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Effect of Metal Doping on Bandgap of Titanium Dioxide Anatase Nanoparticles

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ABSTRACT: In this study, nanoparticles of undoped titanium dioxide were prepared using precursor Titanium tertbutoxide via Sol gel technique. Using a single process, Co, Cu, Fe, Ni and Zn doped TiO2 nanoparticles were prepared by simply changing the precursor dopant metal salt. The nanostructures were characterised by a Scanning Electron Microscope, XRD, and Ultraviolet visible Spectroscopy. SEM confirmed the size of nanoparticles nearly 9 to 20 nm. XRD analysis proved that the position of peaks was not affected by doping. The band gap for undoped and doped samples are estimated using the (αEphot)^2 versus Ephot plots. Metal doping decreases the band gap of anatase titatnium dioxide nanoparticles is confirmed with our results.

Keywords: Band gap; SEM; Titanium dioxide nanoparticles and transition metal doped.

INTRODUCTION: Titanium dioxide is very useful because of its resistance to photochemical erosion. It is convenient to handle and is comparatively cheaper. It is used in photocatalytic application as it can be prepared easily. Its photostability is high. Its holes have strong oxidizing power. Large surface area increases amount of photon generated electron hole pairs. Titanium dioxide is most suitable catalyst for organic contaminants.

Titanium dioxide has been used for the photodegradation of organic dyes and decolorization of wastewater. Using TiO2 as photocatalyst has one drawback that it has a wide energy band and its band gap (3.2 eV for anatase phase) falls nearly in the UV range of electromagnetic spectrum. Only UV light forms electron hole pair required for photocatalytic process.

Since UV light is only 3-5% of the solar spectrum, scientist are trying to decrease its band gap so that electron hole formation should occur at the incidence visible light. Undoped titanium dioxide is sensitive to light in the UV spectrum (λ<387 nm). In order that titanium dioxide absorb light in the visible range effectively (λ >400 nm), it can be doped with a wide range of metal and nonmetal impurities [1].

One of the way to shift optical response of TiO_2 to the visible range is by adding a transition metal oxide such as that of copper, zinc, cobalt, nickel and iron in an adequate amount [1] [2] [4] [6]. The recombination of electron hole pairs (photo generated) is reduced due to this doping and causes red shift.

MATERIALS AND METHODS:

Materials: All Analytical grade purity reagents were used without any further purification. Titanium tert-butoxide (98% purity) was the titanium precursor precursor used obtained from Sigma Aldrich. Hydrochloric acid [HCl] was supplied by Highmedia and Analytical reagent grade ethanol was obtained from Changshu Yangyuan Chemical, China.

De-ionized water was used for preparing all standard solution. Loba Chemie supplied Anhydrous ferric chloride ($FeCl_3$), copper sulphate pentahydrate ($CuSO_4.5H_2O$), Cobalt Chloride hexahydrate ($CoCl_2.6H_2O$), Nickel Chloride hexahydrate ($NiCl_2.6H_2O$) and Zinc Acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) of 99% purity.

Method of Preparation: Undoped sample is prepared using sol gel method described in [10][13]. Solution A is prepared with 2.5 mL of Titanium tert-butoxide , 25 mL ethanol added together with constant stirring. Solution B is prepared with 1.25 l. of distilled water, 0.25 mL of Hydrochloric acid and 25 mL ethanol added together with constant stirring. Solution A and B were mixed with continuous stirring for 2 hrs. A sol is allowed to transform into gel which was dried under 80°C for 1 hr. The dry gel was then sintered at 450°C

for 3 hrs to obtain desired undoped TiO2 Nano crystalline particles.

Extra solution 'C' was prepared for metal doped TiO2 nanoparticles,. Solution C was a 0.73 M solution of the dopant metal precursor salt in distilled water. 1 mL of solution 'C' was added to solution B and rest of the procedure is same as above. The amount of metal salt solution used was calculated for a Ti: Metal atomic ratio of 0.05.

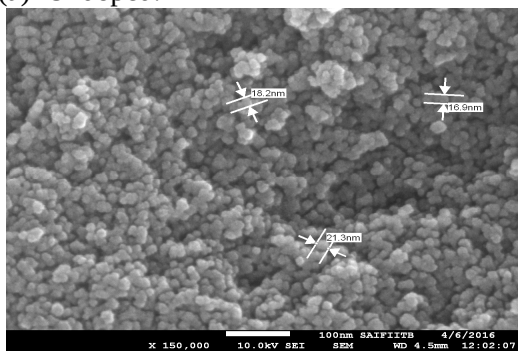
Characterisation: D8 Advance X-ray diffraction meter (Bruker AXS, Germany) was used to characterize the crystalline structure (room temperature, 30 KV, 30 mA), using Cu Ka radiation (=0.15406 nm). The crystal Field Emission Scanning Electron Microscopy (JEDL JSM-7600F) was used to study the morphology and structure of the particles.

Size of nanoparticles was measured. UV/Vis spectrophotometer Perkin Elmer Lambda XLS+ was used to study the absorption spectra of the TiO2 samples.

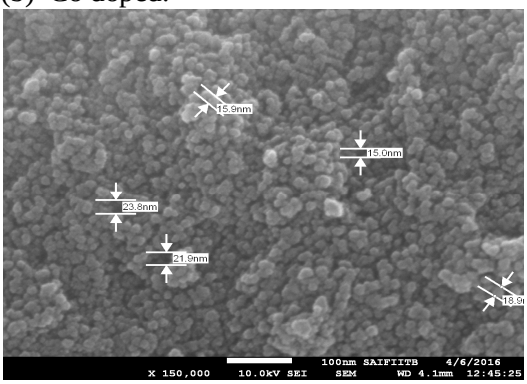
RESULTS AND DISCUSSION:

SEM Analysis: "Fig. 1," (a) and (f) shows the SEM images along with the particle size distribution of the synthesized undoped and doped TiO2. SEM imaging of all six samples showed spherical nature of nanoparticles with particle size nearly 11nm to 24nm. Sample 1 (Undoped), Sample 2(Co doped), Sample 3(Cu doped), Sample 4(Fe doped), Sample 4(Fe doped), Sample 5(Ni doped), Sample 6(Zn doped)

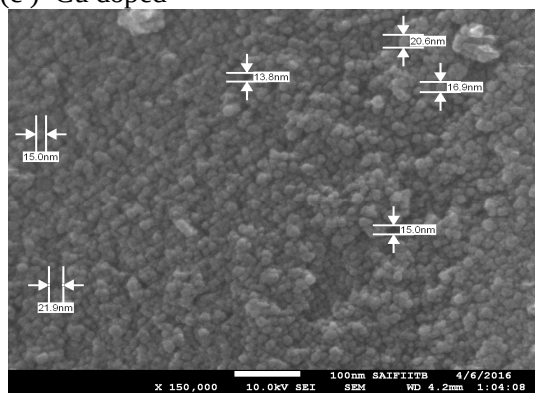
(a) Undoped:



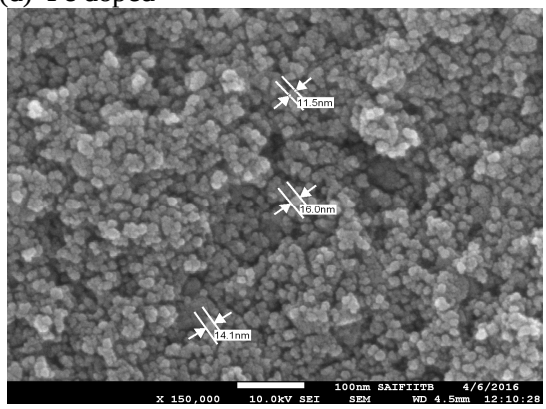
(b) Co doped:



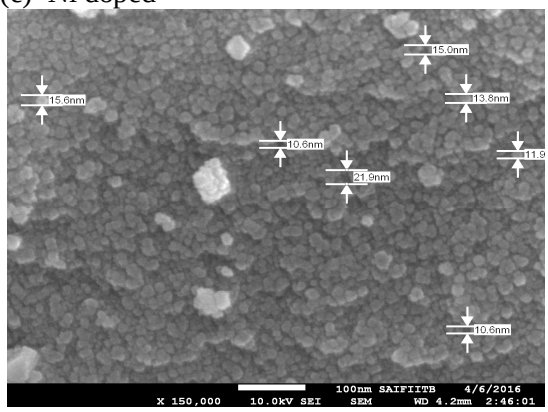
(c) Cu doped



(d) Fe doped



(e) Ni doped



(f) Zn doped

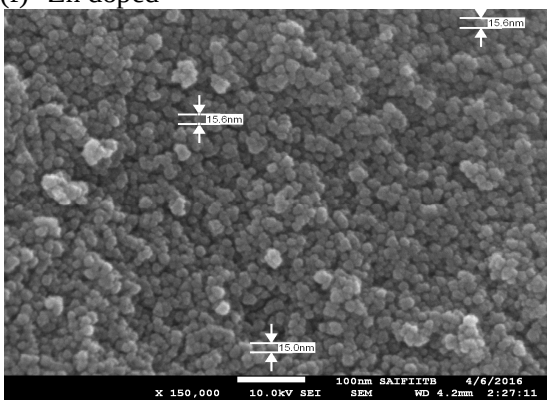
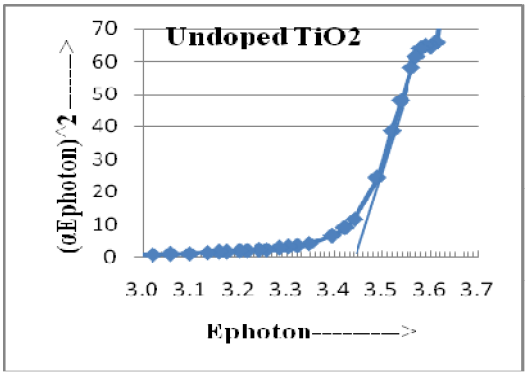
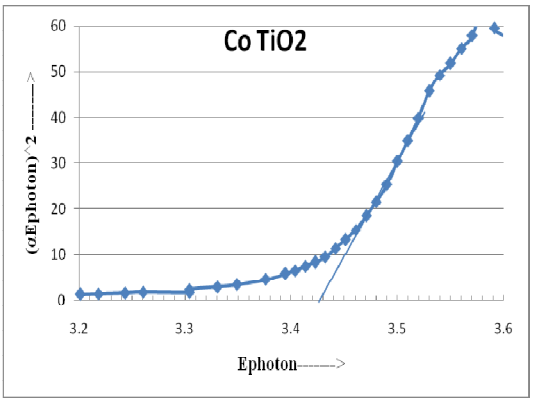


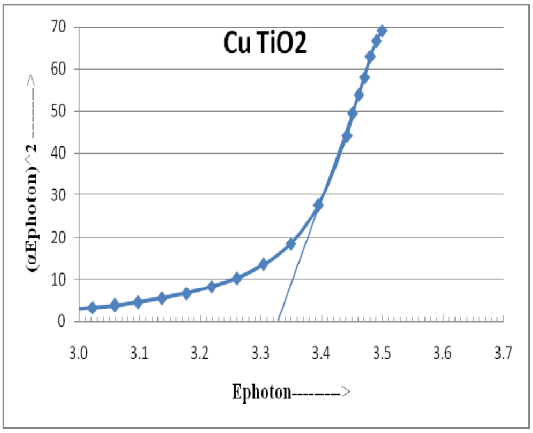
Figure 1: SEM Pictures of Prepared Samples.

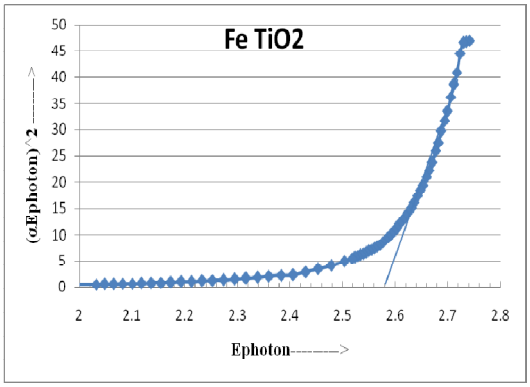
UV-Visible spectra: The band gap calculations are done as per procedure [14][15]. The graph is ploted between (αEphot)^2 versus *E*phot for a direct transition which is most suitable for anatse TiO_2 paricles, where *E*phot is the photon energy, *E*phot= (1239/λ) eV, λ is the wavelength in nm and α is the absorption coefficient . An absorption energy is given by the value of *E*phot extrapolated to α = 0, which corresponds to a bandgap *E*g. The bandgaps of all the six samples were calculated as tabulated below. Our calculated bandgap values are compared with values mentioned in the literature.[2]

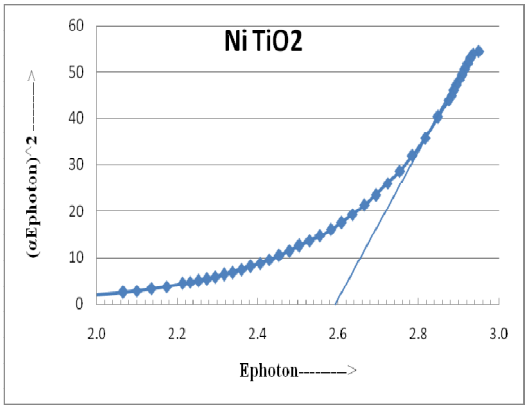
The results showed the band gap of Titanium dioxide was narrowed due to metal doping which improves the photo reactivity of TiO2. Our results matches with the literature i.e. band gap decreases due to metal doping.











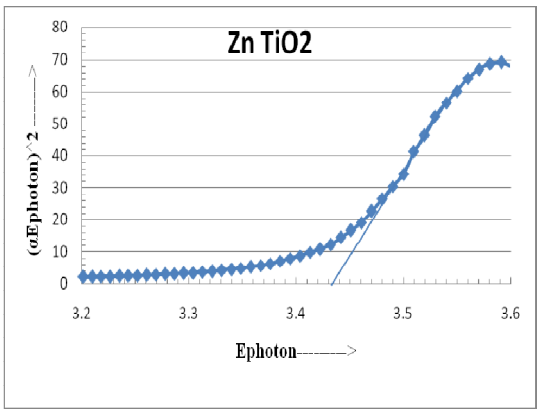


Figure 2: Variation of Absorbance of the Prepared Samples with Incident Wavelength.

XRD analysis: JCPDS-84-1286 was referred to compare the peaks of samples which confirmed its anatase structure at 2θ = 25.4°. Also it is noted that our sample's diffractograms do not have any peak assigned to rutile phase (2θ = 27.36 °). The crystallite size was determined with the help of the Scherrer formula below:

$$G = 0.9\lambda / \Delta(2\theta) \cos \theta$$

where λ is the Cu Kα radiation wavelength and Δ(2θ) is peak width at half-height. The calculated sizes are mentioned below. XRD of all samples showed the peaks are occurring at the same angle that means doping did not cause any effect on anatase nature of TiO2 nanoparticles.

Table 1: Calculated Band Gap of Syntheized Samples.

Sample	Band Gap	Band gap literature	Difference	Maximum absorbance
Undoped TiO_2	3.43 eV	3.23 eV	0.2	Below 370
Fe doped TiO_2	2.58 eV	2.86 eV	-0.28	Below 480
Co doped TiO2	3.42 eV	2.69 eV	0.73	Below 370
Ni Doped TiO_2	2.58 eV	3.25 eV	-0.67	Below 650
Cu doped TiO_2	3.34 eV	3 eV	0.54	Below 370
Zn doped TiO_2	3.41 eV	3.2 eV	0.21	Below 380

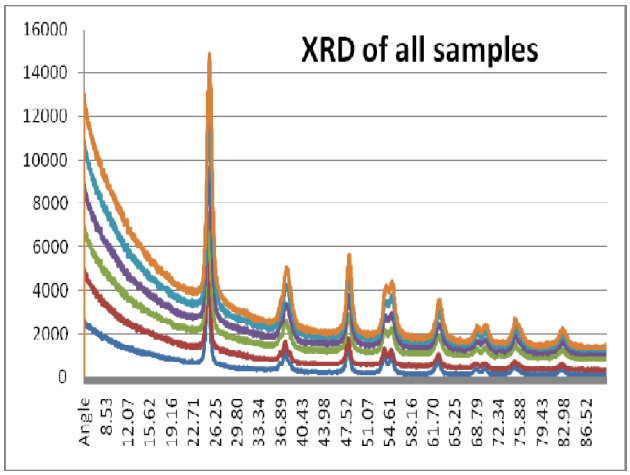


Figure 3: XRD Spectrum of Prepared Samples.

Table 2: Sample Size Calculations of Synthesized Samples.

Sample	Size in nm
Undoped	62.93
CO doped	44.98
Cu doped	62.53
Zn doped	19.67
Ni doped	12.11

CONCLUSIONS:

- SEM pictures of samples show uniform morphology with spherical particles.
- The particle size 11 nm-24 nm which matches with the size calculated using XRD.
- The prepared TiO_2 sample's absorption spectra exhibited strong absorptions below 370 nm for undoped, Cu doped and Co doped samples, below 380 for Zn doped, below 480 for Fe doped, below 650 for Ni doped.
- The band gap of 3.4eV of the prepared sample confirmed its nano crystallite size as larger band gap have smaller crystallite size. Bulk sample of TiO2 has band gap of 3.2 eV.
- XRD pattern revealed that the prepared titania composed of predominantly anatase phase. The position of peaks was not affected by doping.
- Band gap decreases due to metal doping in Anatase TiO_2 nano particles.

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