RAMAN AND FTIRCHARACTERIZATION OF NICKEL DOPED TITANIA NANO PARTICLES

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ABSTRACT

The effects of doping of Nickel into Titanium Oxide (TiO_2) by sol-gel synthesis were investigated. Four samples (pure, 5%, 10% and 15% doped TiO_2) were made. Characterization of the particles were carried out using Raman and FTIR. 10%Ni doped nanoparticles show better structural,and morphological properties.The Microstructure and elemental identification was carried out by SEM with EDX analysis.

Keywords: nanomaterials, photocatalyst, doping, titanium isopropoxide.

INTRODUCTION

Titanium dioxide (TiO_2) is one of the most important metal oxide semiconductors, which find applications in various fields of solar energy conversion, water purification, PEC splitting of water into Hydrogen and Oxygen, photocatalysis, ceramic material, filler, coating, pigment[1] and cosmetics[2] etc. Reports of TiO_2 with different shapes such as nanoparticles, thin films[3], nanorods, nanowires and nanotubes have spurred a great interest in studies on TiO_2 nanostructure synthesis and their applications. Nanomaterials with different shape and structure generally possess varied chemical, optical and electrical properties. Shape control has been a significant concern in nanotechnology. Properties also vary as the shapes of the shrinking nanomaterials change. The specific surface area and surface-to-volume ratio increase dramatically as the size of a material decreases [4]. The performance of TiO_2 based devices is largely influenced by the size and shapes of the TiO_2 building units, apparently at the nanometer scale.

As the most promising photocatalyst, [5]TiO_2 materials are expected to play an important role in helping solve many serious environmental and pollution challenges. TiO_2 also bears tremendous hope in helping ease the energy crisis through effective utilization of solar energy based on photovoltaic and water-splitting devices. It is reported that the Ni doping can improve the visible light responsive activity in environmental organic pollution degradation and hydrogen evolution [6]–[8]. Moreover, Ni doping can introduce an impurity energy level above the valence band of TiO_2, and the CB is maintained to be negative. Therefore, Ni-doped TiO_2 may show visible light response.

SYNTHESIS

*Methods.*For the synthesis of Ti(1-x)NixO_2 (where, x = 5, 10 and 15%) nanopowder, Titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) and Nickel nitrate hexahydrate($Ni(NO_3)_2 \cdot 6H_2O$) were used as Titanium and Nickel sources, respectively. First 90 ml of 2-propanol (C_3H_8O) and Nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$] in 10 ml aqueous solution with different concentrations (5%, 15% and 15%) were mixed drop by drop. The mixture was stirred magnetically at room temp. until a homogenous solution was obtained. Then 0.5M of Titanium tetra isopropoxidewas added drop by drop to the above mixture. The entire sol was continuously stirred for 5 hours using a magnetic stirrer. After stirring gel is formed .The sample is then taken out of the flask and washed several times using deionized water. Pure sample was prepared using same route without Nickel nitrate. The precipitate formed was dried at 80°C for 5 h to evaporate organic residues. Then the dry gel was calcined at 400 °C for 4 h to obtain desired anatase form Ni doped TiO_2 nanoparticles. Then the calcined powders were ground in an agate mortar to avoid agglomeration.

*Characterization.*The FTIR spectra were collected in the 4000–1000 cm^{-1} range, with a resolution of 4 cm^{-1} at roomtemperature by using a Thermo Nicolet IS10 spectrometer provided with single bounce Ge crystalSmart-iTR accessory. In order to complement the FTIR spectra, Raman spectroscopy was performed byusing a LabRAM HR800 spectrometer provided with a green He-Ne laser (534 nm) as the excitationsource. The Raman spectra were collected in the region 3600–100 cm^{-1}, with a spectral resolutionof 0.3 cm^{-1}.

CHARACTERISATION

Morphological Analysis

Figure 1 shows the SEM micrograph of NITI (A), which reveals that the material was formed by aggregates. Dopant concentrations as low as 10 wt.% Ni-TiO_2 did not generate Ni signals in the EDS spectrum, and the authors concluded that the cation incorporated into the lattice [17].SEM micrographs indicate the change in morphology of the synthesized catalysts. Fig. 1 depicts the SEM micrograph of 10wt. % Ni-TiO_2. Fig. 1 shows large number of tiny globular nanoparticles, with reduction in the particle size when compared to that of pure TiO_2. SEM indicates the change in the morphology of the nanoparticles, with enlarged surface area without any agglomeration of the particles. This indicates the role played by surfactant involved during the synthesis of the catalyst. Presence of surfactant leads to encapsulation of the doped titania due to which particle size is restricted from futher growth leading to synthesis of particles with much reduction.This result was important because when nanosized nickel particles were primarily loaded in the anatase phase as a co-catalyst, the particle morphology was determined to be essential for achieving good photocatalytic activity.

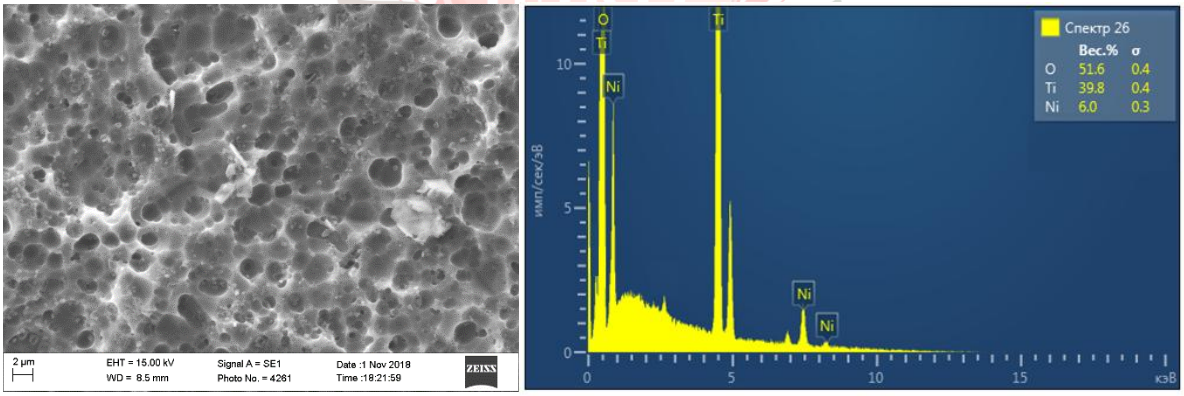

Figure 1. SEM images and EDX results of 10% Ni doped TiO_2

It can be seen in the morphologies of TiO_2 nanoparticles (Fig. 1), the as prepared (sol-gel) sample shows particle with great aggregation. The size of the particle is around 12 nm. The shape of the particle is not uniform and it looks like spherical in shape. The nanostructure of the sample doped with 10% Ni shown in Fig. 1. The formed nanoparticles are visible clearly. Here also the shape of the particle was observed almost sphere like morphology with different size.

FTIR Analysis

The FTIR spectra of the prepared samples are presented in Figures 2-5. The Ni-doped TiO_2 spectrum presented a weak absorption band at around 2340 cm^{-1}.

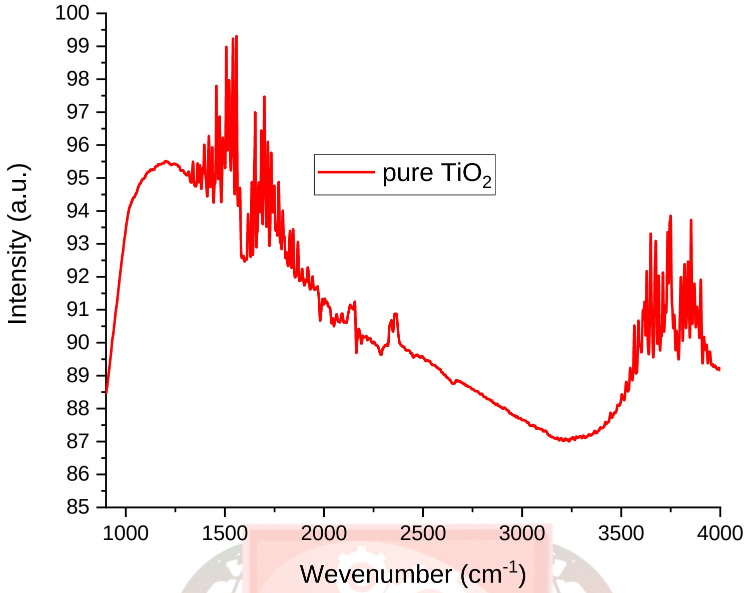

Figure 2. Fourier-transform infrared (FTIR) spectra of (a) pure TiO_2

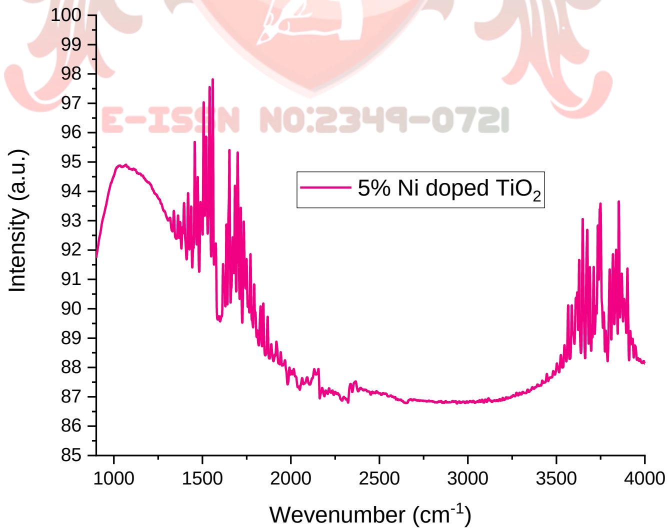

Figure 3. Fourier-transform infrared spectra of 5 wt.%Ni-doped TiO_2 NPs.

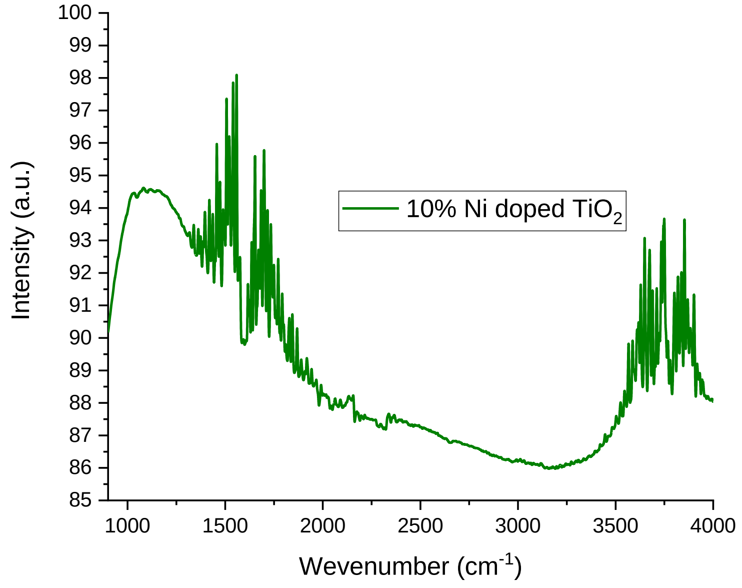

Figure 4. Fourier-transform infrared spectra of 10 wt.%Ni-doped TiO_2 NPs.

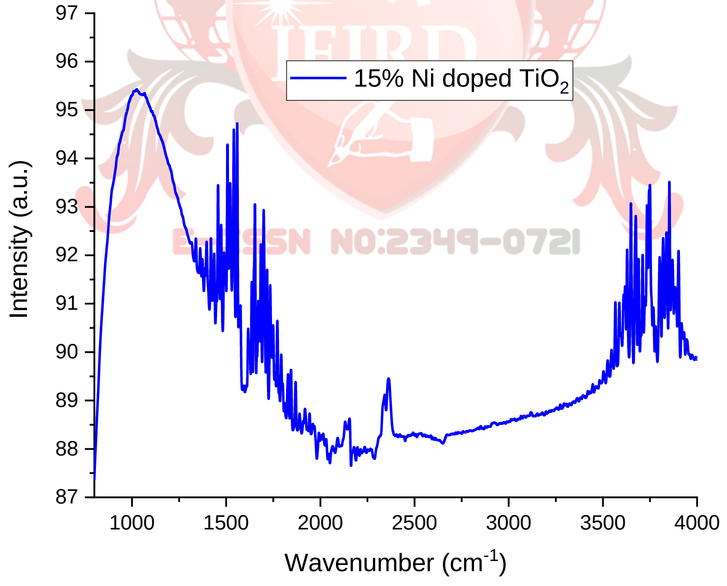

Figure 5. Fourier-transform infrared spectra of 15 wt.%Ni-doped TiO_2 NPs.

The absorption band at 3420 cm^{-1} was attributed to the stretching vibrations of the O-H group adsorbed onto the surface of the nanoparticles, whereas the peak around 1650 cm^{-1} was attributed to the bending vibration mode for the adsorbed water molecules.

Raman Studies

Raman spectroscopy is one of the most efficient analysis techniques to investigate the structural properties of materials. The changes in Raman spectra are related to non-stoichiometry, structure defects, phase changes, and bond modifications. Figures 6-9 show the Raman spectra of pure TiO_2, Ni-doped TiO_2.

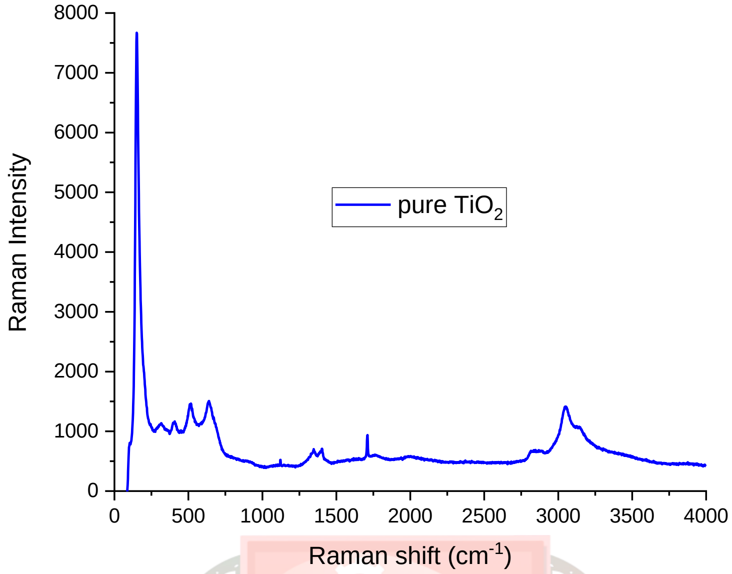

Figure 6. The graphs show the Raman spectra for of pure TiO_2NPs.

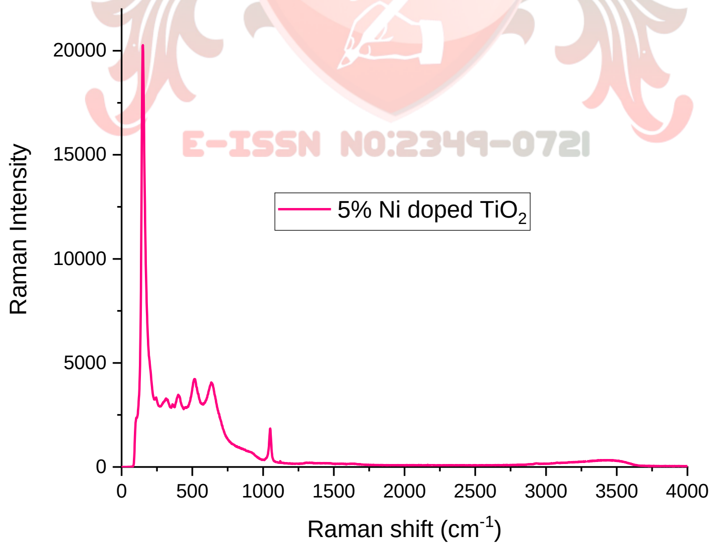

Figure 7. The graphs show the Raman spectra for of 5 wt.%Ni-doped TiO_2 NPs.

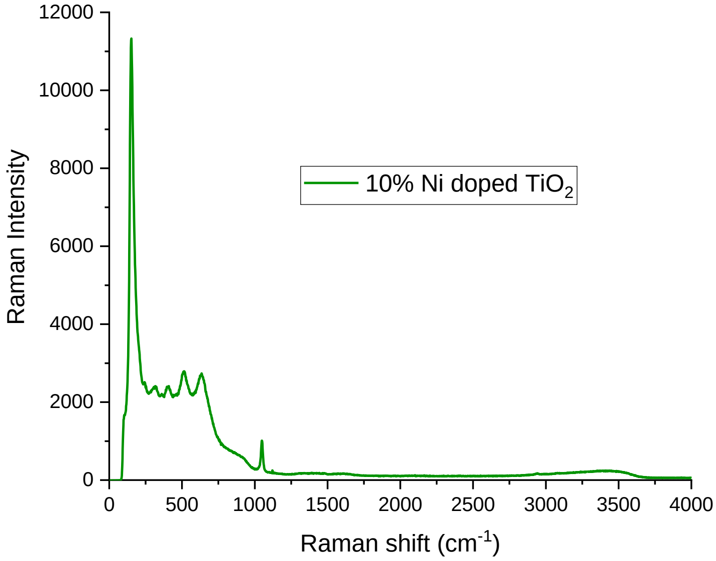

Figure 8. The graphs show the Raman spectra for of 10 wt.%Ni-doped TiO_2 NPs.

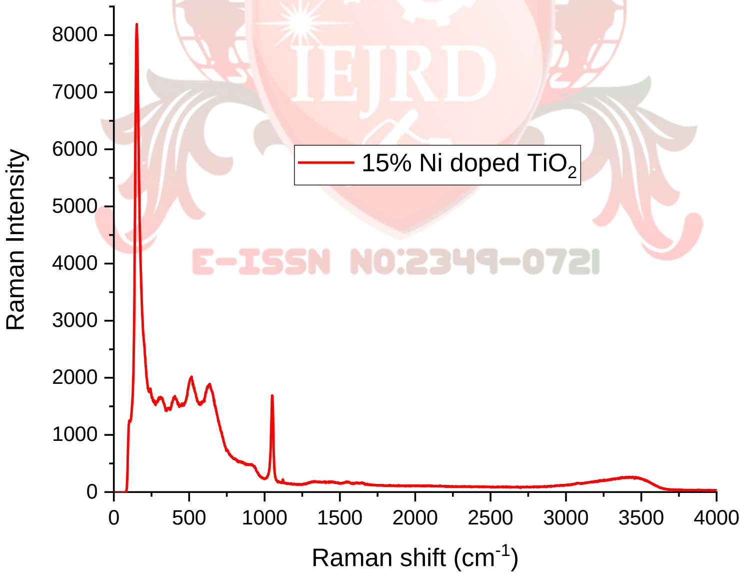

Figure 9. The graphs show the Raman spectra for of 15 wt.%Ni-doped TiO_2 NPs.

All samples exhibited the six Raman active modes, Eg (145 cm^{-1}), Eg (197 cm^{-1}), B1g (397 cm^{-1}), A1g + B1g (516 cm cm^{-1}), and Eg (640 cm cm^{-1}), characteristic of the anatase phase of TiO_2. Nevertheless, the Raman peak position of Eg mode at 145 $cm^{-1}$was slightly shifted toward a longer wave number, accompanied by a slight decrease in the intensity (inset, Figure 2). A similar behavior of Raman mode signals after doping TiO_2 NPs with Ni was elsewhere reported, and it is considered as a sign of structure defect existence, which resulted in the present study from the substitution of Ti^{4+} by Ni^{+2} within the lattice host. These Raman results agree with the literature and confirm those obtained by FTIR.

CONCLUSION

The Ni doped TiO_2 nanoparticles prepared by sol gel method and annealed at 500°C for 3 h. The structure of the prepared nanopowders have been analyzed by Raman and FTIRtechnique which suggesting a high chemical and thermal stability of Ni doped TiO_2 nanoparticles. The sample prepared by 10 % Ni doping showed very good crystallinity than other powders. From SEM, the size distribution was not uniform everywhere for the samples prepared. The particle size was around 12nm. The Ni doped TiO_2 based materials can used for high frequency applications.

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