Evaluation of Li-electroactivity of MnO2 nanoparticles with enzyme-like properties

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1. Introduction

Most of the identified enzymes are proteins that are commonly introduced as catalysts of chemical reactions in biological environments (i.e., biocatalysts). The key feature of these biocatalysts is their high catalytic efficiency and substrate specificity which make them suitable for playing a specific role in biochemistry. Among different types of enzymes, peroxidase enzymes, especially horseradish peroxidase (HRP), are attractive enzymes from both industrial and clinical points of view. In the real world, the practical application of peroxidase enzyme in industrial reactions as the biocatalyst is an interesting field. Up to now, several researches on these enzymes have been carried out to provide useful information about the enzyme structure, and its functional groups, reaction pathways, and active sites [1-15]. Regarding the peroxidase enzymes, the enzyme-specific substrate is hydrogen peroxide (HP) while their function is catalyzing the oxidation of a hydrogen-donating substrate (for example, benzidine). More precisely, hydrogen peroxide is the initiator of the peroxidase-mediated reactions [16]. Oxidation of a wide range of organic compounds (substrates) including aromatic amines, phenols, and their mixtures can be initiated in the presence of hydrogen peroxide or other hydroperoxides and HRP as enzymes. Many chromogenic substrates have been defined as secondary substrates of horseradish peroxidase due to its low selectivity to electron-donating compounds. These chromogenic substrates are called chromogenic electron donors because these compounds show a distinct color change when oxidized by hydrogen peroxide in the presence of the peroxidase enzyme. It is noteworthy that peroxidase and other natural enzymes show some of the following serious disadvantages including: (1) They are sensitive to environmental changes such as pH and temperature changes and are easily denatured. (2) They are digested by protease enzymes. (3) Their preparation and purification are complicated and expensive [16-20]. Fixing these disadvantages is possible through the development of some stable artificial enzymes with high catalytic ability. In this regard, nanotechnology has opened the doors for the development of new enzyme-mimetic materials [21]. In fact, the fast development of nanoscience and material chemistry has increased interest in researching new and innovative synthesis methods to produce new nanomaterials with unique high biocompatibility [22], unique optical properties [23-25], and catalytic activity [26, 27]. In 2007, it was explored that Fe3O4 magnetic nanoparticles (NPs) exhibited significant peroxidase-like activity [28]. This research opened the door for a new branch of nanochemistry called “nanozyme chemistry”. Nanozyme chemistry is -consists of design, synthesis, modification, biochemical characterization, structural characterization, and application of nanoscale artificial enzymes as well as evaluation of the mechanism of nanozyme-based systems [3-21]. Among different areas of nanozyme chemistry, the main researches of nanozyme chemistry are regarding sensing and detection aims, for instance, during the last years, a wide variety of nanozyme-based colorimetric sensors have been developed for the detection and quantification of a variety of analytes for instance, tryptophan [29], glutathione (GSH) [30], dopamine [31], tetracycline [32], metal cations [33], glucose [34], H2O2 [35], explosives [36], and cysteine [37] as well as after first report of COVID-19 in 2019 [38, 39], the nanozyme-based sensing methods for COVID-19 detection were also reported [40]. Although the nanozyme field is focused on sensing and detection, recently, Mu et al. utilized
heme-based nanozymes as redox materials for Li-O2 batteries [41]. This investigation can open a new door in nanozyme chemistry regarding nanozyme application in the energy storage field. In this study, MnO2 nanoparticles with enzyme-like properties were synthesized and then their Li-electroactivity was evaluated. The as-prepared materials showed high Li-electroactivity which makes these nanozymes for applying as cathode materials for Li-ion batteries.

2. Experimental

2.1. Synthesis of MnO2 nanozymes

The MnO2 nanoparticles or more precisely MnO2 nanozymes were synthesized using an one-pot simple, operator-friendly, green, and fast method (the synthesis time was only 5 min). To do this, 450 mg of KMnO4 was introduced into 45 mL water, followed by the addition of 0.5 mL hydrogen peroxide (30%) and 1.0 mL hydrazinium hydroxide (20%). Afterward, the synthesis mixture was stirred for about 5.0 min to complete the synthesis of the MnO2 nanozymes. The nanozymes were then collected by centrifuge, washed with water (5 times), and then dried at ambient conditions.

2.2. Li-electroactivity studies and electrochemical evaluations

Regarding the electrochemical evaluation of the as-synthesized MnO2 nanozymes, onto a copper foil, MnO2 nanozymes, Kynar 2801 binder, and Super P carbon black with a mass ratio of 60:20:20 were cast to prepare the positive electrode films. The Li-metal foil was used as the negative electrode. The electrolyte was obtained by dissolving LiPF6 in a mixed solvent (1:1 v/v) of dimethyl carbonate and ethylene carbonate. Thereafter, the assembled Swagelok-type cell was prepared using positive and negative electrodes and an electrolyte-saturated separator film. This cell was used for galvanostatic cyclic voltammetry at a scan rate of 0.3 mV s⁻¹.

3. Results and discussion

3.1. Investigation of nanozymatic behavior of MnO2 nanozymes

The enzyme-like behavior of the as-synthesized nanozymes was evaluated by the oxidation of 3,3’-diaminobezedine by hydrogen peroxide in the presence of the peroxidase-like MnO2 nanoparticles as the biocatalyst as the standard method for nanozyme activity measurements [42-45]. The oxidation process was then probed by recording the UV-Vis spectrum of the colored product (Figure 2), revealing that in the presence of 3,3’-diaminobezedine, the peroxidase-like MnO2 nanozymes can significantly catalyze the oxidation process of 3,3’-diaminobezedine with hydrogen peroxide to form its corresponding brown-colored indamine polymer which shows a characteristic absorbance at 460 nm. The possible pathway of reaction is represented in Figure 2B, as shown in this figure, during the 3,3’-diaminobezedine oxidation, the peroxidase-like MnO2 nanozymes interacted with hydrogen peroxide molecules and converted them to active hydroxyl radicals which these active radicals, then, react with 3,3’-diaminobezedine molecules to produce an indamine polymer via an oxidative polymerization process, as previously reported in the literature [46-58].
3.2. Application of as-prepared enzyme-like MnO$_2$ nanoparticles as cathode materials for Li-ion batteries

Li-electroactivity measurements for the as-prepared MnO$_2$ nanozymes were performed by cyclic voltammetry to quantify the oxidation/reduction peaks of Mn$^{4+}$-Mn$^{3+}$, against a Li-based anode electrode. In this regard, the cyclic voltammograms of the cathode of Li-ion battery prepared by MnO$_2$ nanozymes as cathode material were recorded for three successive runs in a potential window of 1.5-4.6 V vs. Li electrode at a scan rate of 0.3 mV s$^{-1}$. The results are shown in Figure 3 where it can be seen that the MnO$_2$ nanozymes show a reversible redox behavior in the developed system. The oxidation peak was observed at 3.2 V and the reduction peak was found to be positioned at 2.74 V. According to the results of these experiments, it can be concluded that the electrochemical reactions in the charge/discharge process of the as-prepared nanozymes, when they used as cathode materials for the Li-ion batteries, consisted of lithiation of MnO$_2$ nanozymes in charging step and de-lithiation of MnO$_2$ nanozymes in discharging process [59, 60]. The reversible redox behavior of MnO$_2$ nanozymes in Li-ion batteries pointed out that the MnO$_2$ nanozymes as cathode materials can receive the Li(I) ions and then give it back to the anode (i.e., lithiation/de-lithiation process can be proceed). Therefore, it is consultable that the MnO$_2$ nanozymes can respond well to the charge–discharge tests of Li-ion batteries.
Hence, the charge-discharge tests for the MnO$_2$ nanozymes cathodes were initially performed at slow charge/discharge rates. The charge-discharge tests were carried out at high charge/discharge rates (1000 mAg$^{-1}$). The charge-discharge performance of the as-prepared MnO$_2$ nanozymes as cathode of Li-ion batteries at 1000 mAg$^{-1}$ is shown in Figure 4, revealing that the capacity of the MnO$_2$ nanozymes was not changed at high rates and the as-prepared nanozymes show excellent stability at 1000 mAg$^{-1}$ and can provide stable cycling in both slow and higher rates. It is notable that the charge-discharge tests revealed capacities as high as 164.9 mAhg$^{-1}$ and 46 mAhg$^{-1}$ at 30 mAg$^{-1}$ and 1000 mAg$^{-1}$, in turn, for the as-prepared MnO$_2$ nanozymes cathodes. It is observed that the capacity was decreased by increasing the rate which exhibits a diffusion-controlled kinetic process (i.e., controlled by the diffusion of Li$^+$), as reported [61]. Besides, as previously reported in the literature, at slow rates, the mechanism of charge storage involves the intercalation which is the proven charge/discharge mechanism of metal oxides. In contrast, at higher rates, ions of lithium (Li(II)) may intercalate not so deep into the MnO$_2$ nanozymes and provide a surface-closed intercalation at faster charge/discharge rates.

Figure 2: Cyclic voltammograms of the cathode of Li-ion battery prepared by MnO$_2$ nanozymes as cathode material.
Figure 3: Charge-discharge performance of as-prepared MnO$_2$ nanozymes as the cathode of Li-ion batteries at 1000 mAg$^{-1}$ rate.

4. Conclusions
In this study, MnO$_2$ nanoparticles with enzyme-like properties were synthesized and then utilized as cathode materials for constructing cathode electrode of Li-ion batteries. The as-prepared materials showed high Li-electroactivity which makes these nanozymes for applying as cathode materials for Li-ion batteries. To evaluate the redox behavior of the constructed cathode (Mn$^{3+}$/Mn$^{4+}$) against Li anode, the cyclic voltammetry was used. The results revealed that the enzyme-like manganese dioxide nanoparticles as cathode materials can receive the Li(I) ions and then give it back to the anode. The charge-discharge tests were performed for several successive operational cycles. The results showed that the capacity of enzyme-like manganese dioxide nanoparticles was found to be about 46 mAhg$^{-1}$ at 1000 mAg$^{-1}$.

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Conflict of interest
There is no conflict of interest.

5. References
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