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Morphology of hydrothermally synthesized ZnO nanoparticles tethered to carbon nanotubes affects electrocatalytic activity for H₂O₂ detection

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Abstract

We describe the synthesis of zinc oxide (ZnO) nanoparticles and demonstrate their attachment to multiwalled carbon tubes, resulting in a composite with a unique synergistic effect. Morphology and size of ZnO nanostructures were controlled using hydrothermal synthesis, varying the hydrothermal treatment temperature, prior to attachment to carboxylic acid functionalized multi-walled carbon nanotubes for sensing applications. A strong dependence of electrocatalytic activity on nanosized ZnO shape was shown. High activity for H₂O₂ reduction was achieved when nanocomposite precursors with a roughly semi-spherical morphology (no needle-like particles present) formed at 90 °C. A 2.4-fold increase in cyclic voltammetry current accompanied by decrease in overpotential from the composites made from the nanosized, needle-like-free ZnO shapes was observed as compared to those composites produced from needle-like shaped ZnO. Electrocatalytic activity varied with pH, maximizing at pH 7.4. A stable, linear response for H₂O₂ concentrations was observed in the 1–20 mM concentration range.

Keywords

Electrocatalysis; Cyclic voltammetry; Nanostructure morphology; Zinc oxide; Hydrothermal synthesis; Multiwalled carbon nanotubes

1. Introduction

ZnO, an n-type semiconductor material, due to its high conductivity, exciton binding energy (60 meV), wide band gap (3.37 eV) and high breakdown strength, is an ideal candidate for

biosensing [1,2] materials. Accurate and selective detection of hydrogen peroxide (H_2O_2) is important for a variety of applications such as detecting of the on-set of food spoilage [3], screening of cholesterol in blood to manage cardiovascular disease [4], and monitoring signaling events triggering reactive oxygen species generation [5].

The instability of sensor nanocomposites made consisting of enzyme materials is problematic for practical sample analysis [6]. Chemically modified electrodes have proved to be an effective and sensitive way to detect H_2O_2 both in vivo and in vitro [7,8]. For most electrochemical sensors, the detection of H_2O_2 was achieved at its oxidation potential (+0.6 V vs Ag/AgCl). However, this potential range tends to be susceptible to interferences from extraneous electroactive compounds present in biological fluids, e.g., ascorbate and bilirubin [9], thereby reducing selectivity. Decreasing the oxidation potential or performing analysis at its reduction potential is essential for effective detection; the latter was performed in this study. ZnO nanostructures typically consist of flower-like and needle-like shapes, which can be difficult to control [10–12]. Herein, we report, for the first time, a strong dependence on ZnO morphology in the preparation of electrocatalytically active ZnO-carboxylic acid-functionalized multiwalled carbon nanotube nanocomposites (ZnO/COOH-MWNT) for improved sensitivity and selectivity in the detection of H_2O_2 . When combined, these two materials result in a composite material with a unique synergistic effect.

2. Experimental

With the exception of the COOH-functionalized multi-walled carbon nanotubes, all chemicals were purchased from Sigma–Aldrich, St. Louis, MO and at 99.9% purity. Briefly, a 50.0 mL solution of 1.00 M NaOH was introduced into a 3-neck flask. The flask was then connected to a separating funnel containing 50.0 mL of 0.5 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a condenser and a controlled temperature probe. NaOH was initially stirred and heated to a predetermined temperatures after dripping $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ slowly into the NaOH for 60 min. The white precipitate that formed was stirred continuously for an additional 2 h at pre-selected temperatures, ranging from 30 to 90 °C. The mixtures were filtered, washed with deionized water and dried at 65 °C for 60 min [10]. All ZnO nanostructure synthesis experiments were performed under inert N_2 atmosphere. After synthesis of the ZnO nanostructures, they were attached to COOH functionalized MWNTs (COOH-MWNTs) via ultrasonication described by Fang et al. [13]. Bamboo structure COOH-MWNTs (95+% purity, 30 nm diam.) were purchased from Nanolab, Inc. (Waltham, MA, USA) and used as received. The composite was then incorporated onto a glassy carbon electrode (GCE) as follows. A 10- μL aliquot of the composite suspension was cast onto the mirror-like finished GCE, and dried in an oven at 80 °C for 15 min. After drying, a 10- μL drop of 2 wt% Nafion solution in absolute anhydrous ethyl alcohol (AAEA) was applied onto the as-modified GCE, followed by additional drying in an oven at 80 °C for 15 additional min to obtain Nafion/ZnO-MWNTs/GCE sensor. The ratio of the nanocomposite-to-Nafion film was 1:5. Control experiments using known concentrations of uric acid were also performed. A detailed description of the CV along with nanocomposite characterization via transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) and X-

ray excited Auger spectroscopy (XAES) analysis are described in the Supporting Information.

3. Results and discussion

A series of electrochemical sensing nanocomposites incorporated onto GCE surfaces via Nafion film for voltammetric analyses of H_2O_2 , were synthesized using two steps: (i) hydrothermal synthesis of ZnO nanostructures controlling size and morphology, followed by (ii) attachment to COOH-MWNTs. Pure ZnO nanostructures, verified by XPS, XAES (Figs. S5 and S7, ESI) and lattice fringes observed in high resolution TEM, were synthesized at pre-determined hydrothermal treatment temperatures, ranging from 30 to 90 °C. Hydrothermal treatment temperature markedly affected ZnO nanostructure morphology with lower temperatures (~30 °C) producing a high needle-like to a rough semi-spherically shaped morphology while higher temperatures (~90 °C) resulted in predominantly semi-spherically shaped nanostructures.

TEM images of the hydrothermally synthesized ZnO nanostructures produced are shown in Fig. 1. The diameter size distribution of the ZnO nanostructures produced from hydrothermal treatment temperatures ranging from 30 to 90 °C were analyzed and summarized in the Supporting Information (Fig. S3, ESI). ZnO nanostructures produced from 40 to 90 °C hydrothermal treatments are shown in Fig. 4. Average diameter sizes (nm) of 31 ± 8 for 40 °C, 33 ± 5 for 50 °C, 34 ± 8 for 60 °C and 56 ± 18 for 90 °C were observed. Increasing size also correlated with an increase in UV-vis absorbance with decreasing peak width at higher temperatures (Fig. S1, ESI), indicative of greater uniform size distribution of the ZnO. Hydrothermal treatment at 40 °C and 50 °C yielded two types of nanostructures: (1) needle-like and (2) a rough semi-spherically shaped ZnO nanostructures. The needle-like nanoparticles dominate at 40 °C and then a transition from needle-like to semi-spherically shaped nanoparticles was observed at 50 °C. TEM images (Fig. 1) revealed agglomeration or cluster formation of nanostructures, attributed to the hydrophobicity of ZnO nanostructures in aqueous environment. It is known that Zn–O–Zn bonds form between ZnO nanoparticles under aqueous conditions, resulting in hard agglomerates [14].

Fig. 2 shows the relative percent population of needle-like-to-semi-spherically shaped ZnO nanostructures as a function of hydrothermal treatment temperature. From the investigation of the relative populations of the two types of nanostructures, we observed that the increase of the semi-spherical shaped with increasing reaction temperature, maximizing at 60 °C. Beyond this hydrothermal treatment temperature, the needle-like nanoparticles greatly diminished; at 60 °C, none were observed. This temperature denoted the transition state temperature of the conversion of needle-like shaped to rough semi-spherical shaped nanoparticles. A sharp transition occurred at ~55 °C (Fig. 2) in which the ZnO needle-like morphology was no longer present. Each of the ZnO nanostructures were then attached to carboxylic acid functionalized bamboo structured multi-walled carbon nanotubes (COOH-MWNTs) ~30 nm in diameter via ultrasonication in AAEA to produce the electrochemical sensing nanocomposites for H_2O_2 detection with the carboxylate groups serving as stable tethering points of the ZnO nanostructures to the MWNT support [15].

STEM and EDX verified the presence of ZnO tethered to the MWNT surface after the ultrasonication [step 2 of the ZnO/COOH-MWNT nanocomposite synthesis] (Fig. 3). EDX results show the presence of Zn, O, and C on the surface of the nanotubes, which confirm the presence of attached ZnO. Ni emanated from the sample holder. The P and K peaks emanate from trace impurities from the hydrothermal synthesis step. STEM images of ZnO/COOH-MWNTs composite at various hydrothermal treatment temperatures of ZnO nanostructures are shown in Fig. 4. Additional EDX spectra (Fig. S8, ESI) confirmed that the white structures emanated from ZnO while the flexible strands denote COOH-MWNTs. The observed, marked increase in electrocatalytic activity, comparing the 40 °C hydrothermal treatment to the 90 °C treatment in the first step of nanocomposite synthesis (Fig. 5), was attributed to enhanced bonding of the ZnO to the MWNT substrate as compared to those of ZnO nanostructures hydrothermally synthesized below 90 °C temperatures. The quality of the ZnO attachment to the MWNTs varied. The resulting ZnO/COOH-MWNT nanocomposite generated from the 40 °C ZnO hydrothermal synthesis showed ZnO sparsely populating the MWNT surface (Fig. 4A); most of this catalyst surfaces were comprised of MWNTs unattached to ZnO. When 60 °C hydrothermally synthesized ZnO were used, more of the MWNT surface was covered, but approximately half of the MWNTs surface remained exposed (Fig. 4B). When 90 °C hydrothermally synthesized ZnO nanostructures were used to form the nanocomposite, the MWNT surface was completely covered, showing no exposure of the underlying nanotubes (Fig. 4C and D). It can be inferred from Fig. 4C that the MWNT surface was fully covered by ZnO nanoparticles. Hence, we observe a strong correlation between ZnO nanostructure morphology in step 1, with completeness of surface coverage after step 2 of the nanocomposite synthesis procedure. Needle-like shaped ZnO nanostructures resulted in poor attachment to COOH-MWNTs via ultrasonication (Fig. 4A and B).

Fig. 5 shows the effect of hydrothermal treatment temperature of ZnO nanostructures on the electrocatalytic activity of ZnO/COOH-MWNT nanocomposites (incorporated onto GCEs using 2 wt% Nafion film) towards the reduction of H₂O₂. The increased peak-to-peak heights in the CVs denote increased electrocatalytic activity. A 2.4-fold increase in current was observed, comparing the nanocomposites generated from 90 °C hydrothermally synthesized ZnO nanostructures compared to those generated at 40 °C. For irreversible cyclic voltammetry (CV), the peak current is given by the Randles–Sevcik equation (at 25 °C):

$$I_p = (2.99 \times 10^5) n^{3/2} A C D^{1/2} V^{1/2}$$

where I_p is the peak current, in amps, n is the number of electrons, A is the electrode area (cm²), D is the diffusion coefficient (cm² s⁻¹), C^0 is the concentration in mol cm⁻³, and V is the scan rate in V s⁻¹. Using the Randles–Sevcik expression and potentiometric data (Fig. 5 and Table S2, ESI), we observed a ~60% increase in the electroactive surface area of the electrode between 50 °C and 90 °C. We attribute the enhanced electrocatalytic activity for H₂O₂ reduction (a 2.4-fold increase comparing peak-to-peak heights in the CVs comparing 40 °C hydrothermally produced ZnO/COOH-MWNTs with 90 °C ZnO/COOH-MWNTs) to the greater surface area present in the 90 °C nanocomposite produced.

The observed reduction potential peaks for the ZnO/COOH-MWNT nanocomposites prepared using 40 °C, 50 °C, 60 °C and 90 °C hydrothermal treatment temperatures were at -396 mV, -432 mV, -416 mV, and -360 mV, respectively. Also, the overpotential of the reduction of H₂O₂ decreased as the hydrothermal treatment temperature increased from 50 to 90 °C, accompanying higher current response, indicative of high selectivity (e.g., artifacts due to dissolved O₂, ascorbic acid, in samples) would not interfere with H₂O₂ detection. The highest electrocatalytic activity in this series of nanocomposites was observed using 90 °C ZnO nanocomposite precursors. The sharp cathodic current peak was observed at -360 mV vs Ag/AgCl (3.5 M KCl) (Fig. 5A). Noteworthy is the lack of oxidation features in the CVs, typically present in H₂O₂ sensing composites [16–18], rendering our particular composite more selective in the presence of interfering analytes. Although a number of H₂O₂ sensing composites have had CV responses at even low potentials (important for analyte selectivity), at the ca. -200 mV region, it is significant that materials used in our electrocatalyst neither included precious metals, e.g., Au, Ag, Pt, typical of H₂O₂ composites [4,19,20] nor doping of organometallic materials [16] or enzymes [17,18], which are likely more susceptible to decomposition than the simpler ZnO/COOH-MWNT composition under robust sampling conditions. The effect of buffer pH on the detection of H₂O₂ is shown in Fig. 6. The cathodic current response of the composite increased from pH 3.0 to 7.4 and then decreased from pH 7.4 to 10.0 with a slight increase at 11.0. The maximum cathodic peak current of H₂O₂ is observed at pH 7.4 in 70.0 mM phosphate buffer saline (PBS) solutions. Noteworthy is that maximum current response coincides with physiological pH, rendering this nanocomposite practical for the electrochemical detection of H₂O₂, a by-product of many reactions catalyzed by oxidases.

The 90 °C ZnO/COOH-MWNT composite generated was stable and has a linear response within a 1–20 mM concentration range for H₂O₂ current response measured from the composite is shown in Fig. 7A; the inset shows a linear response with concentration ($R^2 = 0.9789$). Compared to previous literature reports of ZnO-based composites [21–23], our results show a wider linear range extending into higher concentration regions. The low overpotential observed in the CV denotes selectivity of the H₂O₂ from a host of other interfering analytes such as acetaminophen, lactate and glucose. Uric acid is a notable interfering analyte created by the breakdown of purines, which eventually passes through the kidneys and is found in urine, prevalent in biological testing samples. A series of CVs for uric acid is shown in Fig. 7B. Current responses observed in the 350–750 mV region (oxidation potential) as a result of uric acid are well separated from that of H₂O₂ (reduction potential) observed at -360 mV, and unlikely to interfere with detection.

4. Conclusions

In summary, the facile technique of hydrothermally synthesizing high purity ZnO nanostructures followed by attachment to COOH-MWNTs to rapidly form the nanocomposite was accomplished with a 90% reaction yield. In step 1, the morphology of ZnO nanostructures changed from needle-like to semi-spherical shape with increasing hydrothermal treatment temperature, with a sharp transitional change between the two populations at ~55 °C. These results show that needle-like shape-free ZnO produce sensitive electrocatalysts at physiological conditions (pH 7.4). This fabrication route, which

eliminates needle-like ZnO nanostructure morphology prior to MWNT attachment, represents an important strategy for sensor design.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations

COOH-MWNTs	carboxylic acid functionalized multi-walled carbon nanotubes
CV	cyclic voltammetry
EDX	energy X-ray dispersive spectroscopy
GCE	glassy carbon electrodes
MWNTs	multiwalled nanotubes
PVA	polyvinyl alcohol
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
XAES	X-ray excited Auger electron spectroscopy
XPS	X-ray photo-electron spectroscopy
ZnO	zinc oxide
ZnO/COOH-MWNT	zinc oxide carboxylic acid functionalized multi-walled carbon nanotubes

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2013.02.028>.

Fig. 1. TEM images of ZnO nanostructures produced at hydrothermal treatment temperatures of 40 °C, 50 °C, 60 °C and 90 °C prior to incorporating into COOH-MWNT nanocomposites.

Fig. 2. Relative percentages (obtained from a composite count of nanostructures) of needle-like to semi-spherical (particle-like) shaped ZnO nanostructures produced as a function of hydrothermal treatment temperature.

Fig. 3.
(A) EDX; and (B) STEM of ZnO in ZnO/COOH-MWNT nanocomposite.

Fig. 4. STEM images of (A) 40 °C ZnO/COOH-MWNTs, (B) 60 °C ZnO/COOH-MWNTs; and (C and D) 90 °C ZnO/COOH-MWNTs.

Fig. 5.

(A) CVs of Nafion/ZnO/MWNTs/GCE in N_2 saturated 70 mM PBS solution containing 10 mM H_2O_2 at pH 7.4, 25 °C and scan rate of 50 mV s^{-1} using ZnO nanostructures prepared using hydrothermal temperatures at (a) 40 °C, (b) 50 °C, (c) 60 °C ZnO and (d) 90 °C; and (B) current response of the nanocomposites versus reaction temperature.

Fig. 6. Cyclic voltammograms of (a) bare GCE, (b) Nafion/COOH-MWNT/GCE and (c) Nafion/ZnO/COOH-MWNT/GCE with 10 mM H_2O_2 in N_2 saturated various pH buffer solutions at a scan rate of 50 mV s^{-1} .

Fig. 7.

(A) CV responses for H_2O_2 detection at (a) 0.5, (b) 1.0, (c) 5.0, (d) 7.5, (e) 10.0, (f) 12.5, (g) 15.0, (h) 17.5, and (i) 20.0 mM concentrations. Experimental conditions identical to those in Fig. 5 were applied. Inset shows a linear relationship between current and H_2O_2 concentration; (B) CV responses for various concentrations of uric acid, ranging from 0.1 to 20 mM.