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Investigation on Structural and Optical Properties of Manganese Dioxide Nanoparticles by Microwave-Assisted Solution Method

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Abstract- Manganese dioxide (MnO_2) nanoparticles have been successfully synthesized by microwave-assisted solution method. Powder X-ray diffraction method is used to the structural analysis of MnO_2 nanoparticles and finds that MnO_2 nanoparticles have a tetragonal structure. Crystallite grain diameter were estimated from powder X-ray diffraction and confirmed by High Resolution Transmission Electron Microscope. The crystalline grain size is 20 nm. Vibration spectra studies confirms that MnO_2 nanoparticles using FTIR spectra. The band gap energy of nanoparticles is 2.25 ev. It was found from Ultra Violet spectroscopy studies. The absorbance wavelength of MnO_2 nanoparticles was found from Ultra Violet spectroscopy studies. Thermal analyses are carried out of the MnO_2 nanomaterials.

Index Terms- Nanopartilces, Microwave, Wavelength, Thermal.

1. INTRODUCTION

Nowadays, Research interesting has increased by nanoparticles. The nanoparticles have unique size dependent properties. Metal oxides have exhibit advantageous properties in nanoparticles size and are being investigated intensively[1]. Physical vapor deposition (PVD), Solution growth process, and Reverse micelle method etc., are some of the methods used by preparation nanoparticles. Among the various physical/chemical methods to synthesize nanoparticles, co-precipitation, hydrothermal, micro emulsion[2], Solution phase method [3] and micro-oven assisted method [4] is commercially used because of its very less cost. Micro-oven assisted method gives advantages like, simple, easily control temperature, composition and particle size can be made in this method. Micro-oven method of various salts (nitrates, sulphates, chlorides, per chlorates etc.) under a good control of pH by using NaOH solutions yields corresponding metal dioxide nanoparticles. In this present study, MnO_2 nanoparticles were synthesized by microwave - assisted method. MnO_2 nanoparticles are very nice inorganic materials because of it have good chemical properties and physical properties. MnO_2 nanoparticles are many applications in electrochemical electrodes, biosensor, and particularly, energy storage. In this work, preparation of mno_2 nanoparticles and its characterization by TGA/DTA, UV- visible spectroscopy, FTIR, HRTEM and XRD techniques were discussed.

2. EXPERIMENTAL

2.1. Materials and Methods

The MnO_2 had been synthesized in microwave assisted solution technique and finally got brown color powder [5]. The used materials are NaOH, $MnSo_4$, MnC_2O_4 and De-ionized water.

2.2. Instrumentation

The Powder X-ray diffraction pattern of the Manganese dioxide nanoparticles samples were characterized using powder XRD (XPERT-PRO using CuKα1, λ=0.15 nm radiations). The prepared sample was scattered the angle of 2θ (10^0 - 80^0). The shape and size of the MnO_2 nanoparticles carried out the

High Resolution Transmission Electron Microscope using JOEL JEM 2000. The FT-IR spectra of the MnO_2 powder samples were recorded using Fourier Transform Infra-Red spectroscopy (FTIR) (JASCO FTIR-4100). The optical spectra of the MnO_2 powder samples were recorded using UV Visible spectroscopy (UV-2600) in the wavelength range 200-1200 cm^{-1}. TGA/DTA of the MnO_2 nanoparticles of this study was carried out simultaneously using Seiko thermal analyzer in air atmosphere at a heating rate of 25^0C/min for a temperature range of 30–820^0C. The alumina crucible was used.

3. RESULTS AND DISCUSSION

3.1. X-RD Studies - Structural characterization

Fig.1 shows powder XRD study of Manganese dioxide nanoparticles. MnO_2 was purely crystalline in nature. The reflection peaks of prepared nanoparticles were observed and it is perfect match with JCPDS File No. 44-0141.

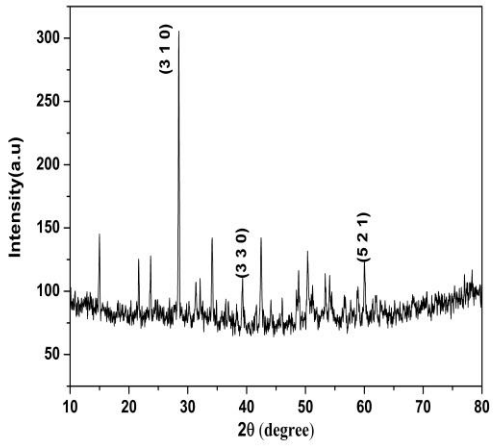

Fig 1. X-ray diffraction pattern of manganese dioxide nanoparticles.

The XRD peaks of the MnO_2 nanoparticles is (3 1 0), (3 3 0), and (5 2 1), It is confirm tetragonal structure of MnO_2 nanoparticles. The obtained value in this study in very good agreement with the value was reported by some articles[6]. The unit cell parameters of the MnO_2 nanoparticles are found and the observed values are a=9.78Å, b=9.78Å and c=2.86Å and a = b = c = 90^0 [7]. The average size of manganese dioxide nanoparticles was 24 nm [8]. The crystalline size of MnO_2 nanoparticles was found 20 nm as calculated by Debye Scherrer's equation (Crystallite size D = 0.9λ/β Cosθ) [9].

3.2. High Resolution Transmission Electron Microscope (HRTEM)

The Information such as particle size, size distribution, shape, degree of agglomeration etc of MnO_2 nanoparticles are obtained from HRTEM. Fig.2a is presented of images in HRTEM. It was concluded that the nanoparticles are uniform size and shape. HRTEM microscope images are observed that the shapes of most of the MnO_2 particles are nearly spherical and slightly elongated.

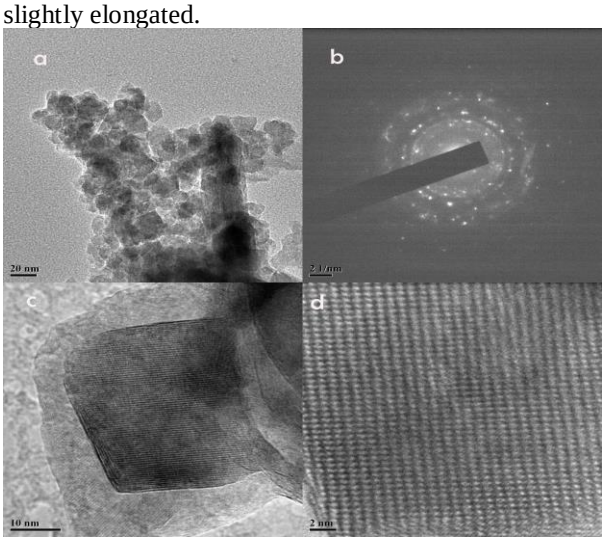

Fig 2. HRTEM image and SAED pattern of the MnO_2 nanoparticles

The selected area electron diffraction (SAED) pattern of the MnO2 nanoparticle is shown in fig 2b. The Debye Scherrer diffraction ring in the SAED pattern is pronounced in MnO2 nanoparticles highly crystalline nature, it can be assigned to the reflections (3 1 0), (3 3 0), and (5 2 1) of a tetragonal structure of the MnO_2. The high resolution images were recorded to get further insight into the atomic order of the MnO_2 nanoparticles. We manually measured the crystalline grain size for 50 particles to ensure a reliable representation of the actual size distribution. The crystallite grain diameter is around 18 to 22 nm as estimated from the HRTEM micrographs [10]. The particle grain size is around 20 nm, It is from XRD patterns and which is in nearly equal to measurable grain size of MnO_2 nanoparticle in HRTEM. The lattice planes of the nanopartcles are shown in the Fig.2c. Fig. 2d shows arrangements of atom in the lattice plane of the nanoparticles. It is clearly that the atoms are arranged in three dimensional lattices.

3.3. FTIR Spectroscopy

Functional groups of prepared MnO_2 nanoparticles were effectively found to using

FTIR spectra. Figure 3 shows FT-IR spectrum of manganese dioxide nanoparticles.

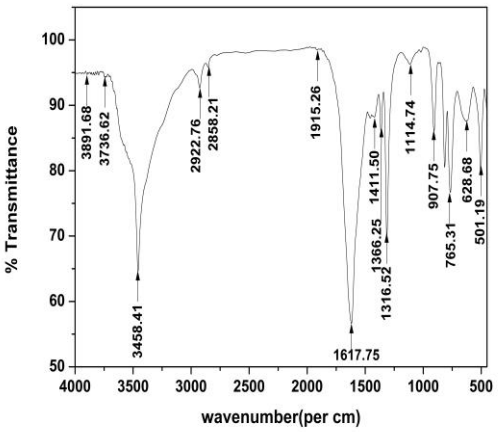

Fig 3. FT-IR spectra of manganese dioxide nanoparticles

The peak 501.19 cm^{-1} is Mn-O vibrations bond and allowed us to estimate of the relative amount of Mn present in our samples [11]. The broad absorption bands located around 3458.4 cm^{-1} and 1617.7 cm^{-1} corresponds to the O-H and H-O-H vibration of residual hydroxyl groups and water. Some absorption band located at 500 cm^{-1} to 900 cm^{-1} is the characteristic band of Mn-O bending vibration of octahedral in MnO_2[12]. The bands at about 752.69 cm^{-1} are attributed to the Mn-O vibrations of MnO_6 octahedra [10]. The FT-IR peaks at about 1114.7, 1316.5, 1336.2, 1411.5, 1915.2, 2858.2, 2922.7, 3736.6 and 3891.6 cm^{-1} are similar to MnO_2 Nanoparticles.

3.4. UV - Visible Spectroscopy

Figure 4 & 5 shows UV-Visible spectra of manganese dioxide nanoparticles prepared as a function of wavelength. The room temperature ultraviolet-visible spectra of MnO_2 nanoparticles sample was recorded absorption (Fig.4a). The absorption peak placed at 297.99 nm is shown fig. 4a. The peaks at 297.99 nanometer and peaks in the spectra placed at 200-400 nm are measured to be shifted towards lower wavelength side.

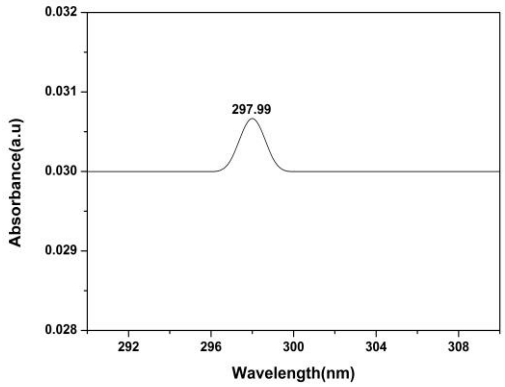

Fig 4. UV-Visible spectra of manganese dioxide nanoparticles

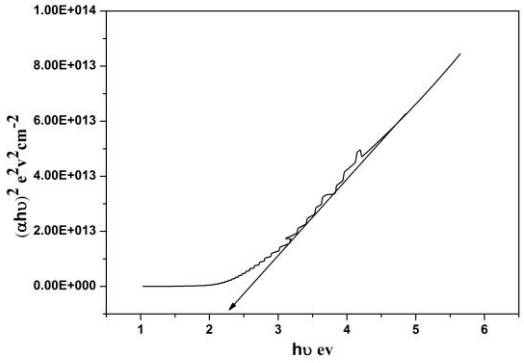

Fig 5. Band gap energy of manganese dioxide nanoparticles

To be find the value of band gap energy from the fundamental absorption, this corresponds to electron excitation from the valence band to conduction band. The relation between the α and $h\gamma$ can be written as: $\alpha h\gamma = A(h\gamma - E_g)$. Where A is a constant, $h\gamma$ is a incident photon energy, α is a absorption coefficient and E_g is a band gap energy of the materials and the transitions are direct so we taken as n = 1/2. Band gap energy can be found accurately from the plots of hν against $(\alpha h\nu)^2$ [13]. The straight line portion of the plot (hν vs $(\alpha h\nu)^2$ to $\alpha = 0$) may be obtained by band gap energy. Band gap energy of manganese dioxide nanoparticles was 2.25 ev as calculated using figure 5.

3.5. Thermal analysis

The thermal stability of MnO_2 nanoparticles were carried out between 30 and 800◦C by thermal gravimetric (TG) and differential thermal analysis (DTA). Figure 6 shows TGA/DTA behavior of MnO_2 nanoparticles. The actual content each component in

samples is determined the actual content by TGA. The variations of the TGA thermogram of MnO_2 nanoparticles are shown in the temperature range of 31-135, 135-315, 315-400, 400-525, 525-590, and 590-800 °C. The first weight loss at 31-135°C related to dehydration of the MnO_2 nanopaticles. The second weight loss in the range of 135-315, 315-400, and 400-525 °C could be related to the water molecule removing from the MnO_2 nanoparticles. However, the small weight loss in the ranges of 525-590 °C was observed in the TGA thermo gram, could be associated to the omitting the oxygen from manganese oxide lattice, due to the phase transition of MnO_2. The TGA analysis of MnO_2 shows a sharp mass loss from 315-400 ^{o}C, which is related to evaporation of the surface adsorbed water from materials. This is in agreement with DTA results where endothermic peak corresponding to the phase transition of layered to tunnelled MnO_2 is observed at 145 ^{0}C. The sharp exothermic is observed at 365 ^{0}C.

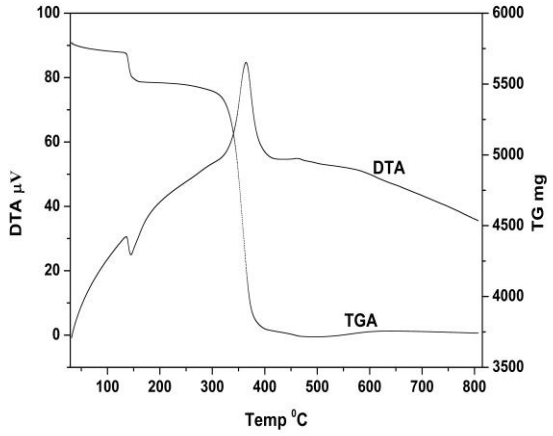

Fig 6. TG/DTA thermogram of MnO_2 nanoparticles

4. CONCLUSION

MnO_2 nanoparticles have been synthesized by microwave-assisted solution method and they were characterized by varies studies. XRD spectra predicted the average crystalline boundary size and structure of MnO_2 nanoparticles. HRTEM studies conformed the crystallite size of the MnO_2 nanoparticles, The functional group of the MnO_2 nanoparticles was identified from FT-IR spectra. The UV-visible absorption was found threshold and band gap energy due to MnO_2 nanoparticles. The thermal stability of the samples was studied by TG/DTA analysis.

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REFERENCES

[1] Vaidyanathan Subramanian.; Eduardo E. Wolf,; Prashant V. Kamat. 2004: Catalysis with TiO2/Gold Nanocomposites. Effect of Metal Particle Size on the Fermi Level Equilibration. Journal of American Chemical Society, **126**(15), pp. 4943-4950.

[2] Baohua Li.; Guangyao Gao.; Dengyun Zhai.; Chunguang Wei.; Yanbing He.; Hongda Du.; Feiyu Kang. 2013: Synthesis, Characterization and Electrochemical Performance of Manganese Dioxide in a Quaternary Microemulsion: the Role of the Co-surfactant and Water. International Journal of Electrochemical Science, **8**, pp. 8740-8751.

[3] Deogratius Jaganyi.; Mohammad Altaf.; Isaac Wekesa. 2013: Synthesis and characterization of whisker-shaped MnO_2 nanostructure at room temperature. Applied Nanoscience, **3**(4), pp. 329–333.

[4] Kumar, E.; Muthu Raj, D.; Vella durai, S.C.; Karthiga Devi, S.; Jenufa Begam, A. 2015: Synthesis and Structural Investigations of Titanium Di-oxide (TiO_2) Nanoparticles by Microwave Assisted Method. International Research Journal of Engineering and Technology, **2**(9), PP. 458-461.

[5] Kumar, E.; Vella durai, S.C.; Guru Prasad, L.; Muthuraj, D.; Bena Jothy, V. 2017: Preparation and Investigation on Structural, Spectral and Electrical Properties of Polyaniline/Manganese Dioxide Nanocomposites. Journal of Material and Environmental Science, **8**(10), 3490-3495.

[6] Senthilkumar, M.; Balamurugan, B.G.; Jeyaprakash. 2013: Hydrothermal Synthesis of MnO_2 Nanoparticles using Teflon Lined Autoclave. Research Journal of Pharmaceutical, Biological and Chemical Sciences. **4**(4), pp. 1627-1632.

[7] Devaraj, S.; Munichandraiah, N. 2007: Electrochemical Super capacitor Studies of Nanostructured α-MnO_2 Synthesized by Micro emulsion Method and the Effect of Annealing.

Journal of Electrochemical Society, **154**(2), pp. A80-A88.

[8] Harish Kumar.; Manisha.; Poonam Sangwan. 2013: Synthesis and Characterization of MnO_2 Nanoparticles using Co-precipitation Technique. International Journal of Chemistry and Chemical Engineering. **3**(3), pp. 155-160.

[9] Vella Durai, S.C.; Guru Prasad, L.; Kumar, E.; Muthuraj, D.; Bena Jothy, V.; Structural, Optical, and AC Conductivity Properties of Polyaniline/Manganese dioxide nanocomposites via In Situ Polymerization. International Journal of Research in Advent Technology, **6**(5), pp. 460-464.

[10] Muthuchudarkodi, R.R.; Vedhi,C. 2015: Preparation and electrochemical Characterization of manganese dioxide- zirconia nanorods. Applied Nanoscience, **5**(4), pp. 481–491.

[11] Cuentas – Gallegos, A.K.; Gómez – Romero, P. 2005: In-Situ Synthesis of Polypyrrole-MnO_{2-x} Nanocomposite Hybrids. Journal of New Materials for Electrochemical Systems, **8**(3), 181-188.

[12] Juan Yang.; Linda Zou.; Huaihe Song. 2012: Preparing MnO_2/PSS/CNTs composite electrodes by layer-by-layer deposition of MnO_2 in the membrane capacitive deionisation. Desalination, **286**, pp.108–114.

[13] Rahdar, A.; Arbabi, V.; Ghanbari, H. 2012: Study of Electro-Optical Properties of ZnS Nanoparticles Prepared by Colloidal Particles Method. World Academy of Science, Engineering and Technology. **61**(1), pp. 657-659.