Structure and Band Gap Energies of Nano Titanium Dioxide
Doped With the Fifth Group Elements
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Abstract
Titanium dioxide powders were synthesized by adding different fifth group elements precursors to titanium (IV) isopropoxide followed by calcination at 500-600 °C. Diffractograms showed the presence of anatase phase accept for phosphorus which has amorphous- poly crystalline phase then established a rutile phase among heating above 500 °C. Particle size distribution and AFM images indicate the nano dimensions of the studied powders. Particle size distribution varied appreciably in comparison with crystallite size (L) calculated from Scherer formula. Band gap energies calculated from Uv-Vis spectra of thin films deposited on one side of quarts substrate. The band gap energies of TiO₂ – Fifth group elements of this work ranged from 2.83 eV for N – TiO₂ to 2.83 eV for Bi – TiO₂ with a steady increase according to atomic radii accepts for antimony which deviated from that behavior

Keywords: TiO₂, Doping, fifth group, Diffractograms, AFM, Band gap

1. Introduction
The large band gap energy $E_g \approx 3.2 \text{ eV}$ of TiO₂ anatase crystalline phase (Zaleska 2008) has imposed significant limitations on its application particularly in the interior places. Titanium dioxide can utilize only a limited portion of solar radiation, the UV fraction which is at most about 5 percent (Janczarek et al 2007). Titanium dioxide is an n-type semiconductor, and that behavior arises due to oxygen vacancies and creation of Ti⁴⁺ sites (Pelaeza 2012). Rutile phase posses a wider 3d band gap compared to anatase due to localisation of Ti 3d states (Di valentine and Pacchioni 2004). In spite of rutile phase has a band gap 3.0 eV compared to 3.2 eV of anatase phase, yet anatase considered to have superior photocatalytic activity because of its larger surface area (Scifiani and Hermann 1996). Extending the absorption of light to the visible range and improving photocatalytic activity require the modification of the band gap.

Implementation of metal and non-metal ions into the lattice of TiO₂ as dopant will bring about a significant lowering of gap energies. Several methods including various types of dopant (Zaleska 2008, Xz and Fa 2001, Hsuan-Chung et al 2012), those dopants include d- orbital’s transition metals, but more recently non-metals including S, N, C, B, P and F. Also various preparation methods were suggested including chemical vapor deposition (Ding et al 2001) sol gel films (Briker and Sherar 1990) multilayer deposition (Saciu et al 2009) and pyrolysis of sprays (Raut et al 2009). Anatase titanium dioxide has a tetragonal crystal structure. $D_{4h}^{14}$, a = 3.733 Å, c = 9.370 Å while rutile, has a tetragonal crystal structure $D_{4h}^{2}$, a = 4.594 Å, c = 2.959 Å. The presence of d-orbital and anionic dopants impair pronounced effects on the titanium dioxide properties (Hanaor and Sorrell 2010). Those effects might lead to reduction of the band gap by creation of new trapping sites which may also control phase transformation to rutile. Cationic dopants may replace Ti⁴⁺ of the anatase lattice or may fall on the boundaries of unit cells (Mackenzie 1975). In contrary anionic dopants might replace oxygen of the lattice (Asahi et al 2011). However influence of doping on geometric structure of TiO₂ and virtually optical mechanisms have been calculated by many researchers, (Guo and Du 2012) utilized Cambridge Serial Total Energy Package (CASTEP) to study Cu, Ag and Au doped anatase TiO₂. Density functional theory calculations were used to characterize the doping effects of $\mathcal{S}$ substituting for $\mathcal{O}$ in anatase TiO₂ (Tran et al 2011). The phase stability in doped TiO₂ was carried out using all- electron atomic orbital’s methods with local density approximation (Hanaor 2012). The effect of N doping on the surface properties of anatase and rutile TiO₂ were performed using photon - energy range UPS (35 - 110 eV) which is extremely surface sensitive (Batzell et al 2006). Substantial efforts have been subjected toward the commercialization of doped TiO₂ photo catalyses of self cleaning for organic and inorganic compounds in the environment (Fujishima et al 2006).

In this work the TiO₂ band gap was modified by doping with the elements of the fifth group including N, P, As, Sb and Bi using a well established sol- gel method. The structure of prepared powders, particle size and their distribution were identified by XRD and AFM microscopy. The band gap energies were calculated from the UV spectra.

2. Experimental
2.1 Materials
Titanium dioxide anatase (Degussa, purity 99%) used as received without any further treatments. Doped titanium dioxide powders were synthesized as follow: to 10 ml titanium (IV) tetraisopropoxide (Aldrich Purity 97%)
appropriate amount of dopants precursors were added, stirred (Magnetic stirrer LMS100) at 30 °C forming a viscous milky like suspension within 10 minutes, which is then broke down to a powder after 3–4 hours of continuous stirring. The powder filtered, dried (Drying oven Fisher Scientific) at 120°C for an hour. The dried powder calcined at 300–900°C (Muffle furnace LEF1055, Jlabtech) for an extra hour at each preset temperature. The following precursors were added to titanium (IV) tetraisopropoxide, 5 ml of 35% ammonium hydroxide (Aldrich) for N - TiO₂, 5 ml of 1M basic solution of AS₂O₃ (Fluka) for AS - TiO₂, 5 ml of 1M of PCl₅ (BDH) for P - TiO₂, 5 ml of 1M basic solution of Sb₂O₃ (BDH) for Sb - TiO₂ and 5 ml of 1M of Bi(NO₃)₃ (Fluka) for Bi - TiO₂. Prepared doped TiO₂ powders have different color shades depending as well as on the calcinations temperatures.

2.2 Measurements
2.2.1 XRD
Titanium dioxide and doped titanium dioxide powder XRD were recorded on PAN analytical X’pert PRO MPD using Cu kα as a source for X-ray radiation of 1.5406Å from(0 – 70) 2θ.

2.2.2 AFM
Two dimensional and three dimensional particles size and their size distribution were recorded by AA2000 atomic force microscope product of Angstrom Advanced Inc.

2.2.3 Band gap energies
For doped titanium dioxide films were calculated from absorbance spectra recorded on double – beam Uv-Vis spectrophotometer (T90 +) PG instruments. The films were prepared by dipping pre-cleaned quartz substrates vertically in a beaker containing 0.5 g of the synthesized powder suspended in 25 ml deionized water for 30 minutes. The substrate then air dried first and subsequently in an oven at 105 °C for 2 hours. The films deposited on one side of quartz substrates were placed in the sample beam, while uncoated substrate placed in the reference path. The following equation (Mohd et al 2011) was applied

$$A = \frac{k(h\nu - E_g)^2}{h\nu}$$

Where ν is the frequency in nm, h is the plank constant and k is a constant. A plot of $(h\nu)^2$ versus hν (eV) gives the band gap $E_g$ value in eV at the intersection of a straight line drawn as a tangent with the x-axis at the absorbance edge.

3. Results and discussions
The fifth group contains two non-metals N and P, as well as three metals As, Sb and Bi. It’s well accepted that nitrogen among the best dopants narrowing appreciably the band gap of TiO₂. According to many theoretical studies nitrogen and phosphorus also might substitute oxygen in titanium dioxide lattice, while other metal members of the group might replace the titanium atom in the lattice. The entire group’s elements have $x^{5+}2^+3^{1+}$, $x = 2$, $x = 2$ to 6 outer shell configuration with atomic radii ranging from 75 pm for N to 150 pm for Bi. The group’s elements have a correlated opportunity to interact with O $2.52^22^4$ (atomic radius 73 pm) and Ti $4.53^23^4$ (atomic radius 170 pm) of TiO₂ lattice. Therefore the fifth group will present a good model to evaluate the effects of doping. However titanium dioxide provide three possible accommodation sites for dopants, the two substitution site for titanium and oxygen already mentioned above, and the third to interstitial site. The effects of doping include phase transformation from anatase to rutile, and to induce alteration in the electronic structure leads to band gap narrowing. Both effects were quite evident in forthcoming results.

Figure 1 shows XRD patterns of anatase TiO₂ and different calcined doped TiO₂. Strong diffraction peaks at 2θ = 25.3455°(101), 37.8298°(103), 37.9331°(004), 38.6406°(112), 48.0772°(200), 53.9206°(105), 55.1004°(211) for anatase TiO₂. Doping with the fifth group elements by the stated above method brought some major differences into peaks positions characteristic of bare TiO₂.

$$2\theta = 27.7930°$$

In N - TiO₂ the two small peaks at 37.8298° and 38.6406° appear on the shoulders of the strong peak at 37.9331° of bare TiO₂ are being not clear indicating some structural changes. P - TiO₂ showed a rather different peak position at 2θ = 29.4227°(110), 33.1973°(101), 36.3764°(200) indicating rutile phase even at early stages of calcinations which was evident at the higher calcinations temperatures. Anew peak positions were noticed for As at 2θ = 28.7235°, 31.8942°, 32.8073° and 2θ = 25.9203°, 33.4925°, 41.5923° for Sb. Neither N - TiO₂ nor Bi - TiO₂ showed rutile phase. The ambiguity regarding the effects of the fifth group dopants on the transformation from anatase to rutile may stem from increased density of anion vacancies as in As and Sb dopants as a result from substitution of Ti in anatase lattice. Nitrogen as many researchers have agreed might replace oxygen in the anatase lattice efficiently while phosphorus behaved differently. Figures 2 and 3 showed the effect of calcinations from 300 – 900°C for N and P doped TiO₂. For N - TiO₂ (Fig 2) heating up to 600 °C will bring about a new weak peak at 2θ = 27.7930° referring to emergence of rutile phase. Heating up to 800 °C will turn the powder totally to a
rutile phase which also accompanied by other characteristic rutile peaks at $2\theta = 29.78931^\circ, 36.3422^\circ, 55.5562^\circ$. The diffraction pattern of $P - TiO_2$ (Fig 3) is rather different, at low calcinations temperatures up to 500 the powder is irregular polycrystalline amorphous with low intensity, however the prevailing phase was rutile and it's more pronounced above $600^\circ C$ probably due the formation of well defined crystal dimensions suitable for XRD measurements.

Particle size distribution and AFM images Figures (4, 5, 6, 7, 8 and 9) indicate the nano dimensions of the studied powders. Several measurements have been performed to assure the data. The AFM images showed distinguished regular, smooth and generally round shapes of particles; however particle size distribution varied appreciably in comparison with the crystal size (L) measured by Sherar formula (Monshi etal 2002, Ahmed etal 2014) from XRD diffraction patterns namely for $N - TiO_2$. 
Where $k$ is the Sherrer’s constant, in the present calculation a value of 0.94 were adopted. $\lambda$ is the wavelength of X-ray source ($0.1548\,\text{nm}$), while $\beta$ is the width of half maximum intensity corresponding to Bragg’s angle $FWHM/2^\circ$. Results of average particle size (nm) and the average diameters (nm) from AFM measurements as well as the crystallite size $L$ (nm) were listed in table 1.

Table 1: Measured average particle size, their size distribution by AFM and calculated crystallite size $L$, band gap energies

<table>
<thead>
<tr>
<th>Code</th>
<th>Particle Size range(nm)</th>
<th>$D_{\text{avg}}$(nm)</th>
<th>$L$(nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>anatase $\text{TiO}_2$</td>
<td>60-135</td>
<td>84.19</td>
<td>62.63</td>
<td>3.2</td>
</tr>
<tr>
<td>$N-\text{TiO}_2$</td>
<td>50-150</td>
<td>95.68</td>
<td>26.03</td>
<td>2.81</td>
</tr>
<tr>
<td>$P-\text{TiO}_2$</td>
<td>80-180</td>
<td>130.75</td>
<td>59.64</td>
<td>2.83</td>
</tr>
<tr>
<td>As$\text{TiO}_2$</td>
<td>30-135</td>
<td>90.98</td>
<td>59.62</td>
<td>2.85</td>
</tr>
<tr>
<td>Sb$\text{TiO}_2$</td>
<td>70-140</td>
<td>91.24</td>
<td>49.17</td>
<td>2.84</td>
</tr>
<tr>
<td>Bi$\text{TiO}_2$</td>
<td>55-120</td>
<td>78.69</td>
<td>59.62</td>
<td>2.95</td>
</tr>
</tbody>
</table>

Figure 4: Two and three dimensional AFM images and particle distribution of anatase $\text{TiO}_2$

Figure 5: Two and three dimensional AFM images and particle distribution of $N-\text{TiO}_2$
Figure 6: Two and three dimensional AFM images and particle distribution of $P - TiO_2$

Figure 7: Two and three dimensional AFM images and particle distribution of $As - TiO_2$

Figure 8: Two and three dimensional AFM images and particle distribution of $Sb - TiO_2$
Figure 9: Two and three dimensional AFM images and particle distribution of Bi – TiO₂

Figure 11 shows the absorbance spectra of TiO₂ thin films (the curves donated f, g are excluded and they don’t belong to the fifth group elements). All of the films were considered transparent above about 460 nm although insignificant absorption tails are still present which probably due to scattered Uv light caused by the thin films themselves (Salah 2013). From figure 11 the extracted absorbance data were plotted as \((\frac{A}{\lambda})^2\) vs. photon energy \(h\nu(eV)\) and presented in figures 12, 13, 14 and 15. Band gap energies of TiO₂ – Fifth group elements of this work ranged from 2.83 eV for N – TiO₂ to 2.95 eV for Bi – TiO₂ with a steady increase according to atomic radii accepts for antimony which deviated from that trend. Although many researchers reported rather lower values for N – TiO₂ and P – TiO₂ powders which may attributed to the measurements of powder instead of films and also to the different experimental conditions such as type of precursors, method of annealing and measurement technique. However doping with the fifth group elements brought about a noticeable correlated narrowing of the band gap energies compared with that of bare TiO₂. Janezarek et al 2007 suggested a control on the band gap energy by varying nitrogen contents through the control of calcination temperatures rather than varying the nitrogen precursor. Recent study (Hreniak et al 2014) found similar trend for the influence of silver on optical properties of TiO₂ powder.

Figure 10: Uv-Vis spectra of doped TiO₂ films with the fifth group elements a) N – TiO₂ b) P – TiO₂ c)As – TiO₂ d) Sb – TiO₂ e)Bi – TiO₂
Figure 11: $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for the $N-TiO_2$ Film

Figure 12: $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for the $P-TiO_2$ Film

Figure 13: $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for the $As-TiO_2$ Film

Figure 14: $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for the $Sb-TiO_2$ Film
4. Conclusions
Doping of TiO$_2$ with the fifth group elements brought a noticeable correlated decrease in the band gap from 3.2 eV for bare anatase phase to about 2.85 eV. Synthesized powders have a nano dimensions and almost anatase phase except for phosphorus which has amorphous – mixed phase turned to be rutile above 500 °C. The method of calculating band gap energies gave sharp and easily distinguishable values.

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