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Synthesis and electrocatalytic properties of manganese dioxide for non-enzymatic hydrogen peroxide sensing

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ABSTRACT

Manganese dioxide nanoparticles were synthesized by chemical reduction route at different growth temperatures of 40 °C, 80 °C, 100 °C and were characterized using X-ray Diffraction (XRD), Field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), Cyclic Voltammetry (CV) and chronoamperometry (CA) analysis. FESEM results show that on increasing growth temperature the morphology changes from clusters into mixture of rods and flakes. XPS analysis reveals the formation of MnO_2. Then these particles were immobilized on Pt electrode. A platinum (Pt) electrode modified with low dimensional MnO_2 was investigated as a chronoamperometric (CA) sensor for hydrogen peroxide sensing (H_2O_2). The sample prepared at 100 °C shows good electrocatalytic ability for H_2O_2 sensing when compared with the samples prepared at 40 °C and 80 °C. At an operating potential of 0.3 V vs. Ag/AgCl catalytic oxidation of the analyte is measured for chronoamperometric (CA) monitoring. The CA signals are linearly proportional to the concentration of H_2O_2. It is also found that the morphology of the nanostructure plays a vital role in the detection of H_2O_2.

1. Introduction

Hydrogen peroxide is a very important intermediate in environmental and biological reactions. The monitoring of H_2O_2 with reliable, rapid and economical method is the greatest significance for numerous processes such as calorimetric, and chemiluminesence [1,2]. Various metal oxide particles such as iron oxide, lead oxide, ruthenium oxide,and cobalt oxide have been successfully used for immobilization of enzymes and proteins in the fabrication of H_2O_2 sensor [2,3]. However, there are certain inevitable drawbacks for these enzymatic sensors such as a complex preparation process, time consuming and uneven film coating that are not in close contact with electrodes that may easily shed and are not robust [4,5]. Among all the metal oxide, manganese oxide (MnO_2) is the purest form as well as its combination with other catalysts has been used for different catalytic reactions [6]. MnO_2 are promising low cost material and effective catalyst for the redox reaction in biosensing as compared with other expensive noble metals [7]. Generally crystal structures of MnO_2 have infinite channels with different dimensions and this allows creating more adsorption sites on that surface as compared with other metal oxides [8]. Nano MnO_2 has some unique properties such as ordered pore channels,

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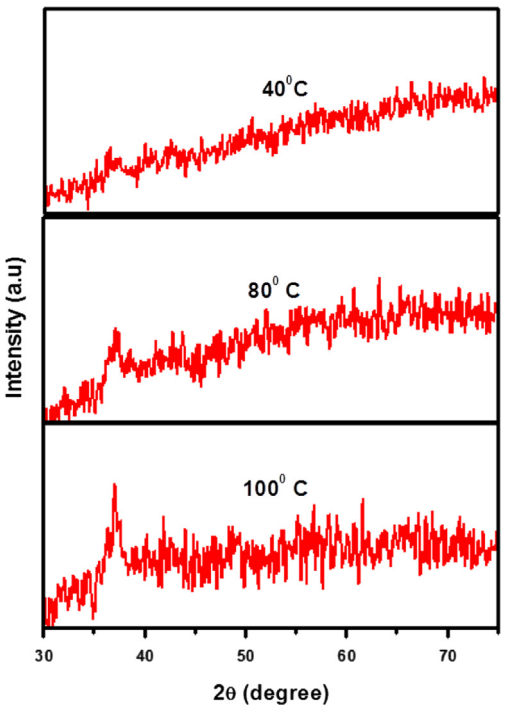

Fig. 1. XRD pattern of MnO_2 nanoparticles prepared at 40 °C, 80 °C, 100 °C.

high surface area, narrow pore size distribution, and good electrical conductivity as compared with the bulk MnO_2 [4]. Therefore, it has attracted special attention due to its distinctive properties and wide applications in catalysis, ion exchange, biosensors, and energy storage. Among the several analytical techniques, electro analytical technique is the suitable one for the detection of H_2O_2 due to their high sensitivity, selectivity, low cost, and operational simplicity [9]. A film of MnO_2 deposited on glassy carbon electrode (GCE), is effective for the electro catalytic oxidation of H_2O_2 and hydrazine compounds. In alkaline medium MnO_2 react with H_2O_2 to form O_2 and H_2O while it is reduced to the lower oxidation state at the same time [10]. Direct electrochemical oxidation of hydrogen peroxide on platinum electrode, yield detection limit of 10^{-6} M [3]. But the direct redox reaction at a bare electrode is not suitable for analytical applications. Also, this requires high positive potentials and this may cause many side reactions. Only few reports are available for chronoamperometric sensing using MnO_2 nanoparticles under static condition. In this work, we mainly focused on non-enzymatic reaction with an effective catalyst. MnO_2 nanoparticles were synthesized using formaldehyde as a reducing agent to obtain different morphology by low temperature reduction approach. This method is one step, simple and cost effective as compared with other methods. It is also found that the morphology of nanostructures changes the sensing capability of MnO_2 nanoparticles. Electrochemical behavior of MnO_2 modified

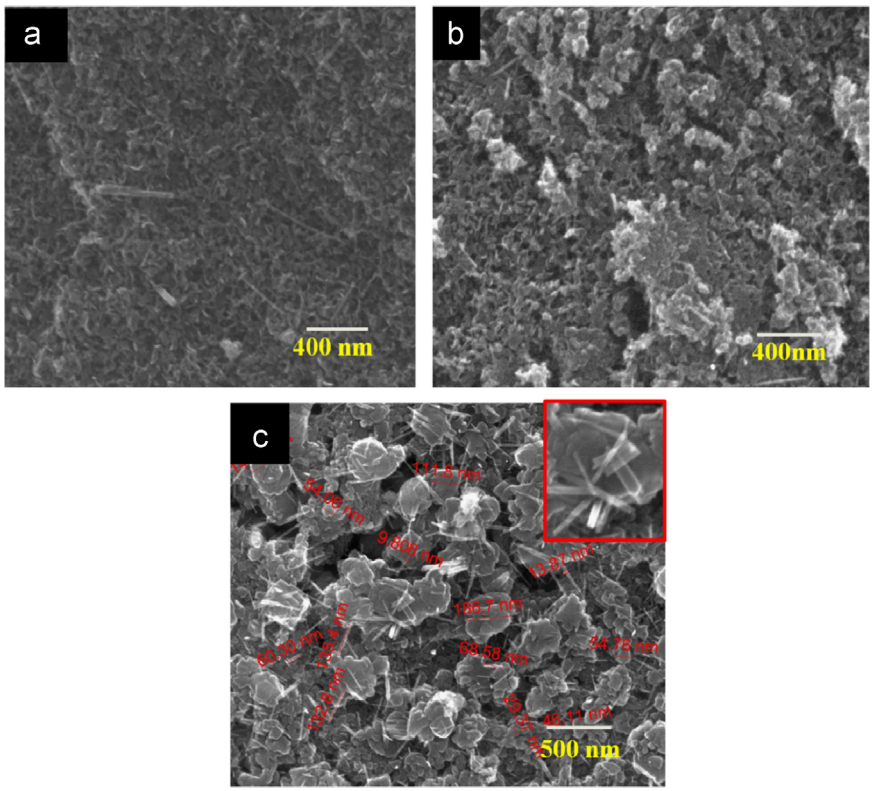

Fig. 2. Field emission scanning electron microscope (FESEM) image of pure MnO_2 particles prepared at (a) 40 °C (b) 80 °C (c) 100 °C. And inset of figure (c) mixture of nanorods and flakes.