Micro pores structured $\alpha$-Mn$_2$O$_3$ and rGO/$\alpha$-Mn$_2$O$_3$

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A room temperature co-precipitation method has been used for the preparation of cubic MnCO$_3$ particles by mixing the aqueous solutions of Mn$_2$SO$_4$ and Na$_2$CO$_3$ in 1:2 molar ratios. The prepared light brownish MnCO$_3$ particles were dried and post heated at two temperatures 300ºC and 600ºC with an appropriate time intervals. This time variation facilitates the uniform cubic $\alpha$-Mn$_2$O$_3$ particles. The as synthesized cubic $\alpha$-Mn$_2$O$_3$ was further investigated by powder X-ray diffraction studies. The as synthesized MnCO$_3$, Mn$_2$O$_3$ and reduced graphene oxide mixed Mn$_2$O$_3$ particles express the rhombohedral and orthorhombic crystal systems. The molecular vibrations of the titled compounds were obtained from FTIR studies. The morphology and microstructures of the synthesized cubic particles were assessed from scanning electron microscopical studies. The elemental composition was obtained from EDAX analysis. The electro chemical performances were assessed by CV measurement; rGO mixed Mn$_2$O$_3$ has higher sweep voltage than pure one. From the AC impedance calibration the rGO composed Mn$_2$O$_3$ has very low $R_c$ value, due to the addition of conducting rGO in to the Mn$_2$O$_3$ matrix. The obtained reduction in resistance and the porous structure may find applications in the field of sensors.

Key Words: MnCO$_3$, Cubic Mn$_2$O$_3$, Co-precipitation method, Electrochemical analysis.

Graphical Abstract

1. Introduction

The controllable synthesis of micro and nano metal oxides with different shapes and morphologies has considerable attention in applications when compared with their bulk counter parts [1]. The properties of nano and microstructures are mainly depends on their chemical composition ratios, crystal structure, size distribution, phase and shape [2-5]. In many cases the physico-chemical properties of the material is tailored by their chemical structure, size and shape. Present case the excess concentration of basicity in the reaction medium induces uniform cubic morphology in the synthesized particles. Nowadays various methods have employed to prepare different nanostructures with unique morphologies, which include nanotubes, nanorods, nanowires, nanobelts, nanoplates and some other nanostructures [6-9]. Recently we devote much attention to synthesize micro structured manganese oxide cubic particles for electrochemical applications. This material is relatively inexpensive, naturally abundant and non toxic. Manganese oxides have some varieties, which is due to its bonding with oxygen. That are named as like MnO, MnO$_2$, Mn$_2$O$_3$ and Mn$_3$O$_4$ [10-12]. The present case Mn$_3$O$_4$ cubic particles were prepared through least expensive co-precipitation method, due to its (Mn$_2$O$_3$) potential applications in electrochemical analysis, catalytic properties in photonics.
and molecules adsorption nature under photochemical degradation process. In addition MnO₃ material was used to prepare soft magnetic materials and further used to prepare electrodes for rechargeable lithium ion batteries [13-15].

Recent scenario the researchers made effort to enhance the cyclic performance of the electrode materials, however they were reducing the particle size, designing special structures, doping and coated carbon based materials over the electrode surface [16-18]. In the present work, MnO₃ and rGO/MnO₃ composite electrode materials were synthesized and electrochemically analyzed successfully. The composition of rGO into the MnO₃ matrix has improved the electrochemical performance. Further, metal oxides with porous structure have attracted much attention as electrode material for electrochemical analysis. The porous metal oxide favors the high specific surface area for the penetration of freely moving electrolyte ions into the electrode surface [19, 20].

2. Experimental Details

2.1. Material Synthesis

Commercially bought analytical grade chemicals were utilized. The adopted typical procedure as follows: 35ml of aqueous solutions of each 1M: MnSO₄·H₂O and 2M: Na₂CO₃ were prepared separately using double distilled water. Then pre-determined quantity of ethanol (7ml) was added drop wise into the MnSO₄·H₂O aqueous solution under constant magnetic stirring for 10 min. After that the 2M: Na₂CO₃ solution was added drop wise into the ethanol-MnSO₄·H₂O aqueous mixture [21]. Light brownish MnCO₃ precipitates were observed after 30 minutes and the reaction mixture was continuously homogenized next three hours by the assist of constant stirring. The precipitated MnCO₃ was centrifuged and dried in open atmosphere at the temperature of 60°C for almost 12 hours. After that the dried product was packed into the muffle furnace and sintered at 300°C for one hour and then the temperature was raised to 600°C and maintained for next one hour [22]. The synthesis of GO was carried out at our laboratory by modified Hummer’s method and it was further reduced by solar exfoliation in the form of rGO. The synthesized rGO was utilized for the preparation of rGO mixed MnO₃.

2.2. Characterization Details

The powder X-ray diffraction patterns of the as synthesized samples were obtained by X’ Pert PRO PANalytical diffractometer equipped with CuKα radiation (30 mA & 40 Kv). The analysis was carried out at the scan rate of 0.02° S⁻¹ in the 20 range from 10° to 80°. The molecular vibrational spectrum was recorded using Thermo Nicolet 380 with KBr pellet method at room temperature. The micro structural images of the prepared samples were obtained from field emission scanning electron microscope (FESEM- FEG Quanta 250). The electro-chemical properties were attained by Metrohm autolab instrument.

3. Result and Discussion

3.1. Powder X-Ray Diffraction Analysis

The crystal structure of the as synthesized compounds named as MnCO₃, MnO₃ and reduced graphene oxide added MnO₃ were examined using powder X-ray diffractometer. The well refined peaks from the analysis show the crystalline perfection of the as synthesized compounds. The corresponding diffraction patterns were shown in figure1. The as prepared MnCO₃ expresses rhombohedral crystal system with the space group of R3c, which was in good agreement with the standard value [JCPDS card no. 44-1472]. The pure α-MnO₃ and rGO doped α-MnO₃ express the orthorhombic crystal system with the space group of Pbc, as per the standard values [JCPDS card no. 73-1826] [22]. The rGO composed α-MnO₃ has resulted maximum diffraction intensity when compared with pure one. The incorporation of one weight percentage of rGO during the synthesis did not have any noticeable shift in the major diffraction peak in the recorded pattern which suggests very low strain due to the introduction of reduced graphene oxide in to the α-MnO₃ molecular structure.

Fig.1. Powder X-ray diffraction patterns of MnCO₃, MnO₃ and rGO-MnO₃

3.2. FTIR Measurement

The molecular structure of the as synthesized compounds was further analyzed by Fourier transform infrared spectral measurements (FTIR). The spectra were recorded in the range of 4000 to 400 cm⁻¹. The figure 2 shows the molecular vibrational spectra for the pure MnO₃ and rGO composed MnO₃ particles. The absorption bands at 576 and 524 cm⁻¹ could be assigned to the metal oxygen binding stretching modes of vibrations. The resulted vibrations at
lower frequency region suggested the formation of Mn$_2$O$_3$ molecular structure. The vibrations at 3442 cm$^{-1}$ was assigned to the O-H stretching of adsorbed water and the absorption bands at 2359 cm$^{-1}$ and 1111 cm$^{-1}$ are due to the molecular vibrations of CO$_2$ and C-O. These water and carbon dioxide contents in the semiconducting nano particles are un-avoidable owing to its mesoporous nature [23]. The molecular vibrational band at 1633 cm$^{-1}$ was related to the O-H bending and C-O stretching vibrations. The very low absorption bands at 2934 and 2858 cm$^{-1}$ are corresponds to the molecular vibration of C-H stretching evidence the low concentration of rGO in the synthesized material.

3.3. SEM with EDAX Studies

Figure 3 shows morphological images of MnCO$_3$, Mn$_2$O$_3$ and rGO doped Mn$_2$O$_3$ at different magnifications. As synthesized MnCO$_3$ expresses well refined cubic structure (figure 3a and 3b). After sintering, the smooth cubic surface was lost and porous nature over the surface was observed (figure 3c). This fact is due to the dissociation of manganese carbonate (MnCO$_3$) to manganese oxide (Mn$_2$O$_3$) form [22]. The cubes with porous surface are clearly shown along with
1D nano whiskers in figure 3d. Introduction of rGO into the host Mn₂O₃ matrix causes the morphology changes from cubic to spherical like morphology (figure 3e) with intense porosity on the surface. It is visibly manipulated in figure 3f that most of the nano/micro cubes in the synthesized compound has been converted into spherical form. This kind of porous morphology may form due to the step degradation of carbon dioxide in the host matrix at the surface. The sintering process at 600°C for 1 hour adopted in the present work may also be attributed to the change in structural morphology which favors surface dissociation in the nano cubes. Such porous could provide more catalytic sites on the surface of Mn₂O₃ and greatly favour the subsequent electrochemical catalytic reaction [24] for sensor application.

Fig. 4. EDAX spectra for Mn₂O₃ and rGO-Mn₂O₃ particles.

Figures 4a and 4b shows the energy dispersive X-ray analysis spectrum of Mn₂O₃ and rGO composed Mn₂O₃ particles. The corresponding elemental ratios were listed below the figures 4a & 4b in table form. This experiment is a key tool to know about the rGO presence in the as synthesized compound. From the EDAX spectrum, the absence of elemental peaks other than the expected in the recorded spectra clearly details the chemical purity of the synthesized compound. Figure 4a has a negligible amount of carbon from the sample holder. This is un-avoidable but intense contribution of carbon in the case of figure 4b clearly establishes the rGO presence in the host material (Mn₂O₃) lattice.

3.4. Electrochemical Analysis

Cyclic voltammetry provides the qualitative information regarding the redox reactions occurred in the electrochemical system. Figure 5 (a-b) shows the cyclic voltammogram of Mn₂O₃ and rGO composed Mn₂O₃ cubic particles. The measurement were taken in different operating voltages (100 mV, 50 mV, 25 mV and 10 mV s⁻¹) in 0.5M concentration of sodium sulphate electrolyte solution. The electrode material were prepared by the assist of 80% host material (Mn₂O₃ and rGO added Mn₂O₃), 10 weight percent of Acetylene black and 10 weight percent of PVDF as binder, which was coated on the 1 cm x 1 cm SS plate with the thickness of 0.5 mm. The prepared electrodes were dried at 80°C over a period of 12 hours in hot air oven, then used as a working electrode and Pt and AgCl were used as counter and reference electrodes respectively in the CV measurement. The achieved 100 mV operating voltage offers large sweep area when compared with other operating voltages for both pure Mn₂O₃ and rGO composed Mn₂O₃. Figure 5c and 5d show AC impedance curves of the pure Mn₂O₃ and rGO composed Mn₂O₃ cubes. The insets of 5c and 5d are the extrapolated images of the corresponding AC impedance plots, and are used for Rₓ calculation. The calculated Rₓ values for pure Mn₂O₃ is 17.469 (Ω) and the rGO composed Mn₂O₃ is 6.72 (Ω). The rGO added Mn₂O₃ has low resistance value when compared with pure one (Mn₂O₃) due to the addition of conducting element (rGO) into the host crystal structure.

Fig. 5. CV curves of a. Mn₂O₃ and b. rGO added Mn₂O₃ and AC impedance plot of c. pure Mn₂O₃ and d. rGO composed Mn₂O₃

4. Conclusion

A room temperature co-precipitation method has been used for the preparation of cubic MnCO₃ nano/micro particles. The precipitated and centrifuged light brownish MnCO₃ nano/micro particles were dried and post heated at 300°C and 600°C at an appropriate time intervals. The
structural details of the as synthesized MnCO$_3$ and Mn$_3$O$_4$ were obtained from PXRD measurement. The as prepared compounds express rhombohedral (MnCO$_3$) and orthorhombic (Mn$_3$O$_4$) and rGO composited Mn$_2$O$_3$ crystal systems. The diffracted peaks were well matched with the standard values. Further the characteristics molecular vibrations of the as prepared compounds was ascertained from FTIR spectral measurement. The microstructure was assessed from scanning electron microscopy. The MnCO$_3$, Mn$_3$O$_4$ and rGO composited Mn$_2$O$_3$ express uniform cubic, cubic with porous surface and spherical with porous surface respectively in nano scale. The porous nature of the surface may provide more catalytic sites on the surface of Mn2O3 and greatly favour the subsequent electrochemical catalytic reaction for sensor application. It is observed that the sintering temperature facilitates the porosity over the nano/micro cubes. The study on the influence of surface porosity on sensing property is in progress. The elemental compositions were calibrated from the EDAX measurement and the presence of rGO in the host matrix was realized. The electro chemical performances were obtained from CV analysis. From the CV analysis rGO added Mn$_2$O$_3$ has maximum sweep potential of 100mV and low $R_e$ value than pure one. In conclusion, the introduction of rGO has not altered the crystal structure of the material, but it enhances the crystalline perfection. It also improved the electrochemical performance due to its electronic conductivity.

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