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Research Article

Manganese Dioxide Nanowires of Tunable Dimensions Synthesized via a Facile Hydrothermal Route

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Manganese dioxide (MnO_2) nanowires of tunable dimensions were successfully synthesized via the facile water-bathing hydrothermal route. Homogeneous solution mixtures of $KMnO_4$ and $MnSO_4$ of varying compositions were being aged in a thermostated water bath under controlled conditions. The dimensional aspect ratios of MnO_2 nanowires formed were readily modulated by varying synthesis parameters such as the initial concentration of chemical precursors, reaction temperature, and aging duration. At fixed initial precursor concentrations, the mean diameter of MnO_2 nanowires decreased slightly from 57 nm to 53 nm with increased reaction temperature from 60°C to 90°C. The mean diameter of MnO_2 nanowires decreased linearly within the range of 104 nm and 35 nm as the initial concentration of both precursors was increased in turn within the range of 10 mmol and 40 mmol at fixed aging temperature and duration. Upon aging for 2 to 24 hours at 80°C, the mean diameter and length of MnO_2 nanowires were observed to vary within the range of 33–55 nm and 0.69–2.68 μm, respectively, which corresponded to the dimensional aspect ratio range of 21 to 49. Henceforth, MnO_2 nanowires of tunable dimensions could be synthesized through optimally controlled synthesis parameters.

1. Introduction

Nanostructured manganese dioxide (MnO_2) has attracted increasing attention as a promising electrode material for the fabrication of electrochemical capacitor due to its abundance, environmentally friendly nature, and lower cost [1–3]. MnO_2 nanowires are expected to exhibit significantly different optical, electrical, and magnetic properties from their bulk 3D crystalline counterparts due to their small diameters, high specific surface area, and unique density of electronic states [4]. MnO_2 nanowires with mean diameter approximately 20 nm and BET specific surface area of 157 m^2/g [5] were synthesized by cathodic electrodeposition and postsynthesis heat treatment. MnO_2 nanowires prepared under hydrothermal condition in the presence of sodium carboxymethyl cellulose possessed mean diameter of 50–60 nm and mean length of around several micrometers [6]. MnO_2 thin films prepared from disordered nanowire networks using self-assembled method have been shown to exhibit substantially enhanced charge capacities [7]. Manganese dioxide nanowires with larger specific surface area were reported to exhibit high capacity and cycling stability as the electrode material of various electrochemical devices such as rechargeable lithium batteries and electrochemical capacitors [8, 9].

Herein, we have reported the facile synthesis of manganese dioxide nanowires with tunable dimensions via the water-bathing hydrothermal route. The effects of synthesis parameters such as reaction temperature, initial concentration of precursor chemicals, and aging duration on the formation, dimensions, and morphological characteristics of MnO_2 nanowires were investigated.

2. Experiment

2.1. Reagent and Apparatus. All chemicals used in this research were of analytical grade and were used as purchased without any further purification. Ultrapure water (~18.2 MΩ·cm, 25°C) was obtained from ELGA Ultrapure Water system (ELGA Ultra Genetic). Potassium permanganate ($KMnO_4$) and manganese sulfate monohydrate

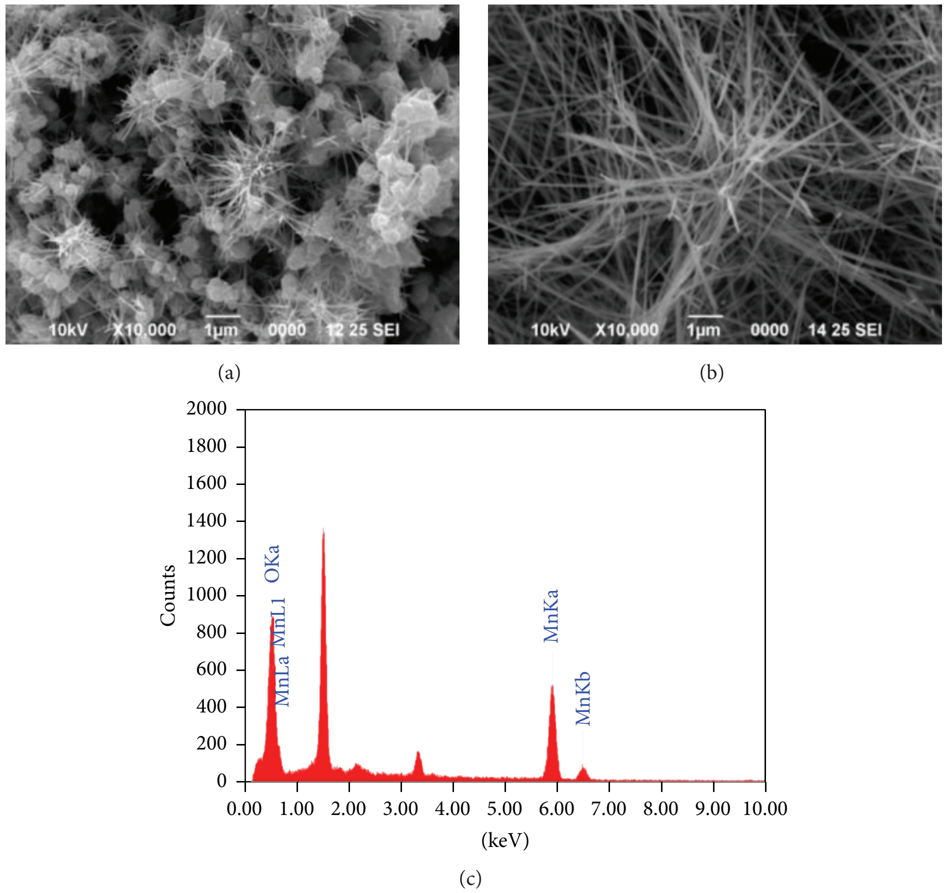

Figure 1: SEM micrographs of MnO_2 nanowires synthesized at reaction temperature of (a) 60°C, (b) 90°C, and (c) EDX spectrum of MnO_2 nanowires.

($MnSO_4 \cdot H_2O$) were purchased from Ajax Chemicals and MERCK, respectively.

2.2. Synthesis of Manganese Dioxide (MnO_2) Nanowires. The synthesis of MnO_2 nanowires was conducted based on the water-bathing hydrothermal route with some modification [10]. 20 mmol of $KMnO_4$ and 30 mmol of $MnSO_4 \cdot H_2O$ were dissolved in 160 mL deionized water and magnetically stirred for about 30 minutes to form a homogeneous solution mixture.

The resulting solution mixture was aged in a thermostated water bath at varying temperatures between 60°C and 90°C for aging durations of up to 24 hours. Upon completion of the desired aging duration, nanowires formed were collected by centrifugation after the solution mixture was allowed to cool to room temperature naturally, washed with ultrapure water and absolute ethanol, and, finally, stored in isopropanol. The effects of synthesis parameters such as reaction temperature, aging duration, and initial concentration of chemical precursors on the dimensions and morphological characteristics of MnO_2 nanowires were investigated.

2.3. Characterization of Manganese Dioxide (MnO_2) Nanowires. Samples of MnO_2 nanowires were characterized using the Scanning Electron Microscope (SEM, JEOL Model JSM-6390LA), Transmission Electron Microscope (TEM, JEOL Model JEM-1230), and energy dispersive X-ray (EDX) spectroscopy.

3. Results and Discussion

3.1. Synthesis of Manganese Dioxide (MnO_2) Nanowires. Brown-black colored MnO_2 nanowires of flat and smooth surface morphology were synthesized at desired reaction temperatures and aging durations according to (1) [10, 11]:

$$3MnSO_4 \cdot H_2O + 2MnO_4^{-} \longrightarrow 5MnO_2 + 3SO_4^{2-} + 4H^{+} + H_2O \quad (1)$$

3.2. Effect of Reaction Temperature. The effect of reaction temperature on the morphological characteristics of manganese dioxide (MnO_2) nanowires is shown in Figure 1. Upon aging for 24 hours, samples consisting of mainly MnO_2 nanoparticles with sparsely and randomly distributed bundles of nanowires were obtained at 60°C, whereas samples with well-defined and fully transformed MnO_2 nanowires of uniform diameters were obtained at 90°C. Energy dispersive

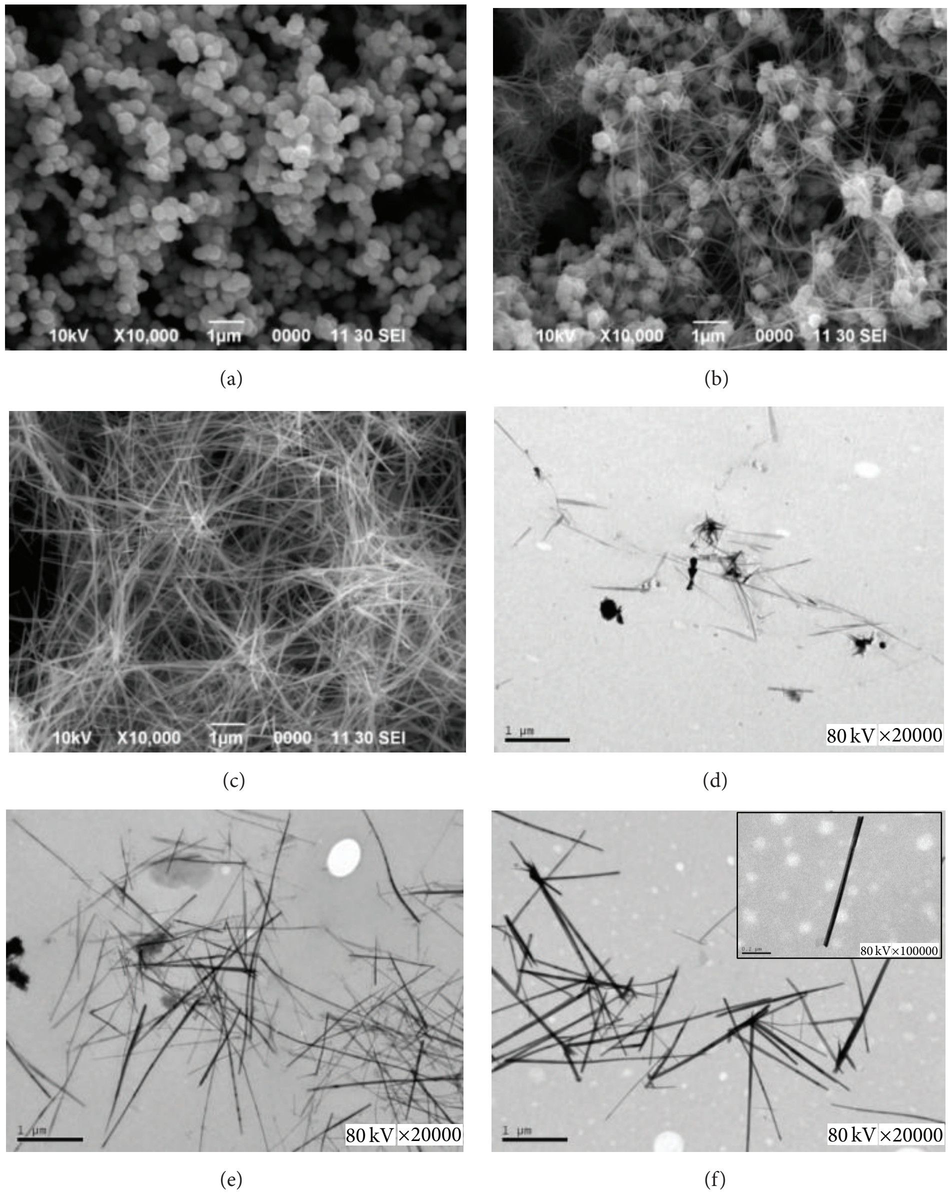

Figure 2: SEM and TEM micrographs of MnO_2 nanowires formed at different reaction durations: (a) and (d) 2 hr, (b) and (e) 6 hr, and (c) and (f) 24 hr. Inset in (f) shows a fully formed individual MnO_2 nanowire.

X-ray (EDX) analysis of MnO_2 nanowires revealed intense peaks which were associated with their elemental composition of manganese and oxygen (Figure 1(c)). These intense and sharp peaks were also indicative of the polycrystalline nature of MnO_2 nanowires formed.

3.3. Effect of Aging Duration. Figure 2 shows the effect of hydrothermal aging duration at 80°C on the morphology and dimensions of MnO_2 nanowires formed. Upon hydrothermal aging for 2 hours, the SEM micrograph showed the presence of MnO_2 nanoparticles only (Figure 2(a)). However, the TEM micrograph revealed a mixture of predominant MnO_2 nanoparticles (mean diameter of about 360 nm) and randomly scattered short nanowires (mean length of about 0.69 μm) (Figure 2(d)). Longer hydrothermal aging durations of 6 hours led to the formation of defined and individually separable nanowires of mean length ranging between 1.22 μm and 1.54 μm as well as sparsely scattered MnO_2 nanoparticles (Figures 2(b) and 2(e)).

Upon prolonged hydrothermal aging duration of 24 hours, fully transformed and well-defined uniform MnO_2 nanowires of mean length about 2.68 μm were obtained (Figure 2(c)). In this case, there was no nanoparticulate MnO_2 visibly observable (Figure 2(f)), indicating the complete transformation of MnO_2 nanoparticles into nanowires. The mechanisms for transformation of MnO_2 nanoparticles into nanowires under controlled hydrothermal conditions had been proposed by Guan et al. (2014) [10].

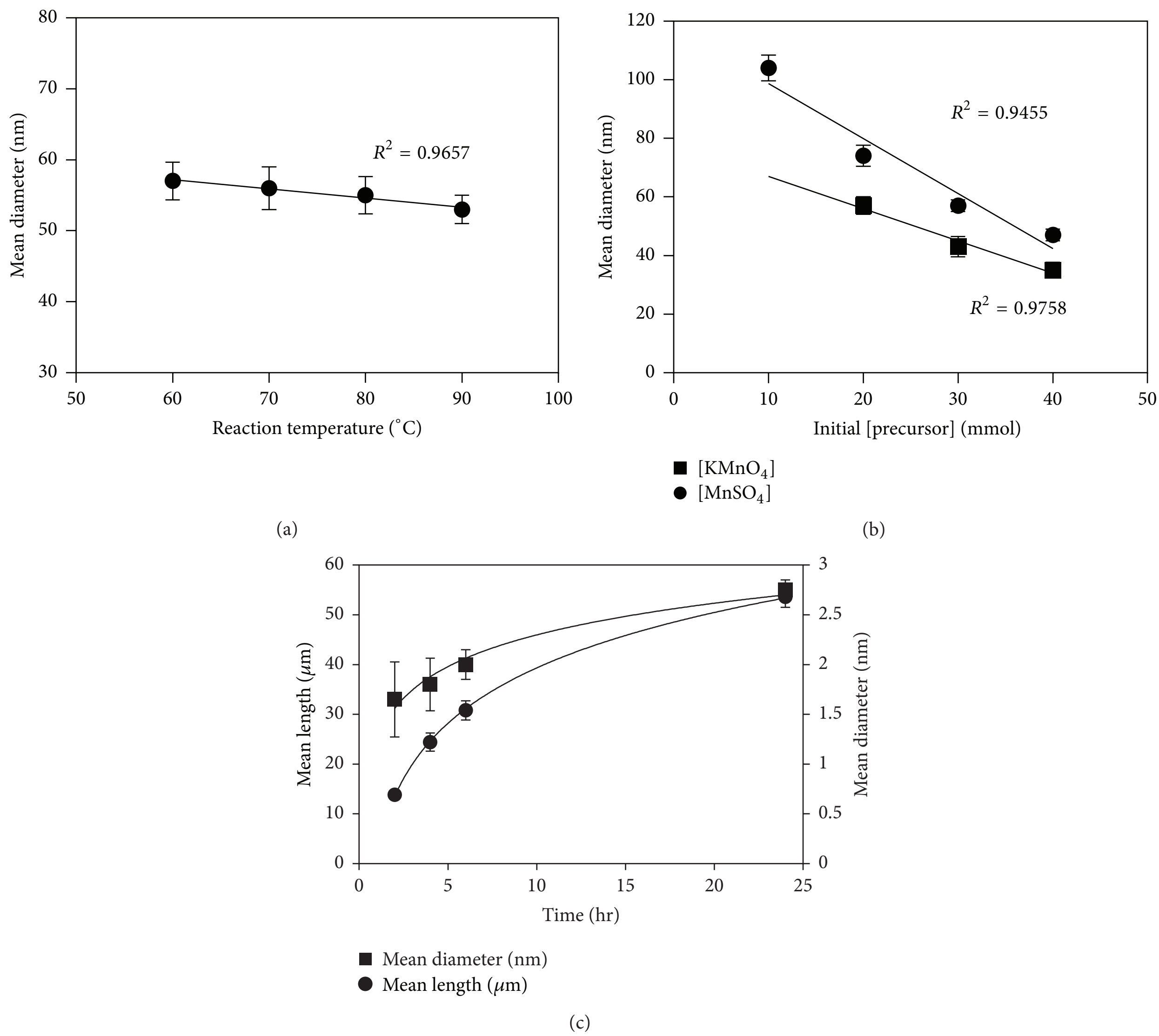

Figure 3: Effect of synthesis parameters on the dimensions of MnO_2 nanowires formed: (a) reaction temperature, (b) initial precursor concentration, and (c) hydrothermal aging duration.

3.4. Dimensions of Manganese Dioxide (MnO_2) Nanowires. Figure 3 shows the effect of synthesis parameters on the dimensions of MnO_2 nanowires formed. The mean diameter of MnO_2 nanowires was observed to decrease linearly, albeit at a rather slow rate, with increased reaction temperature. The mean diameter of MnO_2 nanowires decreased from 57 nm to 53 nm as the reaction temperature was increased from 60°C to 90°C (Figure 3(a)). The initial concentrations of both precursors, potassium permanganate and manganese sulfate monohydrate, were observed to have substantial effect on the mean diameter of MnO_2 nanowires formed upon aging at 80°C for 24 hours. The mean diameter of MnO_2 nanowires was observed to decrease linearly with increasing initial concentration of both precursors. However, the initial concentration of $MnSO_4$ appeared to have a stronger effect on the mean diameter of MnO_2 nanowires than that of $KMnO_4$. The mean diameter of nanowires ranged between 47 nm and 104 nm and between 35 nm and 57 nm as the initial concentrations of $MnSO_4$ or $KMnO_4$ were varied in turn between 10 mmol and 40 mmol, respectively (Figure 3(b)). However, no nanowires could be visibly observable at the initial $KMnO_4$ concentration of 10 mmol or less. This could be attributed to the exceedingly slow rate of redox reaction between Mn^{2+} and MnO_4^- ions which led to the eventual formation of MnO_2 nanowires. In contrast, both mean length and mean diameter of MnO_2 nanowires were observed to increase nonlinearly with increasing hydrothermal aging duration (Figure 3(c)), which varied between 0.69 μm and 2.68 μm and between 33 nm and 55 nm for aging durations of 2 hours and 24 hours, respectively. The dimensional aspect ratio of MnO_2 nanowires was determined to vary between 21 and 49 for the same aging duration.

We envisage that the ability to afford precise control on the morphological dimensions, notably the aspect ratio of

MnO_2 nanowires, should enable microstructural optimization and enhanced electrochemical properties of nanowires-based thin films. Henceforth, systematic studies are currently being undertaken to elucidate effects of morphological dimensions of nanowires on the microstructural parameters such as specific surface areas, porosity, and pore size distribution. Nanowires-based MnO_2 thin films of tailored microstructure and enhanced electrochemical properties such as increased electrical conductivity, charge capacity, and cycling reversibility are therefore highly anticipated.

4. Conclusion

Manganese dioxide nanowires of tunable dimensions were successfully prepared via a facile water-bathing hydrothermal route. MnO_2 nanowires of dimensional aspect ratios between 21 and 49 could be synthesized readily by modulating various synthesis parameters. Synthesis parameters with substantial effects on the mean length and mean diameter of MnO_2 nanowires included the initial concentration of chemical precursors, $KMnO_4$ and $MnSO_4$, and the hydrothermal aging duration. Well-defined manganese dioxide nanowires with a dimensional aspect ratio of 49 were synthesized by reacting 20 mmol potassium permanganate with 30 mmol manganese sulfate monohydrate and upon hydrothermal aging at 80°C for 24 hours. MnO_2 nanowires of precisely controlled morphological dimensions would enable the preparation of nanowires-based MnO_2 thin films with optimized microstructure and enhanced electrochemical properties.

Disclosure

The authors of this paper have no direct financial relation with the commercial entities mentioned in this paper.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

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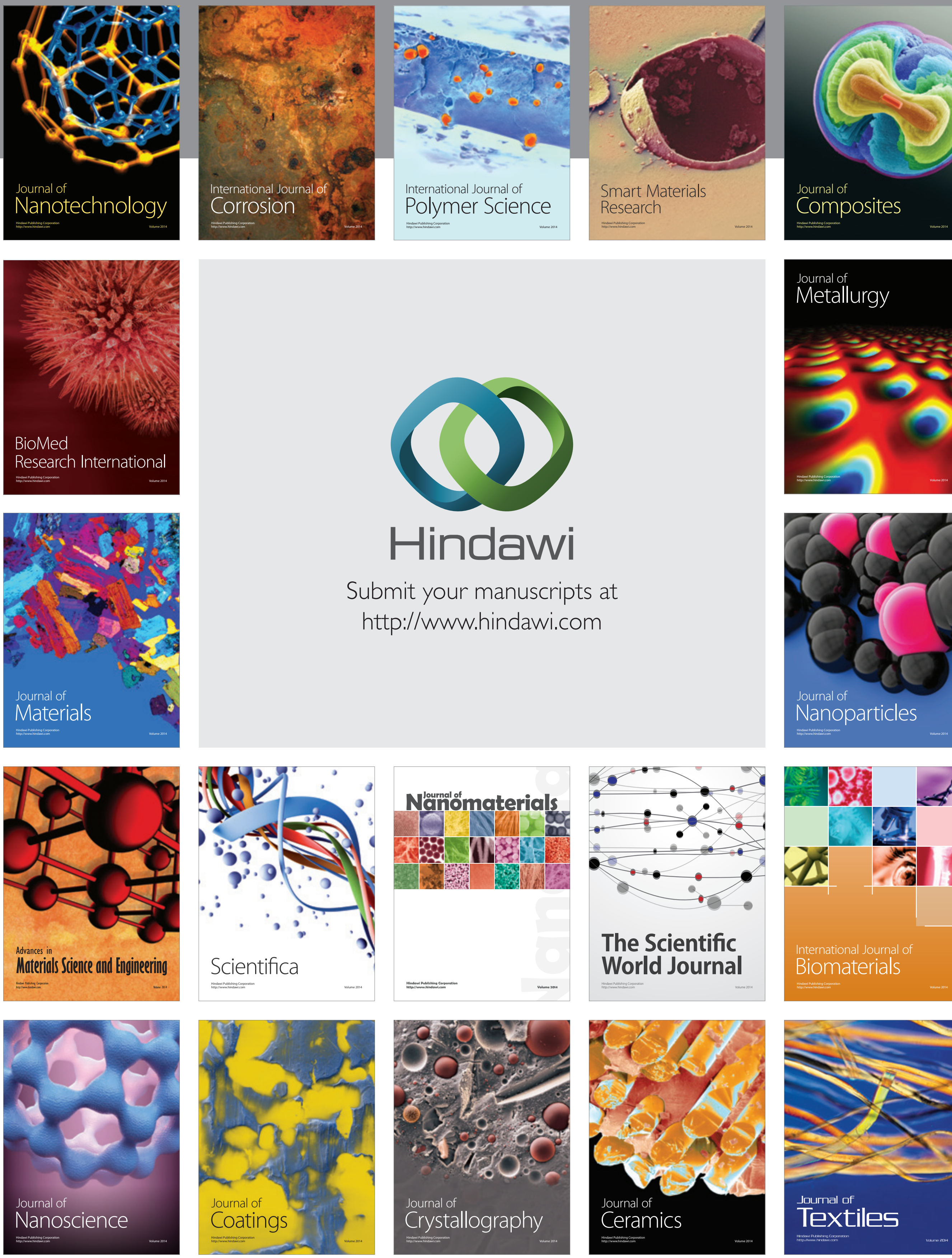
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