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Eco-friendly synthesis of TiO_2, Au and Pt doped TiO_2 nanoparticles for dye sensitized solar cell applications and evaluation of toxicity

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Driven by the demand of pure TiO_2, Au and Pt doped TiO_2 NPs were successfully synthesized using *Terminalia arjuna* bark extract. The eco-friendly synthesized NPs were characterized by UV-Vis-DRS, ATR-FT-IR, PL, XRD, Raman, SEM with EDX and TEM analysis. The synthesized NPs were investigation for dye sensitized solar cell applications. UV–Vis–Diffused Reflectance Spectra clearly showed that the expected TiO_2 inter band absorption below 306 nm, incorporation of gold shows surface plasma resonant (SPR) near 555 nm and platinum incorporated TiO_2 NPs shows absorbance at 460 nm. The energy conversion efficiency for Au doped TiO_2 NPs when compared to pure and Pt doped TiO_2 NPs. In addition to that, Au noble metal present TiO_2 matrix and an improve open-circuit voltage (V_{oc}) of DSSC. Synthesized NPs was evaluated into antibacterial and antifungal activities by disk diffusion method. It is observed that NPs have not shown any activities in all tested bacterial and fungal strains. In this eco-friendly synthesis method to provide non toxic and environmental friendly nanomaterials can be used for solar energy device application.

1. Introduction

Last two decades, nanotechnology is achieving for many fields with a vital role of material science and it has been used to versatile applications. Nanoparticles (NPs) process the unique physicochemical properties, which is due to their high surface to volume ratio. Titanium Oxide (TiO_2) NPs, is a promising semiconductor with wide band gap energy (3.2 eV) and large exciton binding energy [1]. It has been widely used in photocatalytic [2], dye sensitized solar cells [3], wastewater treatment [4], plant tissue culture applications [5] and antimicrobial activity [6]. In addition, important properties of this material are the high visible spectrum transmittance, high chemical stability, low cost and nontoxic towards both humans and the environment [7].

Generally, TiO_2 NPs have been synthesized by various methods such as sol–gel [8], hydrothermal [9], solvothermal [10], flame combustion [11], emulsion precipitation [12], fungus mediated biosynthesis [13] and so on. Noteworthy, most of these techniques are high cost and employed by toxic chemicals. Recently, plant extracts have been reported to show high efficacy

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in TiO_2 NPs synthesis such as *Jatropha curcas* [14], *Aloe vera* [15], *Annona squamosa* [16], *Psidium guajava* [17], *Desmodium gangeticum* [18] *Solanum trilobatum* [19] and *Mangifera indica* [20]. The plant extracts containing rich bioactive components, which act as capping and reducing agent to produce a nanocrystalline nature of metal oxide NPs in different size and morphology. Phytosynthesis method gives a more offer than physical, chemical and microbial methods. In this alternative method, it can produce the cost-effective nanoparticle. So, we have attempt to synthesize noble metals for gold (Au) and platinum (Pt) doped with TiO_2 NPs and its applied for dye sensitized solar cell (DSSC) and biological applications.

Terminalia arjuna (Combretaceae family) it is a large evergreen tree with spreading crown and drooping branches. It is 65–164 feet tall tree distributed in India, Burma and Sri Lanka, particularly found in abundance throughout Indo-sub-Himalayan tracts of South Bihar, Uttar Pradesh, Madhya Pradesh and Deccan regions [21,22]. Since, 1500–800 BCE. it has been used in ayurvedic system of medicine. It's bark powder used as the treatment of coronary artery disease, heart failure and hypercholesterolemia [23]. The phytochemical constituents such as apigenin, arjunic acid, arjun glucoside, arjunetin, tannins, triterpenoids and flavonoids were isolated from the bark of *T. arjuna*. Previously, *T. arjuna* bark extract used as reducing and capping agents for Cu NPs synthesis [24].

In the present investigation, Pure TiO_2, Au and Pt doped TiO_2 NPs were synthesized by *T. arjuna* bark extract. We have studied the structural, optical, DSSC and antimicrobial properties of synthesized nanoparticles. To the best of our knowledge, this may be the first report on the phytosynthesis of Pure TiO_2, Au and Pt doped TiO_2 NPs using *T. arjuna* bark extract.

2. Experimental

2.1. Chemicals

Titanium isopropoxide [$C_{12}H_{28}O_4Ti$ (97%)], Hydrogen tetrachloroaurate(III) trihydrate [$HAuCl_4 \cdot 3H_2O$ (99.9%)], Potassium tetrachloroplatinate(II) [K_2PtCl_4 99.99%] were obtained from Merck (India) and Sigma-Aldrich Chemicals (USA), respectively. Microbiological medias were obtained from Himedia Laboratories, India. Double distilled water, analytical grade chemical and reagents were used for all the experiments.

2.2. Collection of plant material

The *Terminalia arjuna* barks were collected from Endangered Medicinal Plants Conservation Centre, Science Campus, Alagappa University, Karaikudi, Tamil Nadu, India. Taxonomic identification was made by Dr. S. John Britto, The Rapinat Herbarium and Centre for Molecular Systematics, St. Joseph's College, Tiruchirappalli, Tamil Nadu, India. The voucher specimen was numbered (KG-002) and preserved in the Department of Nanoscience and Technology, Alagappa University, Karaikudi.

2.3. Synthesis of pure TiO_2, Au and Pt doped TiO_2 NPs using T. arjuna bark extract

The 10 g of barks were added with 100 ml of double distilled water and boiled at 50–60 °C for 5 min. The obtained extraction was filtered using Whatman No. 1 filter paper and the filtrate was collected in 250 ml Erlenmeyer flask and stored at room temperature for further usage. 3 ml of titanium isopropoxide was drop wise added in 475 ml of distilled water and 25 ml of *T. arjuna* bark extract was added into the solution. This solution was stirred continuously at a temperature of 80 °C for 12 h. The 5 ml of *T. arjuna* bark extract was added to 100 ml of 1 mM $HAuCl_4$ and K_2PtCl_4 solutions at room temperature and reduction of Au and Pt NPs was clearly observed within the next 5 min. The solution has been modified from yellow to reddish wine color and yellow to half black color, which indicates the formation of Au and Pt NPs. In addition, 375 ml of distilled water added in the 100 ml of Au and Pt NPs solutions. After that, 3 ml of titanium isopropoxide was drop wise added in 475 ml of Au and Pt NPs solutions and 25 ml of *T. arjuna* bark extract was added in the solutions. This solution was stirred continuously at a temperature of 80 °C for 12 h. Further, all the precipitates were calcined at 400 °C for 2 h.

2.4. Collection of microbes

Bacillus subtilis (ATCC 6633), *Streptococcus pneumoniae* (MTCC 1936), *Shigella dysenteriae* (ATCC 23513), *Pseudomonas aeruginosa* (MTCC 2642), *Escherichia coli* (MTCC 40) and *Klebsiella pneumoniae* (MTCC 432) bacterial strains as well as *Aspergillus niger, Fusarium solani, Curvularia lunata, Nigrospora oryzae* and *Trichoderma viride* fungal strains were obtained from the PG and Research Department of Plant Biology and Plant Biotechnology, Ramakrishna Mission Vivekananda College, Chennai, India.

2.5. Characterization

The synthesized pure TiO_2, Au and Pt doped TiO_2 NPs were subjected to XRD analysis was recorded by Cu Kα radiation with the wavelength of 1.54060 Å using PANalytical X-PERT PRO diffractometer system. Raman spectra were recorded using laser Raman microscope, Raman-11 Nanophoton Corporation, Japan. Photoluminescence spectra were recorded in the wavelength range from 400 to 600 nm using photoluminescence spectrometer (Varian Cary Eclipse). The morphology of the calcined pure