MnO$_2$ and TiO$_2$ based Nanocomposites for Macroscopic and Individual Nanodevices in Sensing, Energy Storage and Photocatalysis Applications

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Abstract. The present nanotechnological trend is promising for the devices based on nanocomposites. We focus on three application areas, biosensing, energy storage and photocatalyst. A newer frontier trend is related to individual nano-devices based on individual nano-objects giving the exciting advantages. In the present work, the MnO$_2$ and TiO$_2$ nanocomposites were developed by simple and economical means. The MnO$_2$ and Cu/MnO$_2$ were potentiodynamically deposited on stainless steel sheets and ITO coated glass substrates for energy storage and sensing applications. The electrochemically anodized TiO$_2$ nanotubes and Ag nanoparticles decorated TiO$_2$ nanotubes were fabricated on Ti base for photocatalysis. The MnO$_2$ film electrode, Cu/MnO$_2$ film electrode, Ag/TiO$_2$ nanotubes were preliminarily demonstrated as macroscopic devices in capacitors, glucose sensors and photocatalysis water treatments. The specific capacitance of MnO$_2$ film electrode is as high as 135 Fg$^{-1}$and the Cu/MnO$_2$ sensor has the low detection limit of 0.986. For the water purification, the photodegradation efficiency of Ag/TiO$_2$ nanotubes is as high as 95% under UV irradiation.

1. Introduction

Nanostructured materials have gained great attention due to their favourable and enhanced physical and chemical properties which are originated from the high surface area and improved reactive sites. Among oxides, the manganese oxide (MnO$_2$) is an interesting material having a wide variety of structures with large surface area. These diverse structures and associated chemical properties owe not only to their fundamental scientific significance but also the potential applications in cation-exchange, adsorbents, sensor, supercapacitors, battery and catalysis [1-4]. Other than MnO$_2$, the nano-TiO$_2$ is also very well-known and possesses unique chemical and physical properties. The photocatalysis is one of its promising applications since they have wide bandgap, chemically stability, nontoxicity and more importantly, the ability to break molecular bonds leading to photodegradation of organic pollutants under ultraviolet radiation [5-6]. Among the various shapes of nanostructures, the high aspect ratio nanostructures like nanotubes are more effective due to their higher surface area (both inside and outside areas of tubes), more light harvesting due to scattering within the tubes and high interfacial charge transfer rate. Adding-on these, decorating the metal (Ag or Au) nanoparticles on top of the base nanostructures (TiO$_2$) would modulate the sub-band states influencing the optical and electrical properties of composite. Moreover, it would tune the absorption feature of TiO$_2$ composite exploiting the phenomenon of surface plasmon resonance (SPR).

Nowadays, in the fields of the devices for biosensing, energy storage and photocatalyst based on nanocomposites, a new promising nanotechnological trend had appeared. This new frontier trend is
related to individual nano-devices based on individual nano-objects, like nano-particles, nanowires, nanotubes, nanorods and so on [7-20]. These new bio-nanosensors as individual nanodevices based on single nano-objects have exciting advantage compared to the current biosensors [7-10]. Bio-nanosensors based on individual nano-objects can reach maximal high selectivity and sensitivity up to 1 femtoMolar (fM) [10] and up to single virus detection [8] and single molecule. Such extreme sensitive and selectivity of the bio-nanosensors that allow recognise specific viruses and molecules for medicine, ecology and life science is based on single nanowire as the main building block [10].

At present, the new trend related to development of individual nano-devices based on single nano-objects is growing up also in the devices for energy storage [11 - 21]. Such devices have many advantages compared to traditional energy storage devices. In [15], the batteries produced from individual V$_2$O$_5$ nanowires with morphology changing from micro- to nanocrystalline were studied. During the study of the evolution of the cycling ability of those batteries it was shown that the capacity and cycling stability of nano-samples are obviously superior to that of micro-samples. The trend of improving of the functional properties for devices with nanostructure in comparison with the devices with microstructure exists in many research areas [7-21]. That is why together with the energy storage devices based on nanocomposite with MnO$_2$ and TiO$_2$ nanoparticles it is very interesting to study individual nanodevices based on single nano-objects - like nanoparticle and nanowires [11-21]. Recently first such nanodevices were created and discussed in [11-21].

First study of the correlation between the functional properties and parameters of nanoscale-objects used for the creation of the energy storage devices was shown in 1999 in [11]. Single nano-devices have been exploited to demonstrate a powerful diagnostic tool, which allow us to study the direct correlation of the electrochemical property of the same nanoscale-objects [11]. This fruitful idea was further elaborated in [12, 13]. Until now the fundamental mechanisms of capacity damping and the relationship between electrical transport, structure and electrochemistry of different electrode materials, also nanowire electrode material stays unknown. This missing of knowledge is especially critical for the creation and optimization of high-energy density battery electrode materials. In [14], the creation and study of the smallest all-solid electrical energy storage devices based on single nanowire was reported. The single nanowire electrode devices designed as a unique platform for in situ probing the intrinsic reason for electrode capacity fading in Li ion-based energy storage devices. A single nanowire working electrode in this device used single V$_2$O$_5$ nanowire and single Si/a-Si-core/shell nanowire. Electrical transport of the single nanowire was recorded in situ to detect the evolution of the nanowire during charging and discharging. In [14], it is shown that single nanowires device are very effective in providing insights on the mechanism for electrode capacity fading which traditional battery test strategies cannot offer. The investigation of the transport in single nano-objects devices can be combined with the electrode electrochemical performance study and this gives possibility to find out the relationship between electrode material composition, structure, transport properties, charge/discharge status, and electrochemical performance. This can be studied at a single nanowire level to reveal the intrinsic reason for fast capacity fading. The work shows not only the concrete processes of intercalation, charge/discharged, conductance changes and so on. But the work also shows that study of single nanowire devices for energy storage provides unique direct relationship between electrical transport, structure, structure change and electrochemical properties. The insight obtained from this study could help understand the intrinsic mechanism of battery capacity fading. This shows that single nanowire device will be a promising and straightforward way for nanoscale battery diagnosis and unique platform that gives possibility to push the fundamental limits of the nanowire materials for energy storage applications.

In [16] it is reported that the development and study of the smallest all-solid electrical energy storage devices is based on single nanowire. The nanoscale electrochemical device was done inside a transmission electron microscope and consists of a single tin dioxide (SnO$_2$) nanowire anode, an ionic liquid electrolyte, and a bulk lithium cobalt dioxide (LiCoO$_2$) cathode. Using this device in situ observation of the lithiation of the SnO$_2$ nanowire during electrochemical charging was carried out. The observations provide important mechanic insight for the design of advanced batteries. All these
works show that study of single nanowire devices for energy storage is very important for understanding the mechanisms of the main functional properties of energy storage devices. That is why for the successful developments of the energy storage devices research and for advance further application and innovation in energy storage devices industry the fundamental study of individual nanodevices based on individual nanoparticles is vital. One of the most important parameters of energy storage devices is light weight and small size. Thus, the miniaturization is one of the most important trends in the development of energy storage device. Extreme miniaturization can be also reached using single nanowires nano-devices. In [18] it was reported the creation and study of the hybrid electrochemical energy storage devices that combine the advantages of both battery and supercapacitors based on parallel array of nanowire. The device provides high energy and power density and shows reversible areal capacity of ~3 μAh/cm² at a current rate of 0.03 mA/cm². In [18] it is shown the ultimate miniaturization possibility for energy storage devices where all essential components can be engineered on a single nanowire. The best possibility to create nanodevices based on single nanowires is mechanical bottom up nanomanipulation and nanoassembling using shape memory alloy nanogripper [19-21].

In the present work, we developed the MnO₂ and TiO₂ nanotubes (NTs) by electrodeposition and electrochemical anodization respectively. In addition, the composite materials, namely, Cu/MnO₂ and AgNPs/TiO₂NTs were also developed. The electrochemical deposition method is used in this work since it can provide a precise control of film thickness, morphology, stoichiometry by means of current or voltage modulation and chemical composition of electrolyte solution, in the case of NTs, electrochemical anodization enables us to easily control the diameter and length of NTs and form the vertically aligned NTs. As a preliminary study, the MnO₂ film electrode, Cu/MnO₂ film electrode, Ag/TiO₂ nanotubes were demonstrated as macroscopic devices in capacitors, glucose sensors and photocatalysis water treatments.

2. Development of MnO₂ and TiO₂ based Nanocomposites

2.1 Electrodeposited MnO₂ on Steel Sheet

The flexible stainless steel sheet (SSS) of grade 304 was cut into the size of 4 cm x 4 cm and used as substrate material for electrodeposition. Firstly, the substrates were polished with emery-paper and then washed with detergent. Secondly, they were then cleaned in ultrasonic bath with 0.1 M NaOH aqueous solution, 0.1M oxalic acid aqueous solution, acetone and distilled water in order for 15 min each. Finally, it was dried in air. The MnO₂ films were potentiodynamically deposited on the cleaned flexible SSS using the solution of 0.1 M of potassium permanganate (KMnO₄) and 0.1 M of potassium nitrate (KNO₃) using a electrochemical workstation (CS350). In potentiodynamic mode, the applied potential varied from 0.5 V to 1.5 V and the deposition rate varied from 25 mVs⁻¹ to 200 mVs⁻¹. A three-electrode electrochemical cell was used where the flexible stainless steel electrode as the working electrode, graphite as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The as-deposited MnO₂ film was annealed at 350 °C for 3 hours forming the black colored MnO₂ films. The surface morphology of MnO₂ films was investigated by using Atomic Force Microscope (Nanosurf Naio AFM, Switzerland). Figure 1 depicts the atomic force micrographs (AFM images) of MnO₂ films on SSS which are potentiodynamically deposited at the rate ranging from 25 mVs⁻¹ to 200 mVs⁻¹. The MnO₂ films display the microporous structures consisting of fine nanosheets.

2.2 Electrodeposited Cu/MnO₂ on Indium-Tin-Oxide Glass

The multilayer Cu/MnO₂ films were prepared by the layer-by-layer (LBL) technique as follows. Solid substrates of indium-doped tin oxide (ITO)-coated glass with the area of 1cm² were cleaned by ultrasonication in detergents, acetone, ethanol and isopropyl alcohol (IPA) subsequently and each cleaning process took 10 minutes. Potassium permanganate (KMnO₄) and copper (II) sulphate (CuSO₄) were separately prepared in 50 ml of deionized water and stirred for 7 minutes. MnO₂ were electrodeposited on the ITO in three-electrode system by potentiodynamic method from 6 mM
KMnO$_4$ solution in the potential window of 0.3 V to -0.5 V at the scan rate of 6 mVs$^{-1}$ for two cycles. The deposition was conducted at room temperature in three-electrode cell in which the ITO glass, saturated calomel electrode (SCE) and Pt electrode were used as the working, reference and counter electrode respectively. The as deposited MnO$_2$ samples were rinsed in deionized water and dried at 100°C for 10 minutes. Following this, the Cu nanoparticles were deposited on the MnO$_2$/ITO substrate in 0.1M CuSO$_4$ solution for 5 cycles in the range of 0.6 V to -0.6 V at the scan rate of 6 mVs$^{-1}$. The composite film was rinsed in deionized water and dried for 10 minutes. The atomic force micrographs were acquired by using Nanosurf Naio AFM. Figure 2 displays the AFM images of MnO$_2$, Cu and (c) Cu/MnO$_2$ films on ITO which are electrodeposited with the rate of 6 mVs$^{-1}$. The MnO$_2$ film was well-deposited and Cu particles are fully covered on underlying MnO$_2$ layer.

Figure 1 AFM images of MnO$_2$ films potentiodynamically deposited at the rate of (a) 25 mVs$^{-1}$, (b) 50 mVs$^{-1}$, (c) 100 mVs$^{-1}$ and (d) 200 mVs$^{-1}$.

Figure 2 AFM images of (a) MnO$_2$, (b) Cu and (c) Cu/MnO$_2$ electrodes electrodeposited with the rate of 6 mVs$^{-1}$.

2.3 Electrochemically Anodized TiO$_2$ Nanotube Arrays coated with Ag Nanoparticles

Titanium foil with an area of 2.5 cm$^2$ and thickness of 0.02 cm (99.7% purity) were used as starting material in order to obtain the titanium oxide nanotube arrays (TiO$_2$NTs). TiO$_2$ nanotube arrays on titanium foil were fabricated by an electrochemical anodization method. Before anodization, the samples were dipped in acetone, ethanol and isopropanol for 10 min each using ultrasonic cleaner. The foils were subsequently rinsed with distilled water and dried under air blow. The anodization process was carried out with magnetic agitation at room temperature in a two-electrode system. The Ti foil and platinum rod were connected to the positive and negative terminal of a dc power supply respectively. The distance between two electrodes was fixed at approximately 2 cm. The electrolyte for anodization was a mixture of ethylene glycol in water (90 wt%:10 wt%) with 0.5 wt% of ammonium fluoride. The anodization voltage was 50 V and the duration of anodization was 3 hours. When the anodization process was completed, the samples were removed from the electrolyte, then rinsed with distilled water and dried under air blow. And the samples were subsequently annealed in a muffle furnace at 500 °C for 3 hours for crystallization. Silver nanoparticles (AgNPs) were loaded on...
the surface of TiO2NTs by photodeposition method. The TiO2NT samples were soaked into silver nitrate aqueous solutions with three different concentrations (0.1M, 0.5M and 1M) for 2 hours. The samples were illuminated under the UV light (24 W) for 2 hours. Through illumination, silver ions (Ag+) which had been adsorbed on the surface of TiO2 are reduced by electrons and then transformed to the silver nanoparticles (Ag0).

The morphology and size of TiO2 nanotube arrays was investigated by using scanning electron microscopy (SEM). Figure 3 shows the scanning electron micrographs of TiO2 nanotube arrays. It can be seen that TiO2 nanotube arrays are well-ordered. The inner diameter of TiO2 nanotubes is 90 - 120 nm and the length of TiO2NTs is around 2 μm. Figure 4 shows the scanning electron micrographs of TiO2NTs/AgNPs (0.1 M), TiO2NTs/AgNPs (0.5 M) and TiO2NTs/AgNPs (1 M). At the silver content of 0.1 and 0.5 M, Ag nanoparticles are fairly loaded on surface of TiO2NTs. When the silver content is too high (1 M), there is silver nanoparticles agglomeration which blocks the tube opening. It is likely that an optimum silver content is 0.1-0.5 M. Size analysis showed that Ag nanoparticles loaded on the surface of TiO2NTs were in small size of 10-20 nm.

3. Application of MnO2 and TiO2 based Nanocomposites in the macroscopic devices

3.1 MnO2 film electrode in capacitor (Energy storage)

The electrochemical properties of MnO2 film as a working electrode along with graphite as counter electrode and saturated calomel electrode (SCE) as the reference electrode in the three-electrode cell were tested for energy storage capacitor application. The cyclic voltammograms (CV) of MnO2 film.
Specific capacitance of 135 F\text{g}^{-1} for lowest scan rate of 5 mVs\textsuperscript{-1}.

![Figure 5 Cyclic voltammograms of MnO\textsubscript{2} film electrodes prepared at the deposition rate (a) 25 mVs\textsuperscript{-1}, (b) 50 mVs\textsuperscript{-1}, (c) 100 mVs\textsuperscript{-1} and (d) 200 mVs\textsuperscript{-1}. For each sample, the CV’s are recorded at different scan rates ranging from 5 mVs\textsuperscript{-1} to 100 mVs\textsuperscript{-1}.](image)

Figure 5 Plots of specific capacitance versus scan rate for MnO\textsubscript{2} electrode prepared at different deposition rates (25, 50, 100 and 200 mVs\textsuperscript{-1}).

3.2 Cu/MnO\textsubscript{2} film electrode as glucose sensor (Biosensing)

The present part describes an application of Cu/MnO\textsubscript{2} film electrode as glucose sensor (Biosensing). Sodium hydroxide (NaOH) and D-glucose were used as electrolytes in these electrochemical experiments. All the experiments were done in three-electrode cell in which the saturated calomel electrode (SCE) and Pt electrode were used as the reference and counter electrodes respectively. The electrocatalytic effect of Cu/MnO\textsubscript{2} nanocomposite was studied in various concentration of glucose (0.25, 0.5, 0.75 and 1 mM) as shown in Figure 7(a). It is obviously seen that the oxidation peak
currents went up with the increasing glucose concentration. Therefore, the increased peak currents of glucose oxidation explain that Cu/MnO$_2$ nanocomposite has high catalytic capability for glucose oxidation. Figure 7(b) illustrates the current density versus glucose concentration curve. It indicates that the oxidation currents linearly increase with the glucose concentration in the linear range of 0.25 mM-1mM. The calculated values of correlation coefficient, sensitivity, and lower detection limit are 0.9840, 0.67 mAmM$^{-1}$ and 0.25 mM respectively. This high sensitivity might be due to the high electrocatalytic active region on the nanocomposite modified electrode.

Figure 7 (a) Cyclic voltammograms of Cu/MnO$_2$/ITO in 50 mM NaOH with increasing glucose concentration (from 0.25 to 1.25 mM) at scan rate of 10mVs$^{-1}$ and (b) Current density versus glucose concentration for Cu/MnO$_2$ composite electrode.

3.3 TiO$_2$NTs/AgNPs as Plasmonic photocatalyst (Photocatalysis for water purification)

For water purification, the photocatalytic activities of TiO$_2$ nanotubes and TiO$_2$NTs/AgNPs (0.5M) have been tested by the photodegradation of methylene blue (MB) aqueous solution with different pH (1, 3, 5 and 7). The degradation efficiencies of TiO$_2$NTs and TiO$_2$NT/AgNPs (0.5M) in MB solutions with different pH are shown in Figure 8 (a) and (b). It can be observed that, the photodegradation efficiencies of TiO$_2$NTs and TiO$_2$NTs/AgNPs (0.5M) were higher in MB solution with lower pH. A similar trend has been followed for TiO$_2$NTs with and without AgNPs. The lower the pH value, the stronger adsorption of negatively charged MB on the TiO$_2$ surface is as a result of the attraction of the positively charged TiO$_2$ with the negatively charged MB. The adsorption of MB onto TiO$_2$NTs and TiO$_2$NTs/AgNPs (0.5M) photocatalysts is stronger at lower pH of 1, resulting in the higher photodegradation efficiencies. At a 5 hr UV illumination, the photodegradation efficiency is as high as 80% and 95% for TiO$_2$NTs and TiO$_2$NTs/AgNPs (0.5M) respectively.

Figure 8 Photodegradation efficiencies of (a) TiO2NTs and (b) TiO2NTs/AgNPs (0.5 M) in MB solutions of different pH.

4. Summary

In the present work, the MnO$_2$ and TiO$_2$ nanocomposites were developed by simple and economical means. The MnO$_2$ and Cu/MnO$_2$ were potentiodynamically deposited on stainless steel sheets and ITO coated glass substrates for energy storage and sensing applications. The
electrochemically anodized TiO$_2$ nanotubes and Ag nanoparticles decorated TiO$_2$ nanotubes were fabricated on Ti base for photocatalysis. The MnO$_2$ film electrode, Cu/MnO$_2$ film electrode, Ag/TiO$_2$ nanotubes were preliminarily demonstrated as macroscopic devices in capacitors, glucose sensors and photocatalysis water treatments. At present, the new trend related to development of individual nano-devices based on single nano-objects is growing up in the devices for the said applications. The nanosensors based on individual nano-objects can reach maximal high selectivity and sensitivity up to 1 femtoMolar (fM). The exploitation of individual MnO$_2$ and TiO$_2$ nano-objects in microscopic nanodevices are under way.

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