Comment on "Carbon nanowalls as material for electrochemical transducers" [Appl. Phys. Lett. **95**, 014104 (2009)]

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In a Letter by Lauis *et al.*,[1] carbon nanowalls were synthesized with a new approach without the presence of any metallic catalyst. Due to the absence of metallic impurities, it has been claimed that this nanomaterial is useful for electrochemical transducers. To this aim, an amorphous carbon was used as the substrate electrode (*a*-C), and the carbon nanowalls were deposited vertically on this substrate to prepare a new electrode called CNW electrode. Then, the basic electrochemical behaviors of these two electrodes (*a*-C and CNW) were compared to prove excellent electrochemical properties of the CNW electrode. Though, this comparison is not appropriate and justified to make this conclusion; there are some serious problems in the electrochemical investigations,

(1) According to the impedance spectra reported in Fig. 3 of Ref. [1], the cell resistance is about 60 and 45 Ω for the *a*-C and CNW electrodes, respectively. Theoretically, the real Z at high frequencies is representative of the electrolyte and electrode (cell) resistance. According to the data reported, coating the amorphous carbon with a new layer of carbon nanowalls has reduced the electrical resistance but according to the second principle of series circuits: the total resistance of any series circuit is equal to the sum of the individual resistances (here plus interfacial resistances). Thus the electrical resistance of an electrode should be increased by coating, and the substrate resistance is normally lesser than that of the coated electrode (having both materials attached in series). The only explanation is the existence of a peculiar behavior on the electrode/electrolyte interface. Thus, the amorphous carbon is not a suitable electrode for electrochemical studies and also using as a comparing case. In general, the electrochemical behavior of this carbon nanomaterial should be compared with a conventional electrode; as it aims to replace available electrodes (not amorphous carbon) for electrochemical applications.

(2) By using the equation $k° = RT/n^2F^2ACR_{ct}$; the rate constant $k°$ was calculated from the data obtained from impedance spectroscopy. Here, the only variable is R_{ct}. Thus, according to the R_{ct} values estimated for the *a*-C and CNW electrodes ($\sim$200 and 60 Ω); the values of $k°$ cannot be 1.3×10^{-3} and 9.0×10^{-3} cm s^{-1}, as reported in Ref. [1].

(3) The classic Randles–Sevcik equation is used to estimate the electroactive surface area. However, this equation is not valid for the system under consideration. The Randles–Sevcik equation has been derived with a key assumption that diffusion toward the electrode surface is one-dimensional.[2,3] A porous film like the carbon nanowalls reported in Ref. [1] are soaked in the electrolyte solution, and the diffusion is three-dimensional through the pores and chancels of this nanostructured material. This is indeed the superior feature of nanomaterials in electrochemical systems.[4] Definitely, the Randles–Sevcik equation can be used for the calculation of electroactive surface area but only when a rigid electrode has surface roughness, not porous films. On the other hand, electron transfer at the electrode/electrolyte interface should be fast enough (to maintain the equilibrium ratio between the reduced and the oxidized forms of the redox couple predicted by the Nernst equation) to consider a reversible electrochemical system.

Moreover, as quoted by the authors, the peak-to-peak separations are higher than that of ideal reversible voltammograms; thus, the systems can be considered as a quasireversible, probably due to slow electron transfer at the electrode/electrolyte interface. In the latter case, the simplified Randles–Sevcik equation is no longer valid.[5]

(4) For rough electrodes, it is well known that the voltammetric behavior does not obey the Randles–Sevcik equation, as the power of scan rate is no longer equal to 1/2 (instead a factor associated with the surface roughness).[6] More importantly, it has been described that the microscopic and macroscopic areas are sensed depending on the applied scan rate.[7] In other words, depending on the width of the diffusion layer formed on the electrode surface (i.e., a factor of the scan rate), the electroactive area sensed in voltammetry is different. This is indeed the basis for the inspection of scale-dependent roughness (fractal structure) of electrode surfaces.[8]

(5) The effective surface areas for the *a*-C and CNW electrodes have been estimated to be 5.8×10^{-2} and 19×10^{-2} cm^2, when the geometrical electrode area is 15×10^{-2} cm^2. This means the rough factor is about 0.4 and 1.3, respectively. For electrochemically deposited surfaces (usually with microstructure), the roughness factor in order of tens is quite usual. For a porous

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nanomaterial, a roughness factor in order of hundreds is expected (cf. Ref. 9). If the values reported in Ref. 1 are correct, this shows that most of the electrode surface is electrochemically inactive; roughly speaking, the physical surface area should be, e.g., 100 times higher.

Apart from comments quoted above, the impedance spectrum of the CNW electrode [Fig. 3b in Ref. 1] shows a depressed semicircle, which is indicative of the fact that the interfacial impedance is in the form of a constant phase element (CPE). Several reasons like surface roughness, nonuniform current distribution, nonuniformity of the material composition, and nonuniform distribution of active sites can be responsible for a CPE.[10] In general, such electrochemical systems are too complicated to be explained by conventional electrochemistry, and need special considerations to adopt well-established electrochemical relations.

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