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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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

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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, MnO₂ 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 MnO₂ 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 MnO₂ decorated in gold coated silicon wafer using electrochemical synthesis (cyclic Voltammetry) show a high capacitance for high energy applications. We have decorated the MnO₂ structure on a gold electrode. The nanoporous gold nanoparticle and the honey-bee MnO₂ structure facilitate fast ion diffusion and serves as a better material for supercapacitor. We obtain the value of 1149F g⁻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 Na₂SO₄ (≥99% purity), (CH₃COO)₂Mn 4H₂O (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 Na₂SO₄ and 0.1 M manganese acetate were dissolved in the 100 ml 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 Na₂SO₄ 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 mVs⁻¹ 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 Å) at 40 kV was used to confirm the formation of MnO₂ and to calculate the particle size. The morphology of nano particles were analyzed using HITACHI SU1510 scanning electron microscope operating at 10 kV. The morphology of MnO₂ decorated in gold electrode was analysed using park system XE70 Atomic force microscope. Electrochemical characterizations were performed using CHI 600 series Electrochemical Analyzer/Workstation.

**Results and discussion**

The MnO₂ 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 Na₂SO₄ and (CH₃COO)₂Mn.4H₂O. Here the role of Na₂SO₄ is to increase the mobility of the Mn²⁺ ions towards the gold electrode. At suitable voltage, the Mn²⁺ ions forms Mn(OH)₃ and oxidises to MnO₂. Since gold particle in the electrode are nanoporous, MnO₂ forms structure like pattern in the electrode. However, the detailed chemistry of the formation of the honey-bee like structures
The colour changes from yellow to brownish black confirm the formation of MnO₂ 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 Mn²⁺ causing nanoparticle deposition in the form of structures.

\[
\text{Mn(CH}_3\text{COO)}_2 \rightarrow \text{Mn}^{2+} + (\text{CH}_3\text{COO})^- \\
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\
\text{Mn}^{2+} + 2OH^- \rightarrow \text{Mn(OH)}_2 \\
2 \text{Mn(OH)}_2 \rightarrow 2\text{MnO}_2 + 2H_2O
\]

XRD of the MnO₂ decorated in gold coated silicon wafer is presented in Fig. 3. The two sharp peaks confirm the presence of MnO₂ 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 MnO₂ decorated in gold coated silicon wafer at different magnifications. It clearly shows that grown MnO₂ 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 MnO₂ was decorated similar to honey-bee structure.

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

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
Electrodeposition of MnO₂ 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 F g⁻¹ which is very ideal value for high power applications.

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