was studied at different solution pH and calcination temperature. The modification/doping of TiO₂ nanoparticles with different amounts of Ag was achieved via impregnation-photoreduction method. TiO₂ nanoparticles with particle size in the range of 8-11 nm were synthesized at pH range of 3-13 and the obtained product was calcined at a temperature range of 200° C-700° C under air. The XRD analysis revealed successful formation of pure anatase phase body centred tetragonal of TiO₂ nanoparticles at pH 3 and calcination temperature of 400° C. The addition of metallic Ag did not cause any phase transformation instead loosely bound well distinct spherical particles dispersed on the surface of TiO₂, and average particle size range between 7-10 nm. BET analysis showed an increased in surface area of the TiO₂ nanoparticles upon doping with metallic Ag.

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