



## Electrochemical reduction of trinitrotoluene on core–shell tin–carbon electrodes

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### ABSTRACT

In this work, we studied the electrochemical process of 2,4,6-trinitrotoluene (TNT) reduction on a new type of electrodes based on a *core–shell tin–carbon Sn(C) structure*. The Sn(C) composite was prepared from the precursor tetramethyl-tin Sn(CH<sub>3</sub>)<sub>4</sub>, and the product contained a core of submicron-sized tin particles uniformly enveloped with carbon shells. Cyclic voltammograms of Sn(C) electrodes in aqueous sodium chloride solutions containing TNT show three well-pronounced reduction waves in the potential range of –0.50 to –0.80 V (vs. an Ag/AgCl/Cl<sup>–</sup> reference electrode) that correspond to the multistep process of TNT reduction. Electrodes containing Sn(C) particles annealed at 800 °C under argon develop higher voltammetric currents of TNT reduction (comparing to the as-prepared tin–carbon material) due to stabilization of the carbon shell. It is suggested that the reduction of TNT on core–shell tin–carbon electrodes is an electrochemically irreversible process. A partial oxidation of the TNT reduction products occurred at around –0.20 V. The electrochemical response of TNT reduction shows that it is not controlled by the diffusion of the active species to/from the electrodes but rather by interfacial charge transfer and possible adsorption phenomena. The tin–carbon electrodes demonstrate significantly stable behavior for TNT reduction in NaCl solutions and provide sufficient reproducibility with no surface fouling through prolonged voltammetric cycling. It is presumed that tin nanoparticles, which constitute the core, are electrochemically inactive towards TNT reduction, but Sn or SnO<sub>2</sub> formed on the electrodes during TNT reduction may participate in this reaction as catalysts or carbon-modifying agents. The nitro-groups of TNT can be reduced irreversibly (*via* two possible paths) by three six-electron transfers, to 2,4,6-triaminotoluene, as follows from mass-spectrometric studies. The tin–carbon electrodes described herein may serve as amperometric sensors for the detection of trace TNT.

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### 1. Introduction

Nitroaromatic compounds, nitroamines and polynitro-esters are known to exhibit well-defined redox behavior and can be reduced electrochemically due to the fact that the nitro-group is an excellent electron acceptor [1]. The reduction of polynitro aromatic compounds is a multistep process, which may occur in two or three steps resulting in amine or nitroso-compounds *via* hydroxylamine derivatives [2]. It is well established that the above process is strongly dependent on several factors, such as the composition of the supporting solution, the number of nitro-groups and their relative position on the aromatic ring, and the nature and position of other groups of the compound [1]. Various elec-

trodes have been used for the electrochemical reduction of TNT. For instance, studies by cyclic voltammetry (CV) of the trinitrotoluene reduction on a glassy carbon electrode in a phosphate buffer solution revealed that sequential reduction of the three nitro-groups results in three well-separated reductive waves [3]. The first CV peak may reflect the 4-electron irreversible reduction of the nitro-group to the hydroxylamine moiety. Wang et al. [4–7] have used bare carbon and boron-doped, diamond-based electrodes for the electrochemical reduction of nitroaromatic compounds. These authors also demonstrated that the modification of a glassy carbon electrode with multi-walled carbon nanotubes resulted in a quantitative TNT analysis down to the sub- $\mu\text{g/L}$  concentration level [8]. Krausa et al. [9,10] developed an electrochemical solid-state gas sensor based on a bare gold-disc electrode for the reduction of nitroaromatic compounds. The sensitivity of the electrochemical reduction of nitroaromatic compounds can be increased (compared to that measured with carbon electrodes) by the use of the Hg-film [11] and carbon/HgI<sub>2</sub> [12] electrodes. As an alternative to mercury

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electrodes, bismuth-film electrodes, which possess a high overpotential for hydrogen evolution and mechanical stability, were studied for the electrochemical reduction of 2-nitrophenol [13]. A comparison of the electrochemical behavior of several nitroaromatic compounds on bare glassy carbon, gold, silver, platinum and nickel electrodes was performed by Hilmi et al. [11] These authors showed that platinum and nickel electrodes were deactivated upon repeated reduction processes of nitroaromatic compounds, while Au, Ag, or Ag/Au electrodes show a stable activity in these processes, and hence, may be useful for the amperometric detection of nitroaromatics. Zen et al. [14] proposed a single-run approach for the electrochemical detection of nitroaromatic compounds at very low concentrations using pre-anodized screen-printed carbon electrode. Filanovsky et al. [15,16] demonstrated the use of chemically modified electrodes, for instance, carbon modified with cobalt(II) phthalocyanine for traces electroanalysis. In a recent review paper [17], Wang concluded that modification of electrodes based on carbon nanotubes [8] or mesoporous SiO<sub>2</sub>-MCM-41 [18] by metallic nanoparticles may enhance the sensitivity of the electrochemical detection of explosives. Generally, nanoparticles of transition and noble metals, which have different properties compared to that of their bulk, are currently being used for the modification of electrodes in electrochemical analysis and catalysis [19]. It was shown, for instance, that electrodes based on gold nanoparticles demonstrated high electrocatalytic activity and sensitivity towards the electrochemical sensing of epinephrine [20]. A new kind of electrochemical sensor for nitric oxide was proposed recently by the electrodeposition of a Pt-Fe(III) nanoparticle film on a glassy carbon electrode [21]. In a recent work [22], we reported on newly developed carbon-paper electrodes modified by porous TiO<sub>2</sub> particles containing inserted/deposited nanoparticles of Ru, Au, or Pt, for the electrochemical sensing of TNT.

In the work reported herein, we aimed at a further investigation of the electrochemical reduction of TNT on a new type of electrodes based on tin-carbon particles with a *core-shell structure*. We focused on core-shell structure particles since they are expected to have unique properties that are not present in either the core or the shell materials [23]. Sn(C) particles with core-shell structure were prepared by a simple route from the precursor, tetra-methyl tin Sn(CH<sub>3</sub>)<sub>4</sub>. To the best of our knowledge, it is the first report on the use of material with such a core-shell structure as the active mass in electrodes for sensing TNT.

## 2. Experimental

A core-shell structure compound, Sn(C) was prepared from a tetra-methyl tin Sn(CH<sub>3</sub>)<sub>4</sub> (Aldrich, >99%) precursor using the RAPET technique described elsewhere [24]. The reactor was assembled from stainless steel Letlok parts (made by the HAM-LET Co. Ziporit, Israel) and a 3/8 in. union part was plugged on both sides by standard caps. 1 mL of tetra-methyl tin was introduced into the reactor under air and the cell was closed tightly at room temperature. The Letlok was heated in a furnace at 800 °C for 3 h, and then was cooled (during 6 h) to room temperature and disassembled. The product thus obtained was a black powder of tin-carbon core-shell Sn(C) particles, a portion of which was additionally annealed during 6 h at 800 °C under argon. The annealed particles are denoted as Sn(C)-a in this paper. Tin-carbon particles were characterized by X-ray diffraction, HR-TEM, SEM, Raman spectroscopy, electrochemical tools, and by gas adsorption followed by analysis of the BET method for determining the surface area. The tin-carbon core-shell particles (40–200 nm) thus produced had a specific surface area of 8 m<sup>2</sup>/g, as measured by the BET method (Gemini 2375, Micromeritics, multipoint mode). Their annealing at 800 °C under

argon only slightly influences their surface area. XRD measurements were performed using an AXS D8 Advance diffractometer (reflection  $\theta$ - $\theta$  geometry, Cu K $\alpha$  radiation, receiving slit 0.2 mm, scintillation counter, 40 mA, 40 kV) from Bruker, Inc., Germany.

For electrode preparation, tin-carbon particles were mixed thoroughly with a polymeric binder, polyvinylidene fluoride (PVDF), 95%:5% by weight, in an *N*-methylpyrrolidone solvent to make a slurry that was spread onto both sides of a nickel foil current collector (99.9%, thickness 0.25 mm) from Goodfellow Cambridge Ltd. The geometric surface area of the working electrode was 1 cm<sup>2</sup>. In order to obtain good adhesion, the nickel foil was pretreated by etching it in a diluted HNO<sub>3</sub> aqueous solution and then rinsing with double distilled water. The electrodes were first dried in vacuum at 80 °C and then in vacuum at room temperature overnight. Their load was usually about 2 mg of tin-carbon active material per cm<sup>2</sup>. We also used electrodes in which the active mass was loaded on nickel (Strem Chemicals, >99%) disks (0.08 cm<sup>2</sup>), embedded in Teflon. Similar electrodes were also prepared from tin nanoparticles (Aldrich, 99.7%, average size 100 nm) and from carbon particles synthesized by the same RAPET method from the tetra-methylbenzene C<sub>6</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub> precursor (TMB) and were tested as active electrodes' material for TNT reduction. Thus produced carbon particles (referred as "carbon-TMB" in this work) were ball-shaped with average size of 2–4  $\mu$ m; their BET surface area was around 5 m<sup>2</sup>/g.

The electrochemical reduction of TNT was studied in three-electrode cylindrical cells, comprising Sn(C) or Sn(C)-a working electrodes, glassy carbon counter electrodes, and Ag/AgCl/3.5M KCl reference electrodes. The background (supporting) solution was 0.5 M NaCl in double distilled water. The electrochemical cell contained ca. 5 cm<sup>3</sup> of the solution. The concentration of 2,4,6-trinitrotoluene in solutions varied in the range of 1–20 ppm. The home-prepared stock solution comprised 47 mg of TNT dissolved in 50 mL of acetonitrile. The electrochemical experiments were performed using a computerized multichannel potentiostat/galvanostat BTU-1470 from Solartron Inc., driven by a CorrWare program (Scribner Associates, Inc.).

Solutions remaining after several prolonged measurements of TNT reduction on tin-carbon electrodes were collected and analyzed using mass-spectrometry. Mass-spectrometric studies of these solutions containing TNT reduction products were carried out with an AutoSpec Premier Micromass Mass-spectrometer DCI (United Kingdom) in both electronic and chemical (methane) ionization modes. For this analysis, 5–10  $\mu$ L of the residual solution were inserted directly to the spectrometer without any pretreatment.

Raman spectra of tin-carbon core-shell particles and carbon particles obtained from tetra-methyl benzene were collected *ex situ* in a back-scattered configuration using a micro-Raman spectrometer HR800 (Jobin Yvon Horiba Inc.) and holographic grating 1800 grooves/mm, with a He-Ne-laser (excitation line 632.8 nm, the power measured on the sample was around 0.3 mW). Spectra were measured from at least 10 different locations on a sample. The value of peak intensities and of full-width-at-half-maximum (FWHM), related to the Raman spectra, was obtained by a fitting to a Lorentzian line shape. HR-TEM images of tin-carbon core-shell structures were obtained using a JEOL-JEM-2011 (200 kV) transmission electron microscope equipped with an Energy Dispersive X-ray Microanalysis System from Oxford Instruments. Sn(C) particles were collected from electrodes (by scraping) after TNT reduction processes and were measured by Mössbauer spectroscopy at room temperature using a conventional constant-acceleration spectrometer and a 5 mCi Ba<sup>119m</sup>SnO<sub>3</sub> source. The spectra were analyzed by a least square fit procedure. The <sup>119</sup>Sn isomer shifts (IS) values are relative to BaSnO<sub>3</sub>, measured at room temperature.

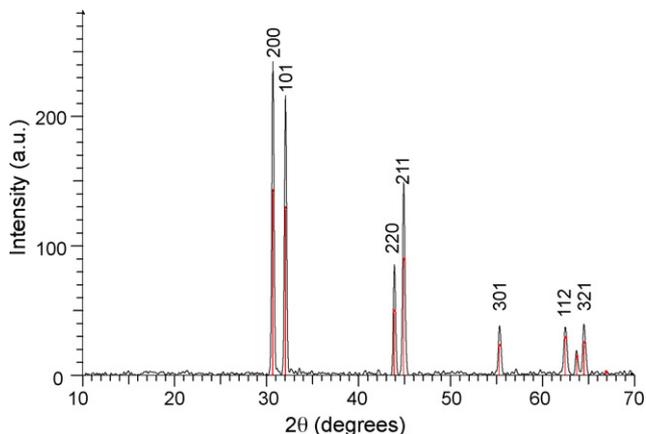


Fig. 1. XRD patterns of the core-shell tin-carbon particles synthesized using the RAPET technique.

### 3. Results and discussion

XRD patterns of an as-prepared Sn(C) core-shell compound are shown in Fig. 1, which demonstrates four sharp major peaks indexed to [200], [101], [220], and [211] at 2-theta angles of 30.63°, 32.01°, 43.86° and 44.89°, respectively. As expected, this pattern is assigned to metallic tin (body-centered tetragonal lattice, matching the PDF 065-0296). Fig. 2 shows HR-TEM images and selective area electron diffraction pattern (inset) of the Sn(C)-a core-shell composite. In Fig. 2a, we present a HR-TEM image of a single sphere-like tin-core particle covered with the carbon shell, while Fig. 2b demonstrates several tin-core particles that are enveloped with carbon shells. The average size of Sn(C) particles was estimated in the range of 40–200 nm and the carbon-shell thickness is around 10–15 nm. The energy dispersive X-ray spectra (not shown here) of these Sn(C)-a core-shell particles demonstrated peaks of carbon and tin at 0.1–0.3 keV and 3.0–4.1 keV, respectively, in the shell and core domains.

Fig. 3 shows the cyclic voltammetric behavior of the Sn(C) electrodes in a background solution (0.5 M NaCl) and in solutions containing various concentrations of TNT. These CVs show three well-pronounced reduction waves in the potential range of –0.50

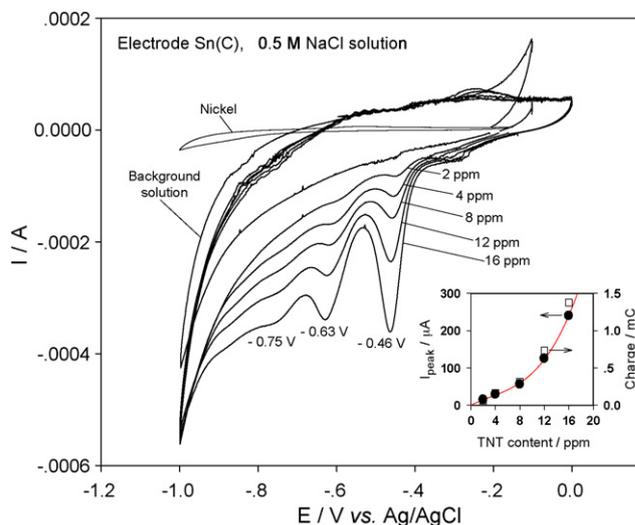


Fig. 3. Cyclic voltammograms (CVs) of a typical electrode comprising an as-prepared Sn(C) core-shell composite, in a 0.5 M NaCl background solution and in solutions containing TNT, as indicated. Solutions were purged with pure argon for 5–10 min prior to electrochemical measurements. The reference electrode was Ag/AgCl/Cl<sup>-</sup>, potential scan rate 10 mV/s. Each CV was recorded after a 30 min rest of the electrode at OCV. Cyclic voltammogram of a nickel electrode (nickel disk embedded in Teflon,  $S=0.08\text{ cm}^2$ ) in 0.5 M NaCl background solution is also shown. Potential scan rate 10 mV/s. Inset is calibration graphs of the voltammetric peak current and charge involved in the first TNT reduction wave, as function of the TNT content in solutions. The values of the current and the charge were calculated using subtraction fitting of the CorrView software. The solid line in this plot represents third order linear regression of the data (confidence interval was 95%).

to –0.80 V (vs. an Ag/AgCl reference electrode), which correspond to a multistep process of the TNT reduction on the Sn(C) electrode. As expected, the peak intensities increase when increasing the TNT content. The inset to this figure shows the calibration graphs of the voltammetric peak current and charge involved in the first reduction wave as a function of the TNT content in solutions; the charge was calculated by integration of the voltammetric peak current vs. time using CorrView software (charge – background fitting). The nickel substrate of the Sn(C) electrode is electrochemically inactive towards reduction of TNT. This is seen from a typical cyclic voltammogram of a Ni electrode in a background NaCl solution (Fig. 3) and

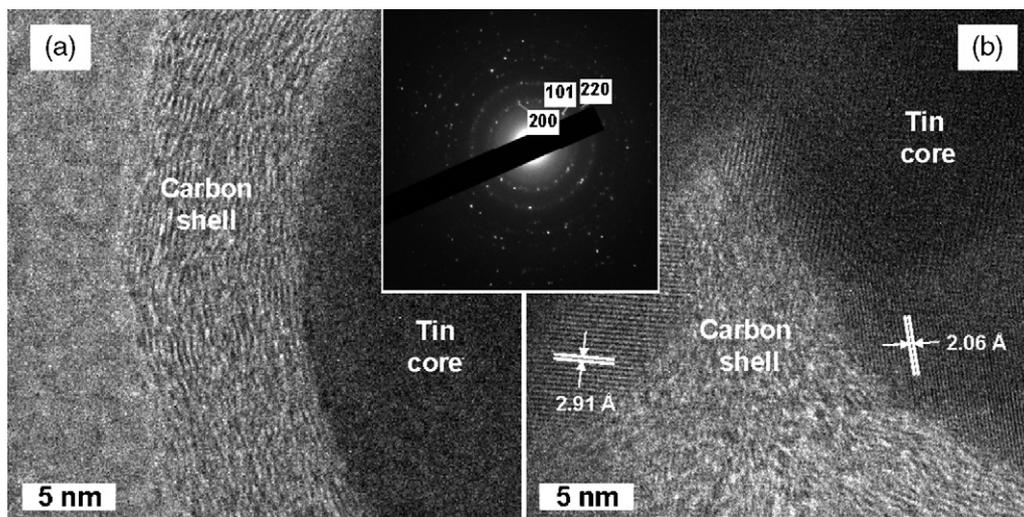
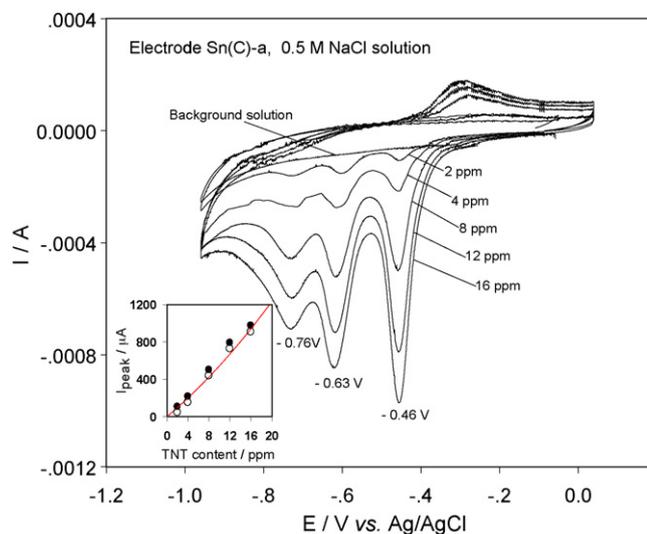


Fig. 2. HR-TEM images of the core-shell tin-carbon compound annealed at 800 °C for 6 h under argon. (a) A single sphere-like tin-core particle covered with the carbon shell; (b) several tin-core particles that are enveloped with the carbon shell. Values of  $d$  spacing related to the [200] and [220] XRD reflections are indicated. Inset is the selective area electron diffraction pattern of the tin-carbon core-shell composite.

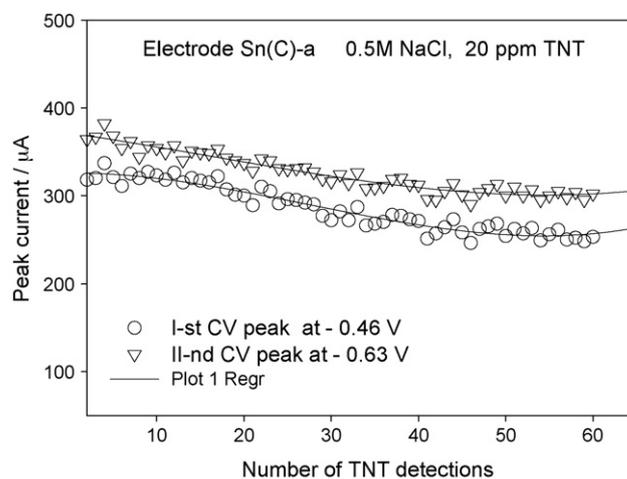


**Fig. 4.** Cyclic voltammograms obtained in a 0.5 M NaCl background solution and in solutions containing TNT, as indicated, from a typical electrode comprising tin–carbon core–shell composite Sn(C)-a annealed at 800 °C under argon. Solutions were purged with pure argon for 5–10 min prior to electrochemical measurements. The reference electrode was Ag/AgCl/Cl<sup>-</sup>, potential scan rate 10 mV/s. Each CV was recorded after a 30 min rest of the electrode at OCV. Inset shows the first cathodic peak current (at -0.46 V) as a function of the TNT content in solutions. Open symbols relate to currents calculated after subtraction of the CV recorded in a background solution while filled symbols reflect the unsubtracted results. The solid line in this plot represents second order linear regression of the data (confidence interval was 95%).

from similar featureless CVs (not shown here) recorded in solutions containing TNT.

We have found that Sn(C) electrodes demonstrate a stable electrochemical behavior for the TNT reduction in NaCl solutions. This was revealed by consecutive CVs of Sn(C) electrodes measured every hour in TNT solutions. Remarkably the Sn(C) electrodes remain stable towards TNT reduction after 24 h rest of the electrode at OCV. This was established by comparison of the CV peak currents as a function of the time interval between each TNT detection. It should be noted that the peak potentials related to the first and second reduction waves also remain stable upon prolonged cycling or prolonged storage of electrodes at OCV.

Fig. 4 shows a family of CVs measured from a Sn(C)-a electrode (comprising annealed core–shell tin–carbon particles) in a background solution and in solutions containing various concentrations of TNT. Comparison of these results with those of Sn(C) electrodes comprising the as-prepared tin–carbon particles (Fig. 3) clearly shows that the Sn(C)-a electrode demonstrates a faster electrochemical kinetics and increased activity towards TNT reduction. Higher voltammetric peak currents and more pronounced second and third reduction waves at the same TNT concentrations of this Sn(C)-a electrode may be attributed to the state of the electrode surface due to stabilization of the carbon shell during annealing of the material at high temperature. It is suggested that annealing of tin–carbon core–shell particles under an inert atmosphere results in removal of various functional groups on the carbon shell which may detrimentally influence the catalytic activity of the surface and adsorption of TNT molecules needed for promotion of their reduction. The inset to Fig. 4 shows the dependence of the voltammetric peak current (at -0.46 V) on the TNT content in solutions; open symbols in this plot relate to peak currents calculated after subtraction of the CV measured in a background solution while filled symbols reflect the unsubtracted results. The solid line in this graph represents the linear regression of the data.

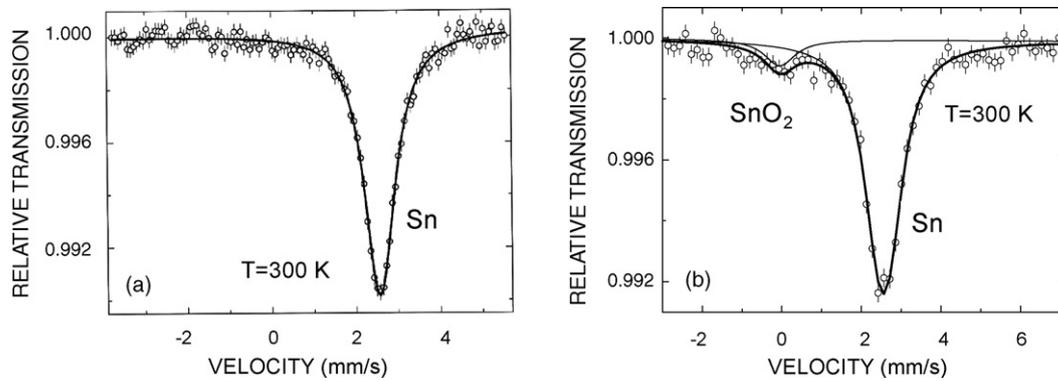


**Fig. 5.** Voltammetric peak currents of the Sn(C)-a electrode as a function of number of TNT detections. Each cyclic voltammogram was recorded every 3 min. Concentration of TNT was 20 ppm. Potential scan rate was 10 mV/s. Symbols are experimental results of the peak currents, while solid lines represent regressions of the data (confidence interval was 95%).

In Fig. 5, we present the results of a typical experiment of repetitive voltammetric TNT detection on the Sn(C)-a electrode, plotted as peak currents vs. number of detections (each CV was measured every 3 min in a solution containing 20 ppm TNT).

We can conclude that electrodes prepared from the annealed tin–carbon material, Sn(C)-a also exhibit electrochemically stable behavior, and provide sufficient reproducibility with no surface fouling through prolonged voltammetric cycling in TNT solutions. We focused on studies of the electrodes comprising Sn(C) particles annealed in argon at high temperatures, because it could be possible that further annealing of the as-prepared tin–carbon particles would be needed in order to stabilize their carbon shell for prolonged and repeated electrochemical measurements. Our experiments showed that electrodes made from both as-prepared Sn(C) and annealed Sn(C)-a particles demonstrated high electrochemical activity and stability towards TNT reduction. The stability of the tin–carbon particles is also reflected by their Mössbauer spectroscopy, as presented in Fig. 6. Despite the exposure of the Sn(C) particles to air, their Mössbauer response shows that the tin in the core is in its pure metallic form. As seen in this figure, the Mössbauer response of Sn(C) particles scraped from the electrodes after prolonged electrochemical reduction of TNT by repeated voltammetric measurements (more than 60 TNT detections recorded every 3 min), shows that the core remains mostly metallic tin, a small part of which was connected to SnO<sub>2</sub>. We suggest that the carbon shell of some of the particles may swell solution and hence allow some of the tin to react with solution species, thus forming tin oxides and hydroxides. However, it is clear from the results thus obtained that the core–shell structure, which includes a stable interface between metallic tin in the core and a thin carbon in the shell is well retained upon voltammetric cycling, and allows a steady catalytic response of the tin–carbon electrodes during repeated TNT reduction cycles, as will be discussed further on.

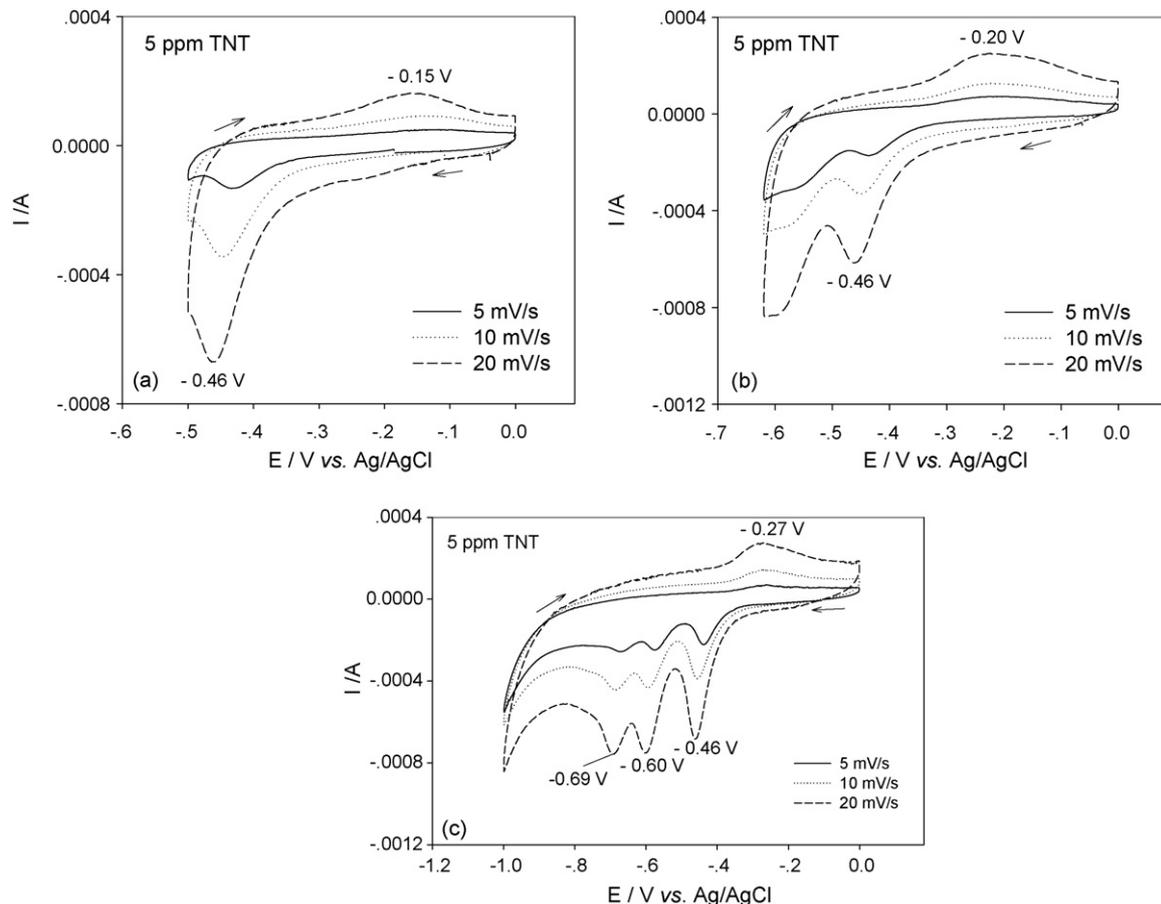
From the electrochemical data thus obtained, it is clear that the reduction of TNT on these core–shell tin–carbon electrodes is an electrochemically irreversible process. However, a partial oxidation of the TNT reduction products in CV measurements occurs at around -0.20 V, as evidenced by the broad peaks appearing during the course of the anodic scan, as seen in Fig. 3. Fig. 7 shows cyclic voltammograms of Sn(C)-a electrodes in TNT solutions measured at different potential scanning rates, where cathodic limits were set at



**Fig. 6.** Mössbauer spectra of pristine Sn(C) core-shell particles (a) and of particles scraped from Sn(C) electrodes after several voltammetric cycles of electrochemical reduction of TNT (b). The isomer shift,  $IS=2.56$  mm/s, is typical of metallic tin, while the  $IS=0.05$  mm/s (the second, smaller peak in (b), relates to  $SnO_2$ ).

–0.50, –0.62 and –1.0 V (Fig. 7a–c, respectively). We have to mention that in this experiment we used the same Sn(C)-a electrode after prolonged voltammetric TNT detection, which demonstrated a remarkable stable behavior (Fig. 5). It is clear from these measurements that the anodic peak around –0.2 V relates to the first cathodic process of TNT, around –0.46 V. We suggest that the potential shift (–0.2, –0.15, and –0.27 V) of the anodic peak in different potential limits can be explained as follows: When cathodic limits of the voltammetric measurements were set first at –0.50 V, then at –0.62 V and, finally at –1.0 V (Fig. 7a–c, respectively), the reduction of TNT results in different reduction products due to the fact that the reduction of polynitro aromatic compounds is a multistep process.

For instance, by setting the cathodic limit at –0.50 V, only the first reductive wave is realized with a cathodic peak at –0.46 V and the hydroxylamine species can be formed at this step. In a multistep reduction process, such products as amine or nitroso-compounds *via* hydroxylamine derivatives can be formed [2]. Accordingly, these different TNT reduction products can be oxidized differently at the anodic potentials ranged from –0.15 to –0.27 V that is reflected by broad anodic peaks in CVs of Fig. 7a–c. Measuring the dependence of the peak currents in the CVs related to the first and second TNT reduction processes (–0.46 and –0.63 V, see Figs. 3 and 7), on the potential scanning rate, shows a linear correlation between  $I$  and  $\nu$  in the logarithmic scale:  $d(\log I)/d(\log \nu) \rightarrow 1$ . This finding means



**Fig. 7.** Voltammetric behavior of an Sn(C)-a electrode in potential ranges of 0 → –0.50 V (a), 0 → –0.62 V (b), and 0 → –1.0 V (c) at different potential scanning rates (indicated). Each CV was recorded after a 30 min rest of the electrode at OCV. The TNT content was 5 ppm in the aqueous 0.5 M NaCl solution (reference electrode Ag/AgCl/Cl<sup>–</sup>). In this experiment, we used the same Sn(C)-a electrode that underwent prolonged voltammetric TNT detection and demonstrated a remarkable stable behavior (Fig. 5).

that the electroreduction of TNT at the Sn(C) electrodes is not diffusion controlled. Hence, the rate determining steps (RDS) may relate to the catalytic charge transfer on the electrode's surface. Such RDS may involve the adsorption of the active species from solution as critical stages. We have calculated the Sn(C) electrode surface coverage  $\Gamma$  using the Laviron's equation [25]:

$$I_{\text{peak}} = \frac{n^2 F^2 S \Gamma \nu}{4RT},$$

where  $S$  is the electrode geometric area ( $\text{cm}^2$ );  $I_{\text{peak}}$  is the peak current (A);  $\nu$  is potential scan rate ( $\text{V s}^{-1}$ );  $F = 9.65 \times 10^4 \text{ C mol}^{-1}$ ;  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $n$  is the number of electrons taking part in the electrochemical reaction ( $n = 6$ );  $T = 298 \text{ K}$ .

From Fig. 3, for the solution containing 16 ppm TNT, and for the first TNT reduction peak,  $I_{\text{peak}}$  was around  $400 \times 10^{-6} \text{ A}$ , while the scan rate was  $\nu = 10 \times 10^{-3} \text{ V s}^{-1}$ . Our calculations give a surface coverage of  $\Gamma = 1 \times 10^{-9} \text{ mol cm}^2$ , or  $10^{-3} \mu\text{mol cm}^2$ . We take into consideration that the number of molecules in 1 mol is  $6.022 \times 10^{23}$  (the Avogadro's number) and  $1 \mu\text{mol}$  contains  $6.022 \times 10^{17}$  molecules. We assume that TNT molecules may be oriented vertically on the electrode surface (with two nitro-groups close to the surface) and that they tend to form  $\pi$ -stacks with each other. In that case, the projection area ("length" multiplied by "width") of the TNT molecule on the electrode can be estimated as  $(12.5 \text{ \AA} \times 2 \text{ \AA}) = 25 \text{ \AA}^2$ . We take into account the following appropriate dimensions of the projection of the TNT molecule on the electrode: the total "length" is around  $7.2 \text{ \AA}$  [26] plus additional  $4\text{--}5 \text{ \AA}$  due to steric effects of the TNT molecules. The "width" of the TNT molecule was estimated as  $2 \text{ \AA}$ . Therefore, the area of  $1 \mu\text{mol}$  is  $25 \times 6 \times 10^{17} (\text{ \AA}^2)$  or  $150 \times 10^{17} \times 10^{-16} \text{ cm}^2 = 1500 \text{ cm}^2$  or  $1.5 \text{ cm}^2$  for  $\Gamma = 10^{-3} \mu\text{mol}$  (the  $\Gamma$  value calculated from the Laviron's equation). Taking into account that the BET specific surface area of the Sn(C) material is  $8 \text{ m}^2/\text{g}$ , the active area of a typical electrode, which contains  $2 \text{ mg}$  active mass, is  $160 \text{ cm}^2$  (ignoring the influence of the complex composition of the electrode, which comprises both Sn(C) and PVdF binder). Based on the above, the electrode's surface coverage is estimated to be  $\theta = 1.5/160 = 0.0094$ , around  $0.94\%$ . For the Sn(C)-a electrode containing annealed tin-carbon core-shell particles, the surface coverage can be estimated as  $\theta = 2.5\%$ , as higher CV currents are measured with these electrodes at the same TNT content in solutions (Fig. 4). The higher value of the surface coverage on the tin-carbon electrodes comprising annealed particles indicates most likely that adsorption of TNT molecules to the active mass may be more facilitated after heat treatment of the material at elevated temperatures, due to removal of surface groups (which is an evident consequence of heating carbonaceous materials in inert atmosphere).

It should be mentioned that trace oxygen reduction is an obvious side reaction in the electrochemical systems described here. Indeed, a first cathodic polarization of Sn(C) and Sn(C)-a electrodes in solutions containing TNT shows a cathodic peak at  $-0.25 \text{ V}$ , which belongs to oxygen reduction. This was verified by reference measurements with solutions containing initially trace  $\text{O}_2$  that was further removed by purging the solutions with pure argon. It is important to note that the reduction of trace oxygen on Sn(C) and Sn(C)-a electrodes occurs at relatively low negative potentials, higher by more than  $200 \text{ mV}$  than the reduction potentials of TNT. This phenomenon seems to be unusual since on regular carbon electrodes, trace oxygen in aqueous solutions is normally reduced at potentials around  $-0.80 \text{ V vs. Ag/AgCl/Cl}^-$  ([17] and references therein) Hence, it is clear that the Sn(C) and Sn(C)-a electrodes exhibit pronounced catalytic activity towards oxygen reduction. This capability of these newly developed tin-carbon electrodes definitely deserves further study due to the importance of  $\text{O}_2$  reduction reactions in so many applications. Sensitivity of the

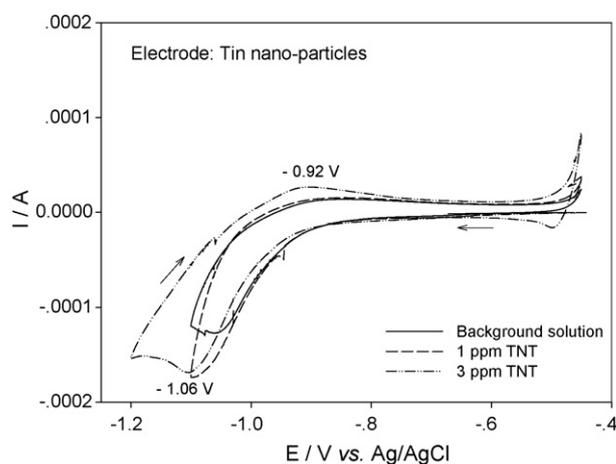
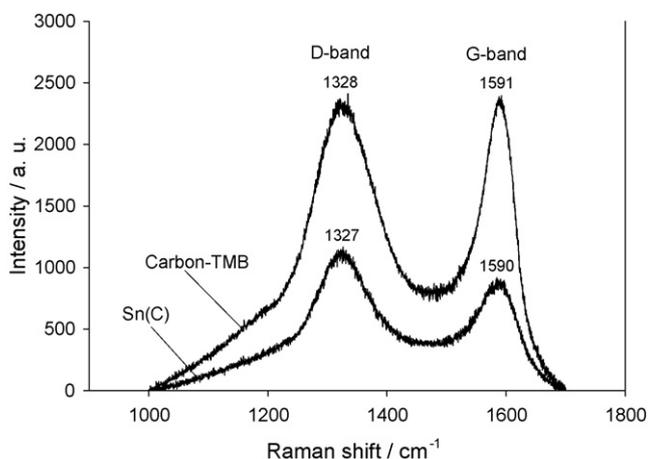


Fig. 8. Typical CVs of an electrode comprising tin nanoparticles, in a  $0.5 \text{ M NaCl}$  solution and in solutions containing 1 and 3 ppm of TNT. Reference electrode  $\text{Ag/AgCl/Cl}^-$ , potential scan rate  $20 \text{ mV/s}$ .

TNT detection ( $dI_{\text{peak}}/dC$ ,  $C$  is the TNT content in solution,  $I_{\text{peak}}$  is the maximal current of the first reduction peak at  $-0.46 \text{ V}$ , calculated by subtraction of the background current) is estimated to be about  $150\text{--}200 \mu\text{A/ppm}$  for the Sn(C)-a electrodes, as follows from cyclic voltammetry at relatively high potential scan rates ( $50\text{--}150 \text{ mV/s}$ ).

The most important questions to be clarified in this work relate to the role of the tin nanoparticles, which constitute the core of the Sn(C) particles, and to the function of the carbon shell for the reduction process of TNT in aqueous solutions? In order to answer these questions, TNT reduction, in the same solutions, was also explored with electrodes comprising tin-nanoparticles (average size  $100 \text{ nm}$ ) as the only active mass, and with electrodes comprising carbon particles produced by the RAPET technique from a tetra-methylbenzene (TMB) precursor, using the same conditions as for the preparation of the Sn(C) core-shell particles. Fig. 8 presents typical CVs of the electrode prepared from tin nanoparticles, in a  $\text{NaCl}$  background solution and in this solution containing 1 and 3 ppm of TNT. These cyclic voltammograms show anodic peak at  $-0.92 \text{ V}$  and an oxidation wave at around  $-(0.60\text{--}0.47) \text{ V}$ , which can be assigned to the formation of Sn(II) and Sn(IV) oxides or hydroxides, respectively [27]. Tin oxides and hydroxides can be further reduced during the cathodic scan with simultaneous evolution of hydrogen. In our experiments, the cathodic process was limited by less negative potentials than those needed for hydrogen evolution. The cathodic peak at  $-1.06 \text{ V}$  is related to the oxidation peaks at  $-0.92 \text{ V}$  and it is not associated with reduction processes of TNT. The formation of  $\text{SnO}_2$  species during TNT reduction on Sn(C) electrodes was definitely confirmed by studies of Mössbauer spectroscopy (Fig. 6) of particles scraped from the Sn(C) electrode after several voltammetric cycles of the electrochemical reduction of TNT. The results thus obtained clearly show that the tin nanoparticles alone have no catalytic effect on TNT reduction. In the next step, the role of the carbon shell was investigated. We have to mention that the electrochemical reduction of TNT on electrodes made from various carbons is well documented in the literature (see, for instance, reference [17]). From this viewpoint, it is important to emphasize that in our work, the idea was to select a carbonaceous material similar to the carbon, which constitutes the shell of the core-shell tin-carbon particles, and to test this material in reference measurements as an electrode's material for reduction of TNT. Thereby, the carbon for these reference measurements was synthesized from the tetramethyl-benzene precursor by the same RAPET technique that was used to prepare the Sn(C) material. This precursor was selected due to the similarity in its structure to that of

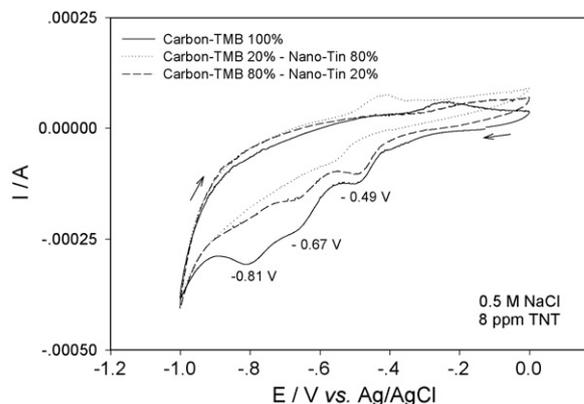


**Fig. 9.** Raman spectra of the Sn(C)-a core-shell particles and of carbon-TMB particles prepared from a tetra-methylbenzene precursor, which were subsequently annealed at 800 °C for 6 h, under argon.

the tetramethyl-tin precursor used for the synthesis of tin-carbon core-shell particles.

**Fig. 9** compares Raman spectra of Sn(C) core-shell particles and of carbon-TMB (both were annealed under argon at 800 °C for 6 h, after synthesis). It is assumed that carbon prepared from TMB, may have properties similar to those of the carbon shell of the Sn(C) particles, and therefore, maybe electrochemically active towards the reduction of TNT. We used Raman spectroscopy in these studies since the Raman spectra of carbons and carbon-comprising materials provide important structural information [28]. The Raman spectra of the Sn(C) core-shell and of the carbon-TMB particles contain two pairs of major bands. Peaks D and G around 1327 cm<sup>-1</sup> and at 1590 cm<sup>-1</sup> in these spectra can be attributed to the in-plane vibrations of sp<sup>3</sup> and sp<sup>2</sup> C=C bonds in disordered carbon and in crystalline graphitic carbon, respectively ([29] and references therein). The ratio of the Raman-band intensities ( $I_D/I_G$ ) was found to be 3.0 and 2.6 for the Sn(C)-a core-shell particles and for the TMB-based carbon, respectively. The average in-plane crystallite size ( $L_a$ ) of the carbon shell of the Sn(C)-a compound and that of the carbon-TMB were calculated to be 1.93 nm and 2.20 nm, respectively using the formulae  $I_D/I_G = C(\lambda)/L_a$  [29] where  $C(\lambda) = 5.8$  nm for an excitation line 632.8 nm of the He-Ne-laser used in our work. Hence, Raman spectroscopic measurements of these materials confirm that carbon shell and carbon obtained from TMB have similar crystalline structure. Will in that case electrodes prepared from carbon-TMB be electrochemically active towards TNT reduction?

**Fig. 10** shows a typical cyclic voltammogram of an electrode prepared from carbon particles synthesized from the tetramethylbenzene precursor, in a 0.5 M NaCl solution containing 8 ppm of TNT. As seen in the figure, this electrode is indeed electrochemically active in the reduction of TNT. Its voltammetric response exhibits three well distinctive reduction waves centered at -0.49, -0.67 and -0.81 V, respectively. Their locations are comparable with those recorded with the Sn(C) and Sn(C)-a electrodes shown in **Figs. 3, 4 and 6**, although they are shifted to more negative potentials, indicating a slower kinetics of the electrodes comprising carbon-TMB particles. It is remarkable that annealing of this carbon at 800 °C under an inert atmosphere does not influence the electrochemical activity of the material towards TNT reduction while is the case of the tin-carbon Sn(C)-a particles. **Fig. 10** also presents the CVs of two electrodes prepared from mixtures containing different amounts of carbon-TMB particles and tin nanoparticles. By comparing the voltammetric responses of electrodes prepared from these two mixtures, one can conclude that the electrode comprising 80%

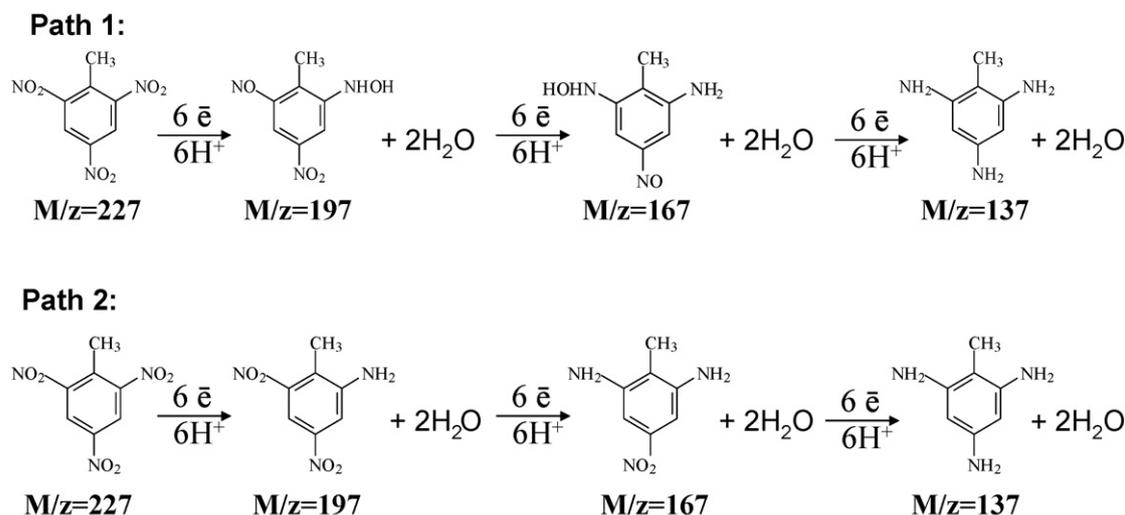


**Fig. 10.** Cyclic voltammograms (10 mV/s) of an electrode prepared from carbon-TMB particles synthesized from tetra-methylbenzene precursor and CVs of electrodes prepared from mixtures of carbon-TMB particles with tin nanoparticles. The TNT content in the 0.5 M NaCl solution was 8 ppm. Each voltammogram was recorded after a 20 min rest of the electrode at OCV.

of nano-tin and 20% of carbon particles is electrochemically inactive towards TNT reduction, while the electrode comprising much more carbon-TMB particles, 80%, and 20% of tin nanoparticles showed electrochemical activity towards TNT, which resembles that of the Sn(C) electrodes. The electrode comprising 20% of the tin nanoparticles is less active towards the reduction of TNT (the peak currents are smaller) compared to the carbon electrode. This can be related to the blocking of the electrode surface by tin nanoparticles, which were shown to be inactive in the electrochemical reduction of TNT.

In order to compare more closely the electroactivity of the electrodes made from carbon-TMB particles with those prepared from Sn(C) particles (**Figs. 10 and 3**, respectively), we have calculated the charges involved in the first CV reduction peaks at -0.49 V and at -0.46 V of these both electrodes, in solutions containing 8 ppm of TNT. Taking into account the specific surface areas of carbon-TMB particles (5 m<sup>2</sup>/g) and that of Sn(C) particles (8 m<sup>2</sup>/g), the normalized charges are 2.03 and 2.10 μC/cm<sup>2</sup> for these electrodes. Although the charges as well as normalized peak current densities of 0.36 and 0.38 μA/cm<sup>2</sup> of these electrodes are similar, the electrode comprising carbon-TMB particles demonstrates slower kinetics of the TNT reduction process. The studies described above clearly show that even though electrodes prepared from carbon-TMB particles are electroactive for TNT reduction, they are much less active towards electrochemical reduction than electrodes made from the annealed Sn(C)-a particles. We have found that for the last electrodes, the normalized charge involved in the first CV reduction peak (**Fig. 4**, solution containing 8 ppm TNT), is around 12.8 μC/cm<sup>2</sup>. Therefore, these core-shell particles have exclusive properties as electrode materials. It is established that the core (tin) is electrochemically inactive and the shell (carbon) possesses reduced catalytic activity for TNT reduction. The specific core-shell structure with tin in the core seems to activate the carbon shell, thus promoting it to a unique catalytic activity. This finding opens the door for further highly interesting work on electrocatalysis by composite materials with core-shell structure. The last state of the work reported herein relates to the analysis of TNT reduction products, which may enable us to sketch the reduction paths of this compound.

The solutions remained after TNT reduction experiments were analyzed by mass spectrometry. This analysis revealed the presence of compounds with  $m/Z = 197$ ,  $m/Z = 167$ , and  $m/Z = 137$  in the remaining solutions, obvious reaction products of TNT. We assume that the process may include two (from several possible) reduction paths, as indicated in the **Scheme 1**. In the first path, nitro-groups



1

**Scheme 1.** A Scheme of possible TNT reduction processes on core-shell tin-carbon electrodes.

of 2,4,6-trinitrotoluene can be reduced irreversibly by three six-electron transfers to 2,4,6-triaminotoluene *via* nitroso- and hydroxylamine derivatives as indicated by the masses of A ( $m/Z = 197$ ), B ( $m/Z = 167$ ) and C ( $m/Z = 137$ ). In the second path, each six-electron transfer may lead to the reduction of one nitro group to amino group resulting in the formation of compounds D, E, and F, which have the same  $m/Z$  values, as compounds A, B, and C, respectively. According to the results thus obtained, we suggest that the aqueous solution provides the necessary protons (Scheme 1) for these reduction steps as the only involvement in these reactions [22].

#### 4. Conclusions

The most significant finding of this work is that nitro-groups of TNT can be successfully reduced on a new type of electrodes based on tin-carbon particles with a *core-shell structure*. Using cyclic voltammetry, we have shown that these functional tin-carbon electrodes exhibit electrochemically stable and reproducible behavior for TNT reduction in NaCl solutions. It was demonstrated that tin nanoparticles, which constitute the core, are electrochemically inactive towards TNT reduction. Nevertheless, we suggest that tin or tin(II) oxide formed on tin-carbon electrodes during TNT reduction may participate in the electrochemical reaction as catalysts or carbon-modifying agents. It is therefore assumed that the specific core-shell structure with tin nanoparticles in the core seems to activate the carbon shell, thus promoting it to a unique electrocatalytic activity. Electrodes comprising tin-carbon particles annealed at 800 °C under argon demonstrate a faster electrochemical kinetics and increased activity towards TNT reduction. A scheme involving two possible paths of the reduction processes of TNT on tin-carbon electrodes was also proposed. We can conclude that the tin-carbon core-shell electrodes studied in this work may serve as amperometric sensors for the detection of trace TNT.

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#### References

- [1] K. Bratin, P.T. Kissinger, R. Briner, C. Bruntlett, *Anal. Chim. Acta* 130 (1981) 295.
- [2] (a) J. Wang, R.K. Bhada, J. Lu, D. MacDonald, *Anal. Chim. Acta* 361 (1998) 85; (b) J.C. Chen, J.L. Shih, C.H. Liu, M.Y. Kuo, J. M. Zen, *Anal. Chem.* 78 (2006) 3752.
- [3] S.C. Schmelling, K.A. Gray, P.V. Kamat, *Environ. Sci. Technol.* 30 (1996) 2547.
- [4] J. Wang, *Anal. Chim. Acta* 485 (2003) 139.
- [5] J. Wang, *Anal. Chem.* 75 (2003) 935.
- [6] J. Wang, *Anal. Chim. Acta* 469 (2002) 253.
- [7] J. Wang, *Anal. Chem.* 74 (2002) 5919.
- [8] J. Wang, S.B. Hocevar, B. Ogorevc, *Electrochem. Commun.* 6 (2004) 176.
- [9] M. Krausa, A. Resnev (Eds.), *Vapor and Trace Detection of Explosives for Anti-Terrorism Purpose*, Kluwer, Dordrecht, The Netherlands, 2003.
- [10] M. Krausa, K. Schorb, *J. Electroanal. Chem.* 461 (1999) 10.
- [11] (a) A. Hilmi, J. Luong, *Anal. Chem.* 71 (1999) 873; (b) A. Hilmi, J. Luong, *Anal. Chem.* 72 (2000) 4677.
- [12] Y. Lu, *Talanta* 58 (2002) 9195.
- [13] E.A. Hutton, B. Ogorevc, S.B. Hocevar, F. Weldon, M.R. Smyth, J. Wang, *Electrochem. Commun.* 3 (2001) 707.
- [14] J.-C. Chen, J.-L. Shin, C.-H. Liu, M.-Y. Kuo, J.-M. Zen, *Anal. Chem.* 78 (2006) 3752.
- [15] B. Filanovsky, Y. Tur'yan, I. Kuselman, T. Burenko, A. Shenhar, *Anal. Chim. Acta* 364 (1998) 181.
- [16] (a) B. Filanovsky, *Rev. Anal. Chem.* 18 (1999) 293; (b) B. Filanovsky, US Patent 7,244,345 (2007).
- [17] J. Wang, *Electroanalysis* 19 (2007) 415.
- [18] H. Zhang, A. Cao, J. Hu, L. Wan, S. Lee, *Anal. Chem.* 78 (2006) 1967.
- [19] X. Luo, A. Morrin, A.J. Killard, M.R. Smyth, *Electroanalysis* 18 (2006) 319 (and references therein).
- [20] L. Wang, J. Bai, P. Huang, H. Wang, L. Zhang, Y. Zhao, *Electrochem. Commun.* 8 (2006) 1035.
- [21] S. Wang, X. Lin, *Electrochim. Acta* 50 (2005) 2887.
- [22] B. Filanovsky, B. Markovsky, T. Bourenko, N. Perkas, R. Persky, A. Gedanken, D. Aurbach, *Adv. Funct. Mater.* 17 (2007) 1487.
- [23] (a) L. Lu, H. Wang, Y. Zhou, S. Xi, H. Zhang, J. Hu, B. Zhao, *Chem. Commun.* 2 (2002) 144; (b) L.J. Fu, H. Liu, H.P. Zhang, C. Li, T. Zhang, Y.P. Wu, R. Holze, H.Q. Wu, *Electrochem. Commun.* 8 (2006) 1.
- [24] (a) S.V. Pol, V.G. Pol, A. Gedanken, *Chem. Eur. J.* 10 (2004) 446; (b) V.G. Pol, S.V. Pol, B. Markovsky, J.M. Calderon-Moreno, A. Gedanken, *Chem. Mater.* 18 (2006) 1512; (c) S.V. Pol, V.G. Pol, A. Gedanken, *Adv. Mater.* 18 (2006) 2023.
- [25] E. Laviron, *J. Electroanal. Chem.* 100 (1979) 263.
- [26] J.N. Barisci, G.G. Wallace, R.H. Baughman, *J. Electroanal. Chem.* 488 (2000) 92.
- [27] B.X. Huang, P. Tornatore, Y.-S. Li, *Electrochim. Acta* 46 (2000) 671.
- [28] A.C. Ferrari, *Solid State Commun.* 143 (2007) 47.
- [29] Y. Ward, R.J. Young, R.A. Shatwell, *J. Mater. Sci.* 42 (2007) 5135.