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High specific capacitance of electrochemically synthesized nano MnO_2 – gold electrodes for supercapacitors

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ABSTRACT

Transition metal ions like MnO_2 are promising materials for electrodes in supercapacitors owing to their high capacitance for storing electrical charges and also eco-friendly with plenty of availability. We have decorated honey-bee like MnO_2 nanostructure over gold coated silicon wafer by electrodeposition. The electrodeposited material was studied by scanning electron microscope (SEM), which reveals the honey-bee like structure. The thickness was found to be in the range of 30–80 nm using atomic force microscope (AFM). The specific capacitance of this electrode is found to be 1149 Fg^{-1}, which is very high and flexible for high power applications. Copyright © 2013 VBRI press.

Keywords: Supercapacitors; electrodeposition; MnO_2.

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V. S. Prabhin obtained his M. Tech. degree (Nanoscience and Technology) from Mepco Schlenk Engineering College, Sivakasi, India and worked under the corresponding author's group. He is presently working in an Engineering college as a faculty.

Introduction

For a huge power surge or instantaneous power release in demanding application such as rocket launching, batteries become unsuitable due to their slow rate of energy release **[1].** Supercapacitors are electrochemical energy storage devices that provide high power density and remarkable energy. Electrochemical supercapacitors can deliver high levels of electrical power and offer long operating lifetimes **[2–9]**. These characteristics are of increasing interest in energy storage applications such as: electric vehicles, backup power systems, electronic components, etc. They are based on a storage mechanism that results from the formation of an electric double layer at the interface between an electronically conductive material and an electrolyte solution **[2, 10]**. But their low energy storage density inhibits the use for high power applications. Basically the electrode materials may be either carbon based or metal oxide or conducting polymer. Conducting polymer may be helpful as they are less expensive and able to store energy through a redox process **[11]**. But its lower cycle life and the low specific capacitance value inhibit its usage for potential applications. Recently D.S. Patil et al. **[12]** reported silver/polyaniline based electrodes for supercapacitors with a specific capacitance of 512 Fg^{-1}. Carbon materials in different forms such as carbon fibres, carbon aerogels, activated carbons and carbon nanotubes are most commonly used in high specific area electrode materials. These materials exhibit various attractive physical and chemical properties such as high conductivity, high surface area, high temperature stability, good corrosion resistance, high porosity, easy processability and

good compatibility with composite materials and relatively low cost **[13]**. In this category, CNT attracted much attention owing to its flexibility **[14–15]**. But the specific capacitances are lower to use it in high power applications. The usage of transition metal oxide proves to be a better idea because they are available in plenty, low cost, nontoxic, etc., **[16–17]** but their low conductivity does not help. In transition metal oxides, MnO_2 could be used to make electrodes in such supercapacitors **[16, 18]**, because they are predicted to have a high capacitance for storing electrical charge but the poor conductivity of MnO_2 limits the charge/discharge rate for high-power applications. To overcome this problem an electrode made of gold could be used. An electrode made of gold nanoparticle facilitates fast ion diffusion between the materials and the electrolytes which can act as double-layer capacitors or bio-sensors **[19]**.

Electrochemical synthesis is a better technique for developing indigenous supercapacitors and also for many other applications such as gas-sensors, bio-sensors, etc. **[20]**. Here, we report that honey-bee structures made of MnO_2 decorated in gold coated silicon wafer using electrochemical synthesis (cyclic Voltammetry) show a high capacitance for high energy applications. We have decorated the MnO_2 structure on a gold electrode. The nanoporous gold nanoparticle and the honey-bee MnO_2 structure facilitate fast ion diffusion and serves as a better material for supercapacitor. We obtain the value of 1149Fg^{-1}, which is close to the theoretical value **[16]**. This value is very high compared to previous reports in the metal based/CNT based/polymer based. It is believed that the honey-bee structure is the reason for the high specific capacitance of our electrode. The other advantage of our report is that we have obtained this value at high scan rate and this facilitates to use this material for high density applications.

Experimental

Materials and methods

Analytical grade Na_2SO_4 (≥99% purity), $(CH3COO)_2Mn{\cdot}4H_2O$ (99.99% purity) and gold wafer were purchased from Sigma Aldrich. All electrochemical experiments were performed using CHI 600 series Electrochemical Analyzer/Workstation. Distilled water was used for the solution preparation. A conventional three-electrode system which consists of a gold wafer as working electrode, an Ag/AgCl (saturated KCl) as a reference and a platinum wire as counter electrode were used. 0.1 M Na_2SO_4 and 0.1 M manganese acetate were dissolved in the 100ml water and the electrolyte solution was prepared. Gold wafer electrodes were immersed in deionized distilled water and kept for ultra-sonication for one hour. After this process, the electrodes were washed thoroughly with deionized distilled water and used for the electrochemical deposition process. Here, the cyclic voltammetry has been employed for the electrochemical deposition process. Pre-treated electrode has been immersed in the 0.1 M Na_2SO_4 solution containing 0.1 M manganese acetate solution and the potential has been fixed from 0 to 0.4 V at the scan rate of 20 mV/s for three cycles and the manganese oxide materials were directly deposited on the electrode surface. Finally the manganese oxide materials was rinsed with deionized water and employed for the electrochemical analysis.

Characterization

XPERT- PRO X-ray diffractometer using Cu Kα Radiation (wavelength λ = 1.54016 A°) at 40 keV was used to confirm the formation of MnO_2 and to calculate the particle size. The morphology of nano particles were analyzed using HITACHI SUI510 scanning electron microscope operating at 10 kV. The morphology of MnO_2 decorated in gold electrode was analysed using park system XE70 Atomic force microscope. Electrochemical charaterizations were performed using CHI 600 series Electrochemical Analyzer/Workstation.

Fig. 1. MnO_2 coated in gold coated silicon wafer for electrodes in supercapacitors.

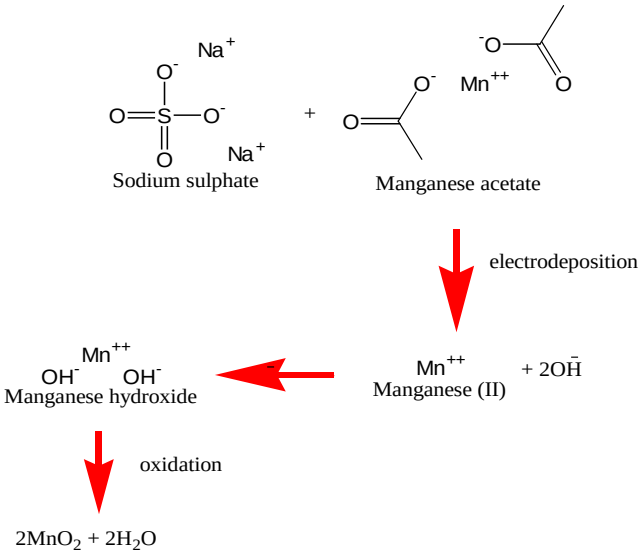

Fig. 2. Schematic representation of MnO_2 deposition process in the gold electrode

Results and discussion

The MnO_2 decorated in gold coated silicon wafer photograph was present in the **Fig. 1**. The schematic representation of electrochemical reaction mechanism was depicted in the **Fig. 2**. In this process, the electrolyte solution is the mixer of Na_2SO_4 and $(CH_3COO)_2Mn.4H_2O$. Here the role of Na_2SO_4 is to increase the mobility of the Mn^{2+} ions towards the gold electrode. At suitable voltage, the Mn^{2+} ions forms $Mn(OH)_2$ and oxidises to MnO_2. Since gold particle in the electrode are nanoporous, MnO_2 forms structure like pattern in the electrode. However, the detailed chemistry of the formation of the honey-bee like structures

is not known. The colour changes from yellow to brownish black confirm the formation of MnO_2 in the gold electrode. The deposition was the result of the below mentioned sequential process. At first, water electrolysis occurred at the gold electrode surface generating OH^-. This OH^- bonds with Mn^{2+} causing nanoparticle deposition in the form of structures.

$$Mn(CH_3COO)_2 \longrightarrow Mn^{2+} + (CH_3COO)^-$$
$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$
$$Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_2$$
$$2\,Mn(OH)_2 \longrightarrow 2MnO_2 + 2H_2O$$

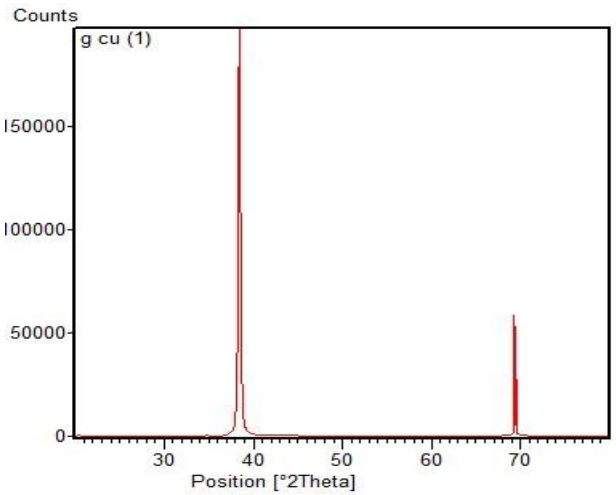

Fig. 3. XRD of MnO_2 decorated in gold coated silicon wafer showing the presence of pure phase of MnO_2 with uniform particle size distribution of 30 nm.

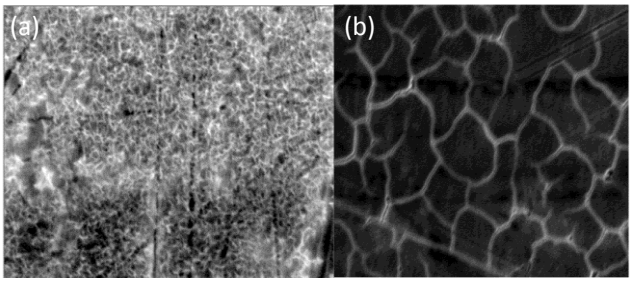

Fig. 4. SEM image of (a) MnO_2 coated in gold coated silicon wafer with different magnification showing clear (b) honey-bee structure.

XRD of the MnO_2 decorated in gold coated silicon wafer is presented in **Fig. 3**. The two sharp peaks confirm the presence of MnO_2 in pure form and no other impurities are found (JCPDS number is #895171). It also reveals the uniform particle size distribution of 30 nm using Scherrer formula. **Fig. 4** shows typical scanning electron microscopy (SEM) of MnO_2 decorated in gold coated silicon wafer at different magnifications. It clearly shows that grown MnO_2 in the gold coated silicon wafer forms a neat porous network. The exact morphology was not seen clearly in 1 µm resolution, though it indicates a new structure formation. **Fig. 4b** shows clearly that MnO_2 was decorated similar to honey-bee structure.

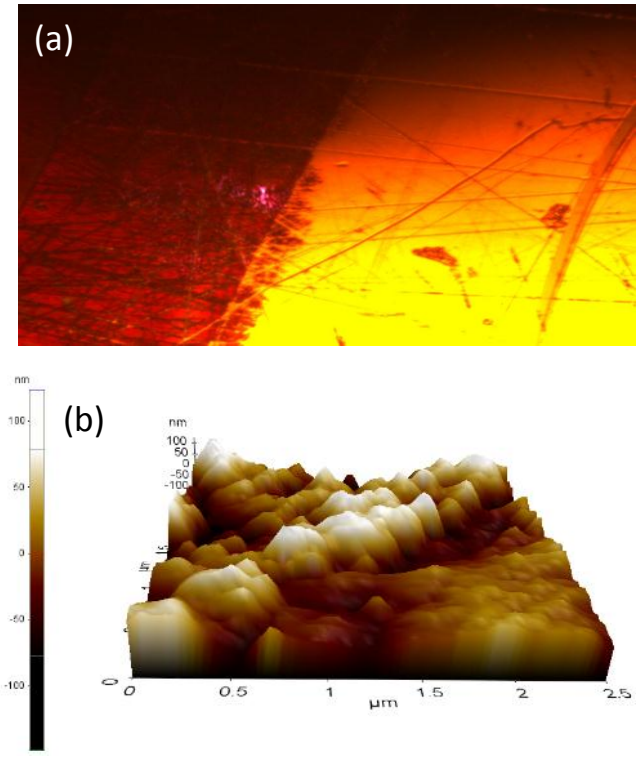

Fig. 5. AFM images of MnO_2 decorated in gold coated silicon wafer. (a)Top image clearly shows difference between coated and uncoated regions which uniform morphology and (b) Bottom is topographical view which shows thickness of coated regime in the scale of 30–80 nm.

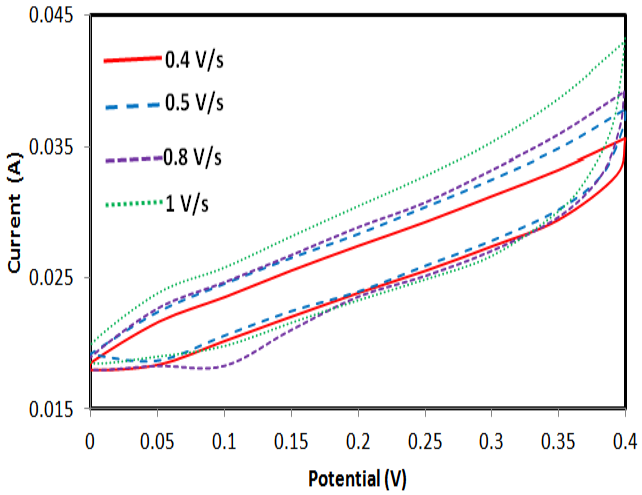

Fig. 6. Scan rate dependence of electrochemical properties. Cyclic voltammograms (current density versus voltage) for a MnO_2 decorated in gold coated silicon wafer electrode (plating time, 10 min) at four different scan rates between 0.4–1 Vs^{-1}.

Atomic force microscopy (AFM) images were presented in **Fig 5**. **Fig. 5** shows the topography view of manganese oxide coated over the gold wafer. Left side of the image shows the manganese oxide coated region which is darkened and the right side of the shows the gold wafer without any deposition. The bottom image of **Fig. 5** shows the top view topography of manganese di-oxide coated over gold wafer. Since the AFM tip is made to scan between the coated and uncoated region, the thickness of the coating is

determined. The thickness is found to be in the regime of 30-80nm. It also shows the uniform deposition of MnO_2 over the gold wafer.

Fig. 6 shows cyclic voltammograms (CV) for MnO_2 plated in gold substrate. The investigations were carried out for all electrodes in Li_2SO_4 solutions at room temperature. The current increases with scan rate for all electrodes. CV shows a rectangular behaviour for all scan rates and shows a good high-rate performance. The electrode shows a high capacitance (~1149 Fg^{-1}) with the plating time of 10 min at the scan rate of 0.01 Vs^{-1} which is very high to the previous reports **[21–23]**.

The capacitance was determined by integrating the area of the cyclic voltammetry graph. The formula is given below,

$$C = \int_{E_1}^{E_2} i(E)\,dE \,/\, 2(E_2 - E_1)mv \qquad (1)$$

where C is Specific capacitance, ∫ i(E)dE is the total voltammetric charge obtained by integrating the positive & negative sweep in cyclic voltammetry, (E2-E1) is the difference in applied potential, m is the difference in mass which is, after and before the deposition of manganese oxide over gold wafer and V is the Potential scan rate. The specific capacitance is calculated by integrating the equation (1) as,

$$C = \frac{Q}{\Delta V \Delta M} \qquad (2)$$

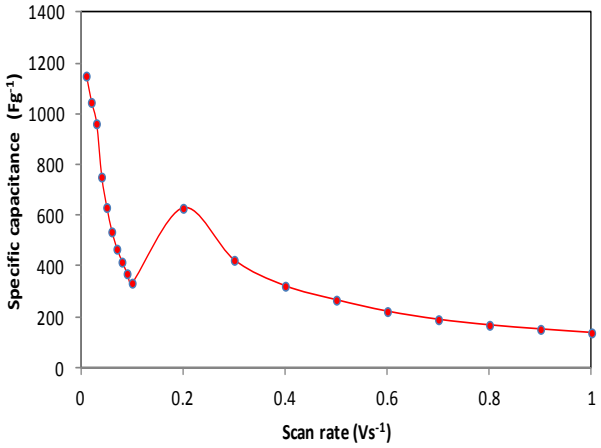

Fig. 7. Specific capacitance of plated MnO_2 versus scan rate. All data are taken in 2 M Li_2SO_4 solutions.

Fig. 7 shows specific capacitance of plated MnO_2 versus scan rate. The specific capacitance was maximum at the scan rate of 0.01Vs^{-1} and decreases gradually up to 0.1 Vs^{-1}. There is sudden increase in the specific capacitance when the scan rate was as 0.2 Vs^{-1}. Beyond 0.2 Vs^{-1}, the specific capacitance decreases very slowly and shows almost constant at higher scan rate. This shows that the electrode is ideal and it can be used for high power applications.

Conclusion

Electrodeposition of MnO_2 in gold coated silicon wafer was performed and SEM shows the formation of honey-bee like structure. Thickness of the deposited structure was analysed from AFM and found to be in 30–80 nm. CV shows a good rectangular behaviour and the current increases with the scan rates. The specific capacitance was found to be 1149 Fg^{-1} which is very ideal value for high power applications.

Reference

1. Intelligent Nanomaterials, Edited by Ashutosh Tiwari, Ajay K. Mishra, Hisatoshi Kobayashi and Anthony P.F.Turner, **2012**,Wiley-Scrivener Publishing LLC,USA,ISBN:978-04-709387-99
2. Winter, M.; Brodd, R. Chem. Rev. **2004**, 104, 4245. **DOI:** 10.1021/cr020730k
3. Conway, B.E. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications **1999,** Kluwer Publications
4. Simon, P.; Gogotsi, Y. *Nature Mater*. **2008**, 7, 845 **DOI:** 10.1038/nmat2297
5. Arico, A.S.; Bruce, P.; Scrosati, B.; Tarascon, J.M.; Van Schalkwijk, W. *Nature Mater*. **2005**,4, 366 **DOI:** 10.1038/nmat1368
6. Miller, J.R.; Simon, P. *Science* **2008**, 321 651. **DOI:** 10.1126/science.1158736
7. Pech D.; et al., *Nature Nanotech.* **2010**, 5, 651. **DOI:** 10.1038/nnano.2010.162
8. Chmiola, J.; Largeot, C.; Taberna, P.L.; Simon, P.; Gogotsi, Y. *Science* 2010, 328, 480. **DOI:** 10.1126/science.1184126
9. Huang, J.S.; Sumpter, B.G.; Meunier, V. *Angew. Chem. Int. Ed.* **2008**, 47,520. **DOI:** 10.1002/anie.200703864
10. Kotz, R.; Carlen, M. *Electrochimica Acta* **2000,** 45, 2483
11. Sharma, A.K.; Sharma, Y.; Malhotra, R.; Sharma, J.K. *Adv. Mat. Lett.* **2012**, 3(2), 82 **DOI:** 10.5185/amlett.2012.1315
12. Patil, D.S.; Shaikh, J.S.; Pawar, S.A.; Devan, R.S.; Ma, Y.R.; Moholkar, A.V.; Kim, J.H.; Kalubarme, R.S.; Park, C.J.; Patil, P.S. *Phys Chem Chem Phys.* **2012**, 14(34), 11886-95 **DOI:** 10.1039/C2CP41757J
13. Pandolfo, A.G.; Hollenkamp, A.F. *Journal of Power Source.* **2006**, 157,11 **DOI:** 10.1016/j.jpowsour.2006.02.065
14. Kumar, N.A.; Choi, H.Y.;Bund, A.; Beak, J.B.; Jeong, Y.T. *J. Mater. Chem.* **2012**, 22, 12268 DOI: 10.1039/C2JM30701D
15. Hu, S.; Rajamani, R.; Yu, X. *Appl. Phys. Lett.* **2012**, 100, 104103 **DOI:** 10.1063/1.3691948
16. Toupin, M.; Brousse, T.; Belanger, D. *Chem. Mater.* **2004,** 16, 3184
17. Chang, J.K.; Tsai, W.T.; *J. Electrochem. Soc.* **2003** 150, A1333.
18. Hashmi, S. A.; Updahyaya, H. M. *IONICS* **2002**, 8, 272
19. Tiwary, A.; Aryal, S.; Pilla, S., Gong, S. *Talanta* 2009, 78 (4), 1401 **DOI:** 10.1016/j.talanta.2009.02.038
20. Tiwary, A.; Gong, S.; *Electroanalysis* **2008**, 20 (16), 1775 **DOI:** 10.1002/elan.200804237
21. Lee, S.W.; Kim, J.; Chen, S.; Hammond, P.T.; Shao-Horn, Y. *ACS Nano* **2010,** 4, 3889. **DOI:** 10.1021/nn100681d
22. Fischer, A.E.; Saunders, M.P.; Pettigrew, K.A.; Rolison, D.R.; Long, J.W. *J. Electrochem. Soc.* **2008,** 155 A246 **DOI:** 10.1149/1.2830548
23. Lee, S.W.; Kim, B.S.; Chen, S.; Shao-Horn, Y. Hammond, P.T. *J. Am. Chem. Soc.* **2009,** 131, 671 **DOI:** 10.1021/ja807059k