Short Communication Wiley Online Library ELECTROANALYSIS

DOI: 10.1002/elan.201700551

Co_2SnO_4/Carbon Nanotubes Composites: A Novel Approach for Electrochemical Sensing of Hydrogen Peroxide

E. Yedinak,[a, b] C. J. Venegas,[a, b] T. P. Brito,[a, b] D. Ruiz-León,*[a] and S. Bollo*[b, c]

Abstract: For the first time Co_2SnO_4 (CTO)/Carbon nanotubes (CNT) composites were prepared and used to modify glassy carbon electrodes for the amperometric determination of hydrogen peroxide. The catalytic activity of composites towards the oxidation of hydrogen peroxide was dependent on the quantity of CNT present in the composite and to the pH of the medium. The pure cobalt stannate phase with a ratio of 3:1 (CTO:CNT) exhibited the best catalytic activity towards hydrogen peroxide oxidation at low potentials (0.200 and 0.500 V). A linear relationship between current and hydrogen peroxide concentration was obtained with a sensitivity of 95 and 258 $\mu A\,mM^{-1}$ and a detection limit of 0.130 and 0.08 μM respectively.

Keywords: Cobalt stannate · carbon nanotubes composites · Hydrogen peroxide oxidation · ceramic oxides · electrochemical

Enzymatic biosensors measurements have the advantage of sensitivity, simplicity, reproducibility, and low cost [1]. However, designs featuring enzyme entrapment suffer from instability and accordingly have been a major production problem. Many recent advances have been dedicated to the enzyme-less detection of hydrogen peroxide, which have applications in chemical, food manufacturing, environment, and textile industries, to name a few [2–4]. Electrochemical detection of hydrogen peroxide suffers from a high polarizing voltage required for the oxidation reaction, thus introducing the possibility of interference from other species such as ascorbic acid and uric acid. The oxidation potential can be reduced, however, with the incorporation of redox active cation such as cobalt on the electrode surface [5–7].

In a previous work, we report for the first time an amperometric non-enzymatic sensor based on the catalytic activity of cobalt-doped stannates/reduced graphene oxide (rGO) composites towards the oxidation of hydrogen peroxide. The catalytic activity of composites was highly dependent on quantity of cobalt in the ceramic compound, and also on the proportion of rGO present [8].

Since their discovery in the early 1990s, much research has been focused on the applications of carbon nanotubes (CNT), from which electrochemical sensors has certainly benefitted from their high surface-to-volume ratio, enhanced electrical properties, low limit of detection, and fast signal response [9–11]. With respect to hydrogen peroxide, the incorporation of nanotubes into electrochemical sensors has allowed lower working potentials, thus suppressing the oxidation or reduction of interfering species, as well.

For this study, it is of particular interest to study the effect of CNTs in a composite material with Co_2SnO_4 (CTO) for the detection of hydrogen peroxide since in our previous work, this was the ceramic compound that showed the greatest electroactivity. To our best knowledge, this study represents the first use of CTO/CNT in the context of hydrogen peroxide sensors and it is believed the activity may be enhanced by changing rGO for CNT. The degree of signal enhancement from the oxidation of hydrogen peroxide was investigated as a function of the proportion of electroceramic to carbon nanotubes, pH of supporting electrolyte, and working potential.

The morphology of the composite materials were examined by scanning electron microscopy (SEM) (Figure 1). As can be seen, the nanotubes appear to surround and encapsulate the stannate particles, thus confirming an intimate contact between the two component materials. Insert of Figure 1 shows the SEM images obtained for pure CTO and CNT (right and left respectively), demonstrating that the each material remain intact after the composite formation.

Electrochemical studies were conducted using CTO/CNT composite material to modify glassy carbon electrodes. Figure 2 show the cyclic voltammograms of 3 mM hydrogen

[a] E. Yedinak, C. J. Venegas, T. P. Brito, D. Ruiz-León
Laboratorio de Fisicoquímica y Electroquímica del estado Sólido, Facultad de Química y Biología, Universidad de Santiago de Chile, Av. Libertador Bernardo O'Higgins n° 3363, Santiago, Chile
E-mail: domingo.ruiz@usach.cl
[b] E. Yedinak, C. J. Venegas, T. P. Brito, S. Bollo
Centro de Investigación de Procesos Redox (CiPRex)
[c] S. Bollo
Advanced Center for Chronic Diseases (ACCDiS), Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile
E-mail: sbollo@ciq.uchile.cl

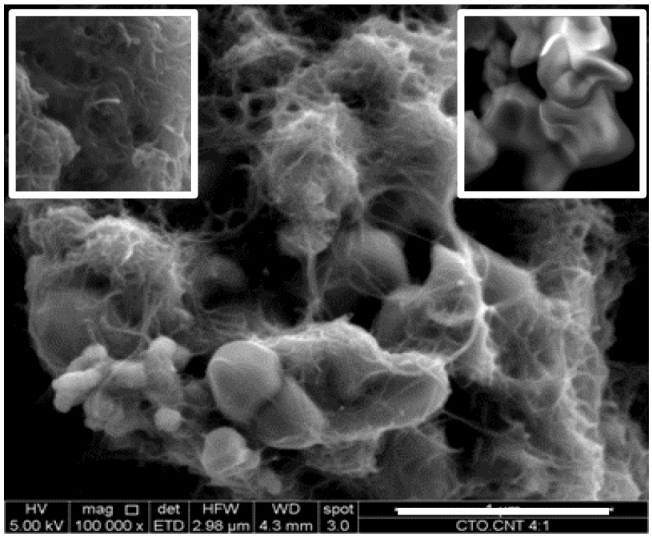

Fig. 1. SEM micrographs of CTO/CNT composite. Scale Bar = 1 µm. Insert: SEM micrographs of CNT (left) and CTO (right) at scale of 2 µm.

peroxide at GCE modified with 3:1 CTO/CNT proportion and each independent material. Clearly it is observed a synergistic effect for the oxidation of hydrogen peroxide when using the mixture of both materials in the form of a composite.

Figure 3A depicts the response sensitivity calculated from amperometric studies conducted at a constant potential of 0.200 V for cobalt stannate composite materials in different proportions with respect to carbon nanotubes. As can be observed, for ratios of cobalt stannate to carbon nanotubes of 1:1, 2:1, and 3:1, there is an increase in the

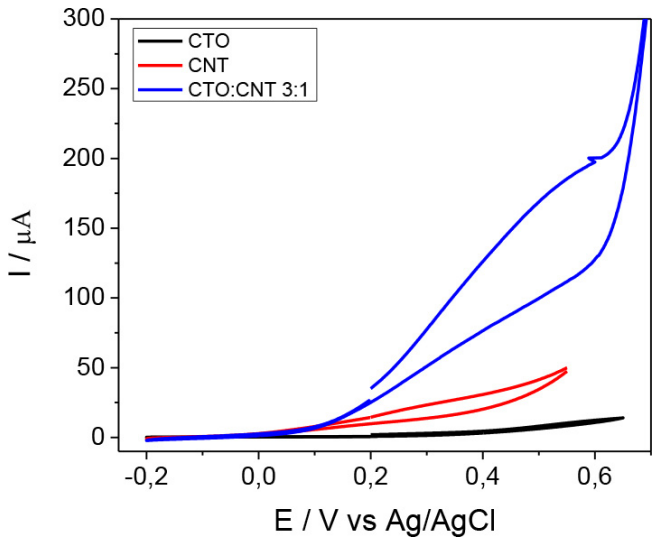

Fig. 2. cyclic voltammograms of 3 mM hydrogen peroxide obtained at 3:1 CTO/CNT proportion and each independent material. Supporting electrolyte NaOH 0.1 M. $E_i = 0.2$ V towards positive range. Sweep rate 0.05 V/s.

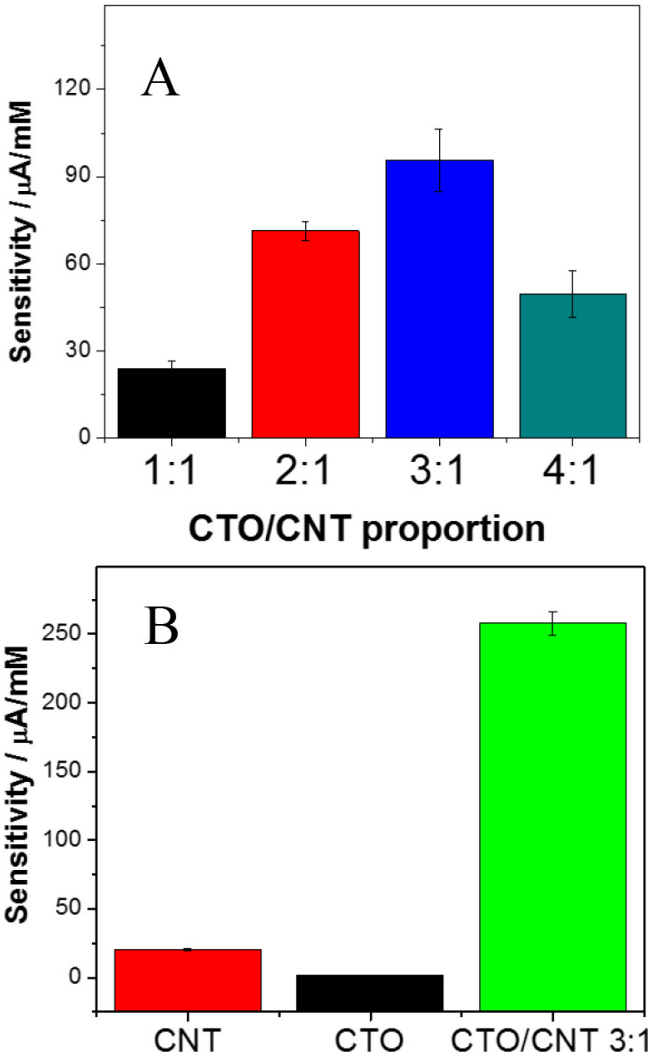

Fig. 3. Sensitivity towards hydrogen peroxide obtained from amperometric experiments at (A) different CTO/CNT proportions at 0.002 V, supporting electrolyte NaOH 0.1 M and (B) 3:1 CTO/CNT proportion and each independent material at 0.500 V. Supporting electrolyte NaOH 1 M.

signal response, presumably due to the increased presence of cobalt stannate. However, for a ratio of 4:1, the signal response decreases dramatically, perhaps due to the insufficient coverage of the carbon nanotubes over the cobalt stannate particles, thus diminishing the synergetic interaction between both materials.

It was also discovered that hydrogen peroxide oxidation on the CTO/CNT composite modified electrode was pH-dependent. Initially, with an increase in pH, the system response also increased. However, after pH of 13, the system appears to saturate and any additional increase of pH will not yield a higher signal response. Thus, the system was optimized in 0.1 M NaOH (pH 13). Figure 3B depicts a comparison of results obtained for CTO/CNT (3:1) in 1.0 M NaOH buffer at a constant potential of 0.500 V with respect to its constituent components. As can be seen, the compo-

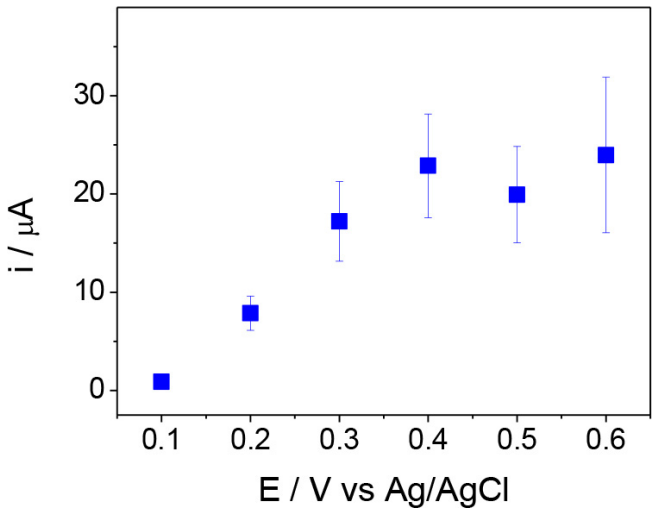

Fig. 4. Hydrodynamic voltammograms for 50 μM hydrogen peroxide at CTO/CNT 3:1 electrode.

site material's response is enhanced compared to either of the two components alone, thus proving the synergic relationship of this composite material.

Figure 4 shows the hydrodynamic voltammograms for 50 μM hydrogen peroxide obtained at CTO/CNT (3:1) modified electrode. For the unmodified GCE, the oxidation of hydrogen peroxide is observed from 0.600 V onwards [12]. For the GCE modified with the composite, there is a decrease in the potential for the oxidation of hydrogen peroxide to 0.200 V. The electrocatalytic effect of the composite on the electrochemical behavior of hydrogen peroxide is clear, and can even be observed using composites containing lower quantities of cobalt (not shown). The selected potentials to develop the analytical method were 0.200 and 0.500 V. The linear range at both potential was 0.060 mM–0.570 mM and the CTO/CNT modified electrode revealed a high reproducibility, with a relative standard deviation of 3.1% calculated from the sensitivities for hydrogen peroxide obtained with four different sensors.

Table 1 shows the results from this work compared with other hydrogen peroxide sensors found in literature that use an alkaline supporting electrolyte. As can be seen, this system has a limit of detection that is lower than other sensors found in literature. It was not possible to determine the sensitivity of the system with respect to surface area due to the highly absorptive properties of the surface of the modified electrode.

Compared with our previously reported composite CTO/rGO (8:1), better analytical parameters were obtained using CNTs. An explanation for these results may be that CNTs are capable of fully encapsulating the CTO particle as can be seen in Figure 1, which produced a closer contact between the catalytic sites of both materials than that occurring between CTO and graphene sheets.

According to previous results obtained from J. Mu et al. [13], a proposed mechanism spinel Co_3O_4 nanoparticle involved the oxidation of hydrogen peroxide at the surface, which was catalyzed by Co^{3+} in the nanoparticles. This mechanism depended both on the concentration of hydrogen peroxide and hydroxide ions. A pH effect was observed for this system, thus offering a possible mechanism for the hydrogen peroxide sensor presented in this work. However, the complexity of this system necessitates further work which is currently being completed to fully understand the complex nature of the composite material and its interaction with hydrogen peroxide. In our case, in CTO only has a single Co^{2+} contribution, therefore for the catalytic effect, Co^{2+} must first be oxidized to Co^{3+} which is the primary catalytic site within the cobalt stannate.

Experimental

Co_2SnO_4 synthesis was prepared and characterized according to our previous reported method [8]. Fresh stock dispersions of 8 mg/mL CTO and 2 mg/mL CNT (Nano Lab, >95% purity, length 1–5 μm, diameter 15±5 nm) were prepared the same day of experimentation. Both CTO and CNT stock dispersions were prepared in 2% Nafion® (Aldrich) with ethanol. The stock dispersions were sonicated for three 10 minute intervals to ensure a homogenous suspension. From these stock solutions, 1 mL solutions of CTO/CNT in proportions of 1:1, 2:1, 3:1, and 4:1 were prepared. The dispersions were sonicated for three 10 minute intervals.

Prior to modification, glassy carbon electrodes (GCE, CH Instrument, 3.0 mm in diameter) were polished using 0.3 and 0.05 mm alumina (Micropolish Buehler) and

Table 1. Comparison of various sensors for the determination of H_2O_2.

Electrode	Potential (V)	Sensitivity ($\mu A\,mM^{-1}\,cm^{-2}$)	LOD (μM)	Ref.
Co_3O_4 nanopart.	−0.70	–	4.40	[13]
CoOOH nanolamines	0.10	99.0	40.0	[14]
Ftalocianine Co(II)/ Porfirine Co(II)	0.55	0.45	6.00	[15]
CTO /rGO (8:1)	0.40	0.43	0.31	[8]
CTO/CNT (3:1)	0.20	95*	0.13	this work
	0.50	256*	0.08	

*$\mu A\,mM^{-1}$

rinsed with deionized water. The CTO/CNT dispersions (10 μL) were dropped onto the polished GCE surface and allowed to dry at 50 °C for 15 minutes.

All electrochemical studies were completed at room temperature using a single cell with a traditional three-electrode system featuring the modified GCE as the working electrode, an Ag/AgCl saturated electrode as reference, and Pt wire as auxiliary electrode. The volume of the supporting electrolyte used was 6 mL. All potentials represented are versus the Ag/AgCl electrode. Amperometric measurements were performed using a PalmSens MultiEmStat Potentialstat/Galvanostat.

Acknowledgements

Financial support from Conicyt-Fondecyt CHILE (Grant 1161225). C.J.V acknowledges the CONICYT scholarship for Ph.D. studies in Chile, T.P.B acknowledges USACH scholarship and E.Y. to Fulbright Program grant sponsored by the Bureau of Educational and Cultural Affairs of the United States Department of State and administered by the Institute of International Education.

References

[1] J. Newman, A. Turner, *Biosens. Bioelectron.* **2005**, *20*, 2435–2453.
[2] J. Jin, W. Wu, H. Min, H. Wu, S. Wang, Y. Ding, *Microchim. Acta.* **2017**, *184*, 1389–1396.
[3] M. Baghayeri, A. Amiri, S. Farhadi, *Sensors Actuators B Chem.* **2016**, *225*, 354–362.
[4] N. Mahmood, C. Zhang, Y. Hou, *Small* **2013**, *9*, 1321–1328.
[5] J. Gerken, J. McAlpin, J. Chen, M. Rigsby, W. Casey, R. Britt, J. McAlpin, *J. Am. Chem. Soc.* **2011**, *113*, 14431–14442.
[6] X. Qi, H. Gao, Y. Zhang, X. Wang, Y. Chen, W. Sun, *Bioelectrochem.* **2012**, *88*, 42–47.
[7] M. Wang, D. Zhang, Z. Tong, W. Ma, X. Xu, *Micro Nano Lett.* **2010**, *5*, 207–210.
[8] C. Venegas, E. Yedinak, J. Marco, S. Bollo, D. Ruiz-León, *Sensors Actuators B Chem.* **2017**, *250*, 412–419.
[9] W. Yang, K. Ratinac, S. Ringer, P. Thordarson, J. Gooding, F. Braet, *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 2114–2138.
[10] L. Goulart, F. de Moraes, L. Mascaro, *Sci. Eng. C. Materials Biol. Appl.* **2016**, *58*, 768–773.
[11] C. Gao, Z. Guo, J. Liu, X. Huang, *Nanoscale* **2012**, *4*, 1948–1963.
[12] D. Pan, J. Chen, L. Nie, W. Tao, S. Yao, *Anal. Biochem.* **2004**, *324*, 115–122.
[13] J. Mu, L. Zhang, M. Zhao, Y. Wang, *J. Mol. Catal. A Chem.* **2013**, *378*, 30–37.
[14] K. Lee, P. Loh, C. Sow, W. Chin, *Biosens. Bioelectron.* **2013**, *39*, 255–260.
[15] K. Ozoemena, Z. Zhao, T. Nyokong, *Electrochem. Commun.* **2005**, *7*, 679–684.

Received: September 11, 2017
Accepted: November 7, 2017
Published online on November 22, 2017

