Synthesis and Characterization (Electrical and Optical) of TiO2 doped with MnO_2

Comment [O.I.1]: TiO_2

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ABSTRACT

TiO_2 is vastly used in several industries due to its several properties, its wide bandgap and poor ionic conductivity has however hampered its application in the energy industry. In this work, TiO_2 has been doped with MnO_2 to produce thin films. The doping was carried out in 5, 10 and 15 wt% of MnO_2 and the resultant films characterized (uv/vis photospectroscopy and 4-point probe conductivity test). It was observed that the electrical conductivity was highly improved as was observed in the conductivity test which showed the conductivity of pure TiO_2 at $0.0100\Omega^{-1}m^{-1}$, increase to 0.0217 $\Omega^{-1}m^{-1}$ at 5wt% of MnO_2 , and to $0.0409\Omega^{-1}m^{-1}$ at 10wt% and finally to 0.0749wt $\Omega^{-1}m^{-1}$ at 15wt% of MnO_2. The improvement in the conducting properties were also made evident by the drastic reduction in the bandgap energy of TiO_2 which reduced for 3.2eV of pure TiO_2 to 2.7eV, 2.2eV and 1.7eV for 5wt%, 10wt% and 15wt% MnO_2 respectively. These bandgap values were obtained from kebulka-monk plots made by the reflectance readings of the UV/VIS.

Comment [O.I.2]: 5, 10 and 15wt%

Keywords: [Doping, Conductivity, TiO_2, Bandgap]

1. INTRODUCTION

Titanium dioxide (TiO_2) is about the most popular white pigment, and this can be attributed to its high refractive index which has made it found vast applications in coatings, photocatalysis, solar cells among others (Rao et al., 2016). TiO_2 like carbon has attracted lots of interest in recent years as a potent anode material for Li-ion batteries. Its environmental benignity, availability, small volume change during charge-discharge cycles(<4%) and low cost has made it attractive for the production of high power lithium-ion batteries. (Liu and Yang,2016).

However, its structural instability and poor ionic conductivity has stood out as a major setback. To circumvent this challenge, different forms of composites, alloying and doping has been done including nanocrystallization, all aimed at improving its characteristics.

Dong, et al (2013), prepared honeycomb-like porous TiO_2/GNs (graphenenanosheets) composites as Li-ion anodes which reports enhancement of both the electric conductivity and structural stability of TiO_2. Based on their electrochemical and physical properties, different components are being combined with TiO_2 in order to achieve a perfect combination for energy related applications. Metal oxides have not been exempted in this attempt. Among various oxides used so far are MoO_3, V_2O_5, CoO, SnO_2, etc.(Armstrong, et al. 2013). These reports suggest that the metallic oxide coatings, not only led to almost zero volume change during cycling but also inhibit pulverization as well as improve li-ion insertion/de-insertion properties of TiO_2 when used as an anode material in Li-ion battery applications.

In this work, MnO_2 is doped with TiO_2 in an attempt to improve the structural stability and electrical properties of TiO_2.

2. EXPERIMENTAL DETAILS

2.1 Synthesis Of Sol Gel Titania

7.38g of $TiCl_4$ was added to 100ml of H_2O at 9^0C under vigorous stirring for 30minutes. At the end, the H_2O temperature rose to 21^0C. It was then rinsed by centrifugation at 400rpm for 10 minutes. Then, 16mls of Ammonia solution was added first to the solution before 10mls was later added to make 26mls of ammonia solution.

After centrifuging for 5 minutes, the supernatant is discarded and the residue retained and mixed with more water and then centrifuged again. This process was repeated 10 times using a total of 250mls of distilled water.

The volume of the mixture was made up to 50ml by adding water. Furthermore, 20ml of 30wt% of HCl was added to the solution and stirred vigorously and at this point the solution became colourless. It was allowed to undergo Alwart's ripening for 24hrs at room temperature.Finally, the sol was centrifuged at 4000rpm to remove oversized particles.

2.2 Synthesis Of MnO_2

8g of $KMnO_2$ was added to 38ml of 35% HCl. The temperature of the mixture was raised to 70^0C and held for 3hrs.

In a separate 250ml beaker, 5g of Na_2CO_3 (All materials are analytical grade) was measured and enough water added to make a saturated solution. At this point, the solutions (in beaker 1 and 2) are mixed together resulting in the formation of insoluble $MnCO_3$ (manganese carbonate).

$2KMNO_4 + 16HCl = 2KCl + 2MNCl_2 + 8H_2O + 5Cl_2$

The manganese carbonate ispurified by centrifugation at 4500rpm, the supernatant is discarded and the residue is stirred with water. This is washed with methanol and centrifuged. This is repeated twice at 4500rpm. This is dried in a drying dish. The dried material is dissolved in nitric acid (50%). 2ml of the solution is extracted, calcined at 500^0C and weighed.2ml of the $Mn(NO_3)$ contains 0.27g of MnO_2, with further dilution with water 0.16g of MnO_2 was gotten.

2.3 Preparation of Tio_2 and Mno_2 Thin Films

Slot coating (or Dr Blading) method of deposition was used to prepare the thin films on a glass substrate.0.02g/mol of TiO_2 mixed with 0.02g/mol of PVA (polyvinyl alcohol) and stirred in a magnetic stirrer for about 10mins to make the mixture homogenous. The PVA is added as a surface agent to enable the film stick to the surface of the slide. This mixture was then deposited on the slide using the slot coating method and blow-dried with a hot air blower. And the slide was further dried at about 200^0C.Furthermore, 0.2ml MnO_2 and 0.2ml of PVA was mixed together and stirred with a stirrer and this was also deposited on another slide and dried. At this stage two thin films were prepared (a pure TiO_2 and pure MnO_2 thin films)

2.3 Preparation of Mno_2 Doped Tio_2 Thin Films.

1.9ml of TiO_2 was put in a beaker placed on a hot plate stirrer, 2ml of PVA was added and finally 5wt% of MnO_2 was gradually added to the mixture and allowed to stir mildly for 5mins. This mixture was then deposited using the slot coating method on the slide and dried at 200^0C. The process was repeated in preparing thin films for 10wt% and 15wt% of MnO_2

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3. RESULTS AND DISCUSSION

The four point probe method was utilized to know the resistivity of the thin films. Table 1.0 shows the obtained results and the corresponding conductivities.

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Table 1. Result of four-point probe test.

Wafer_ID	Composition	Wafer Thickness	Resistivity(Ωm)	Conductivity ($\Omega^{-1}m^{-1}$)
Slide 1	TiO_2 only	50nm	99.8923	0.0100
Slide 2	TiO_2 (5%wt MnO_2)	“	45.9958	0.0217
Slide 3	TiO_2(10%wt MnO_2)	“	24.4677	0.0409
Slide 4	TiO_2(15%wt MnO_2)	“	13.3581	0.0749

From the table Slide 1 which was prepared with only TiO_2 showed high resistivity value of 99.89 Ohm-meter which confirms the semiconductor status of the material. However based on the percentage of doping, significant reduction in the resistivity was observed at 5% , 10% and 15%.

Comment [O.I.32]: Table,

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Following the resistivity values, the formula;

$\sigma = 1/\rho$ 1.1

Where, σ represents conductivity and ρ is the resistivity which is gotten from the resistivity test.

The corresponding conductivity values also as evaluated using equation 2.0 showed significant increments as its value increased from $0.01\Omega^{-1}m^{-1}$in the pure phase to 0.07 in the 15%wt doping.

On a close examination of table 1 we observe that the doping improved the conductivity of TiO_2. At 15%wt MnO_2 doping, the resistivity had dropped to 13.3581Ωm which produced a conductivity of $0.0749\Omega^{-1}m^{-1}$. Further increase of the doping percentage led to irregular readings which suggested that the doping can only go this far for effective use.

Comment [O.I.34]: Table 1

To further confirm the improved electrical properties, optical analysis was further carried out by utilizing the UV/VIS spectrophotometer. From the reflectance values acquired, the bandgap (eV) was estimated by adopting the kebulka-munk approach. By using equations 1.2 and 1.3 below, the bandgap was estimated for each of the samples where eV values are the x-axis intercept of the plots.

Band Gap Energy (E) = hc/λ 1.2

h = Plank’s constant = 6.626 x 10-34 Joules sec

c= Speed of light= 3.0 x108 meter/sec

λ = cut of wavelength which from the spectrophotometer = 300- 600nm

Band Gap Energy (E) = 1240/ λ (eV).

With 1eV = 1.6 x 1019 Joules

From the reflectance data acquired, the kebulka-munk (k/s) equation was used to plot corresponding graphs using Microsoft excel.

$$f(R) = \frac{(1-R^2)}{2R} = \frac{k}{s}$$ (Piketech, 2011) 1.3

Where R represents the absolute Reflectance which is obtained from the percentage reflectance value from the uv/vis data.

k is the absorption coefficient while s is scattering coefficient.

The general units of k/s is the absorption unit (a.u).

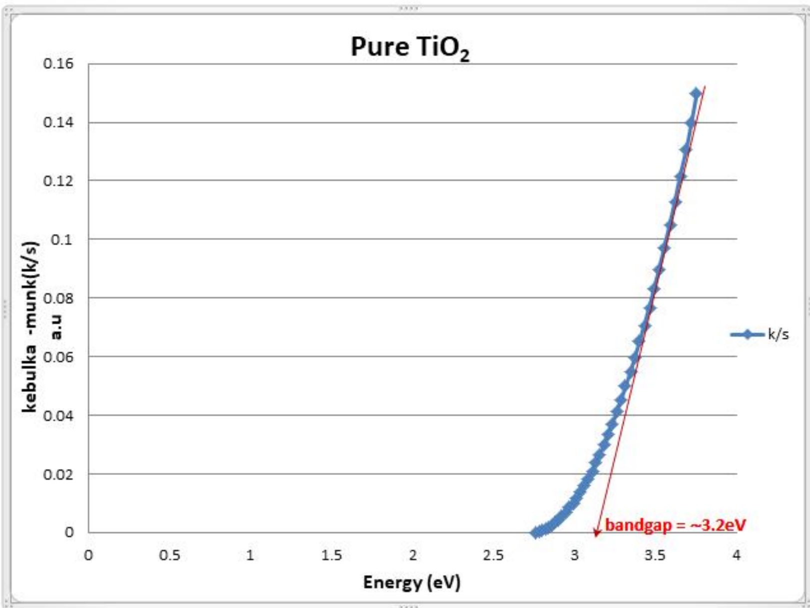

Fig. 1. Estimation of band gap value of pure TiO_2 using kebulka-munk plot

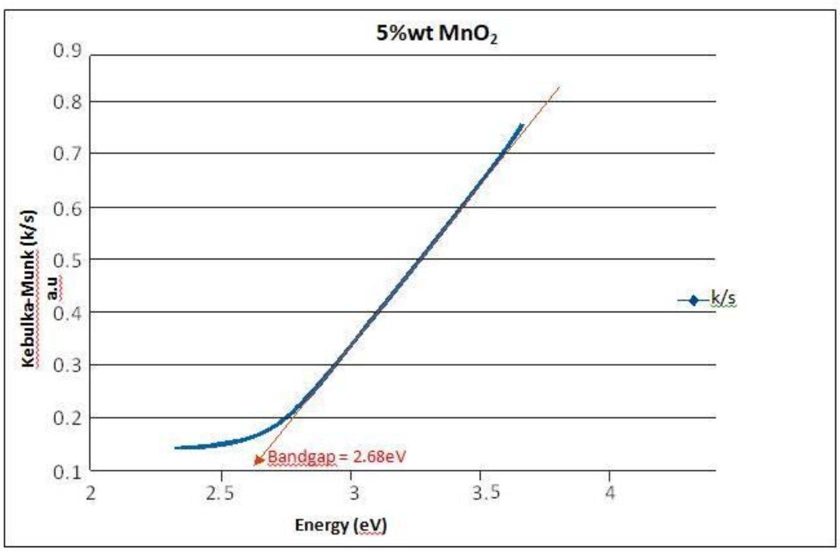

Fig.2. Estimation of band gap value of TiO_2 doped with 5%wt MnO_2 using kebulka-munk plot

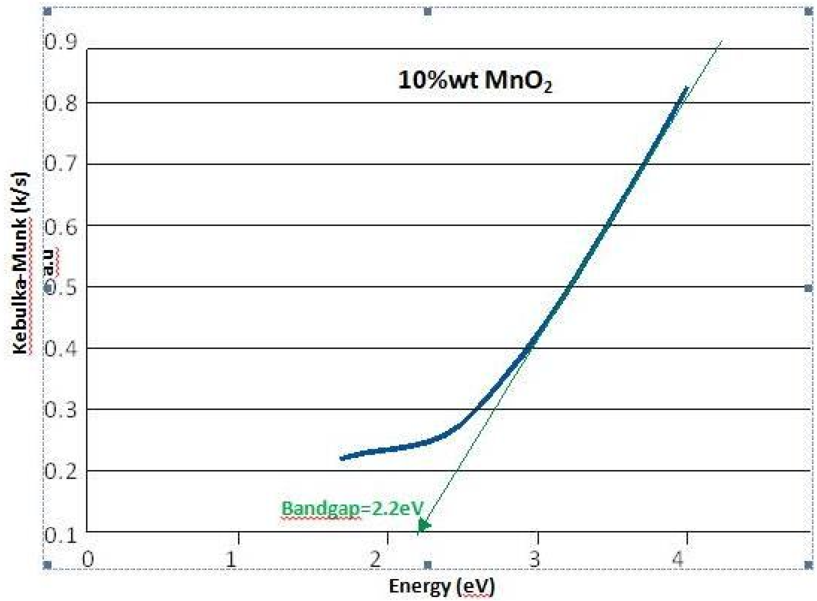

Fig.3. Estimation of band gap value of TiO_2 doped with 10%wt MnO_2 using kebulka-munk plot

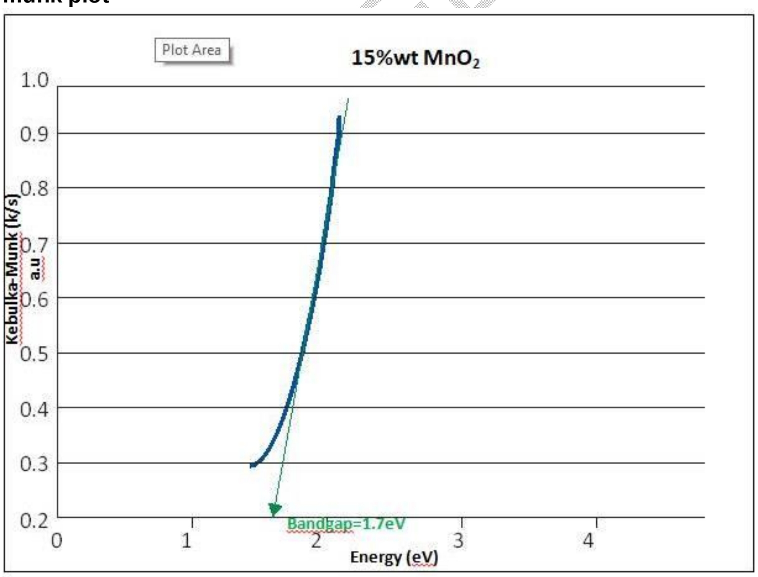

Fig. 4: Estimation of band gap value of TiO_2 doped with 15%wt MnO_2 using kebulka-munk plot

The UV/VIS analysis/characterization of the thin films gave clearer information on the impact of the MnO_2 doping on the TiO_2. Ordinarily, the latter comes with a very wide band gap of about 3.2eV (Dette. et al , 2014) which makes it very difficult for electrons to travel from the valence band to the conduction band. It was observed that the band gap was appreciably reduced due to the effect of the doping as can be observed from fig 1 to fig 4. These are kebulka-munk plots which were done with the help of the % reflectance data gotten from the UV/VIS spectrophotometric reading using equations 1.2 and 1.3. Following the different doping percentages on the thin films, different band gap values were obtained (5%wt =2.7eV, 10%wt =2.2eV and 15%wt =1.7eV).

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4. CONCLUSION

TiO_2 has shown very good characteristics which makes it a potent material for energy applications like li-ion batteries, and its credentials are improved obviously with decrease in particle size to the nano-scale, however its poor ionic conductivity had always hampered its use in the li-ion battery industry. This research has shown that if the right material is used for doping TiO_2, the electronic and ionic features can be greatly improved. MnO_2 was used because of its availability and ease of use in the doping process coupled with other known benefits of transition metal-oxides. The doping was done in 5%wt, 10%wt and 15%wt and was seen to improve both electrical and optical properties of the thin films.

Comment [O.I.36]: 5, 10 and 15%wt

COMPETING INTERESTS

Declaration of competing interest should be placed here. All authors must disclose any financial and personal relationships with other people or organizations that could inappropriately influence (bias) their work. Examples of potential conflicts of interest include employment, consultancies, honoraria, paid expert testimony, patent applications/registrations, and grants or other funding. If no such declaration has been made by the authors, SDI reserves to assume and write this sentence: "Authors have declared that no competing interests exist.".

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