

Magnetic Response in TiO₂ Nanoparticles

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Abstract:

TiO₂ nanoparticles are amongst the widely investigated metal oxide nanomaterials. The materials have unique surface to volume ratio, chemical stability, low toxicity, low cost thereby making them promising materials for environmental remediation, renewable energy, health care and advanced technological applications. The magnetic response of TiO₂ nanoparticles is greatly influenced by particle size, morphology, synthesis condition, defect concentrations and thermal treatment. Understanding the origin of magnetism is essential for developing multifunctional material for spintronics, magnetic sensors. This work highlights the influence of defects and oxygen vacancies in tuning the magnetic property of TiO₂ nanoparticles.

Keywords: chemical stability, low toxicity, renewable energy.

1. Introduction:

Nanostructured materials have structural features such as grain size, particle size and layer thickness that lie within the nanoscale range, typically 1-100 nm. They show unique physical, chemical, optical, electrical, magnetic, and catalytic properties that differ largely from their bulk counterparts. At the nanoscale magnetic properties differ from their bulk counterparts due to finite size effects, surface atoms, quantum effects and thermal fluctuations. They are very important in modern material science because they offer the possibility of tailoring magnetic properties by controlling particle size, shape composition and surface structure.

TiO₂ is one of the most extensively studied nanomaterials. It exists mainly in three crystalline states namely anatase, rutile and brookite [1]. These polymorphs exhibit different photocatalytic performances however anatase phase has the best photocatalytic activity [2]. Magnetism in TiO₂ originates from intrinsic defects such as oxygen vacancies and titanium vacancies or from extrinsic doping with transition metals [3]. In our work we have reported the magnetic behavior of TiO₂ nanoparticles prepared by a simple sol-gel method.

2. Experimental Details

2.1 Synthesis Procedure: The preparation of TiO₂ nanomaterials was carried out with a simple sol-gel method. In a typical synthesis titanium isopropoxide was added to 2-propanol in the ratio of 1:3. The reaction was carried out under constant stirring. This was followed by addition of 1 ml water to initiate the hydrolysis reaction. The prepared material was dried in air at 80 °C and then heat treated at 450 °C to get the desired TiO₂ nanoparticles.

2.2. Characterisation Techniques

The phase structure and particle size of the materials are determined using Rigaku Miniflex CD 10041 XRD unit with copper target and $\lambda=1.54$ angstrom at a scanning rate of $1^\circ/\text{min}$ and in the scanning range of $10-80^\circ$. High resolution transmission electron microscope images for morphology and particle size determination are observed with JEM-2100, 200kV JEOL. Diffuse Reflectance Spectra (DRS) of all samples are taken with Shimadzu-2450 UV-Vis spectrometer. The photoluminescence (PL) measurements at room temperature are recorded with PERKIN ELMER LS 55 fluorescence spectroscopy. Magnetic measurements are carried out in a vibrating sample magnetometer (VSM) using a selection of Varian and Walker electromagnets.

3. Results and Discussions

3.1. Structural and morphological study.

Fig.1 shows the XRD pattern of the prepared nanoparticles. All the diffraction peaks correspond to the tetragonal anatase phase (JCPDS-782486) [4].

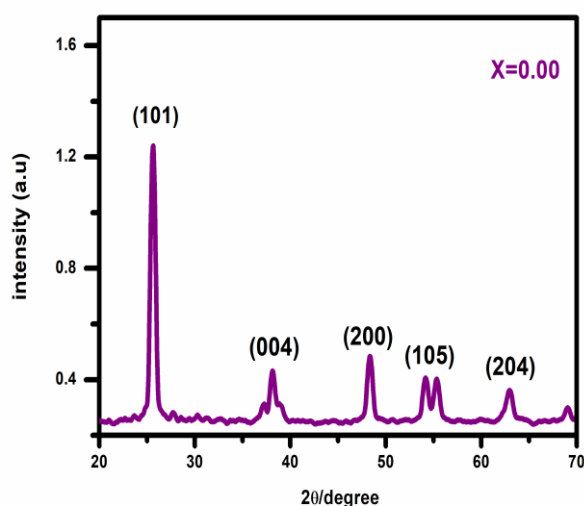


Fig 1: XRD

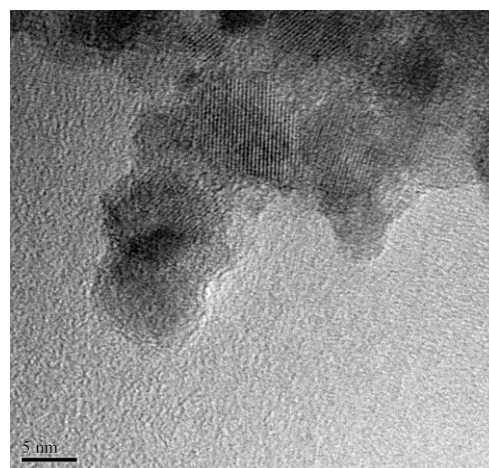


Fig 2: HRTEM

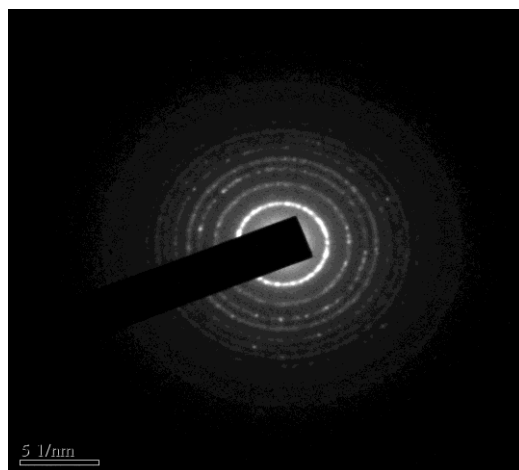


Fig 3: SAED

The sizes (d) of the nanocrystal calculated by using Scherrer's formula :

$$d = \frac{0.9\lambda}{\beta \cos \theta}$$

are found to be 8.8 nm. No traces of brookite or rutile is observed in the peak.

Fig.2 shows the HRTEM analysis. The particle size is 16 nm. It is to be mentioned here that in our work we have obtained difference in size as calculated from XRD and HTEM. These observational mismatch is due to the polycrystalline nature of the samples [5]. The polycrystalline nature is further supported by the SAED (Selected Area Electron Diffraction) that is performed by using a transmission electron microscope (Fig.3).

3.2. Optical Study

The UV-Vis spectra shows prominent peak at 340 nm (Fig 4).

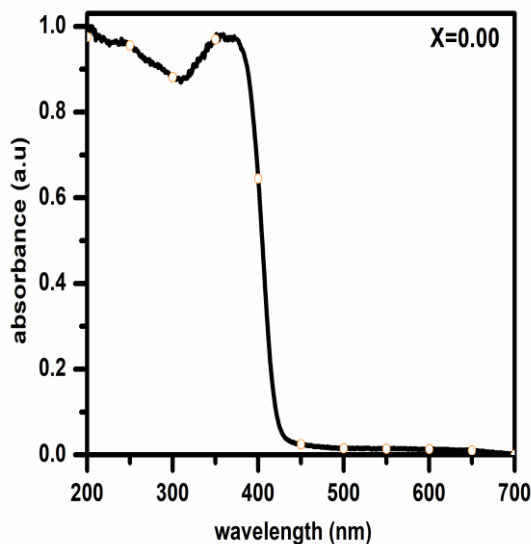


Fig 4: Absorbance Spectra

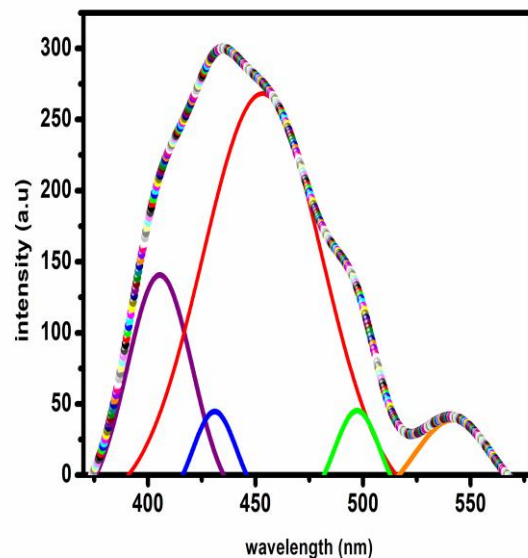


Fig.5: PL spectra

The nanoparticles show absorption peak in the UV region. This peak is mainly due to electronic excitation from the valence band to the conduction band. In the region between 400-700 nm, the peak is almost flat inferring that the material is unsuitable for use in the visible region. To mitigate this often TiO_2 is doped with external impurities so that it can show absorption in the visible region. For this purpose both transition and rare earth ions are added [4,6].

Photoluminescence is the process of emission of light from a material after the absorption of photons. In TiO_2 nanoparticles PL mainly results from the generation and subsequent recombination of photo generated charge carriers. The photoluminescence spectra (Fig 5) are obtained at an excitation wavelength of 360 nm. Gaussian fitting of the peak is performed to have better understanding of the peaks. The peak at 400 nm is the band edge emission peaks[4]. The emission peaks at 492 nm and 530 nm occurs respectively due to the transition from oxygen vacancies with two trapped electrons and one trapped electron to the valence band of TiO_2 [7]. Another peak at 424 nm is attributed to presence of self

trapped excitons (STE). These excitons originate by interactions of conduction band electrons localized on the Ti 3d orbital with holes present in the O 2p orbital of TiO₂ [8].

3.3. Magnetic Study

Fig 6 shows the M-H curve of undoped TiO₂.

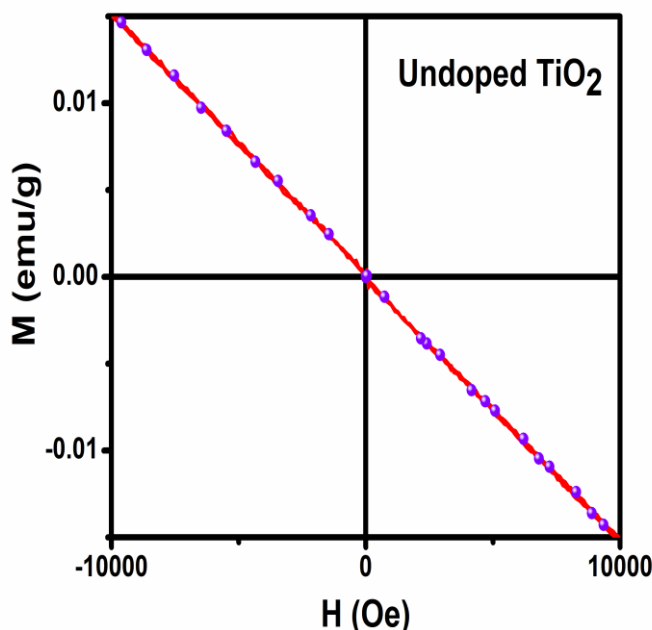


Fig .6: M-H curve

In TiO₂ nanoparticles titanium exists mainly in +4 states. The electronic configuration of neutral titanium is [Ar]3d²4s², while Ti⁴⁺ has the configuration [Ar]3d⁰. Thus in the +4 state titanium contains no unpaired d electron. Similarly O²⁻ ions are paired. When an external field is applied, the paired electron undergo small induced orbital motion that shows a magnetic moment opposite to that of applied magnetic field. This results in a negative susceptibility, which is the characteristic feature of diamagnetism. Although there are reports where undoped titanium di oxide exhibited paramagnetic and ferromagnetic behavior [9,10]. Such magnetic response are due to high surface to volume ratio, surface defects such as oxygen vacancies, titanium vacancies and under coordinated atoms. Presence of oxygen vacancies can also contribute to the magnetic behavior of the nanoparticle.. Thus the diamagnetic nature of the samples in our reported work is due to closed shell electronic configuration of Ti⁴⁺ states and O²⁻ states.

Conclusion:

In conclusion the magnetic behavior is largely governed by electronic structure and intrinsic structural defects. The observed nature of the samples can nevertheless be influenced significantly by nanoscale effects, particularly oxygen vacancies, surface defects and the presence of Ti³⁺ states. These defects can impart localized magnetic moment and may

produce paramagnetic or weak ferromagnetic response.

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