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Carbon Electrodes Modified with TiO$_2$/Metal Nanoparticles and Their Application to the Detection of Trinitrotoluene**

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The preparation of modified, catalytically active, functional carbon electrodes and their application to the electrochemical reduction of trinitrotoluene (TNT) is reported. Modification of the electrodes is performed with composites of nanometer-sized, mesoporous titanium dioxide, which acts as a support containing inserted/deposited nanoparticles of ruthenium, platinum, or gold. These composites are prepared by a novel sonochemical synthesis using simple and low-cost precursors. Cyclic voltammetry shows that 2,4,6-trinitrotoluene can be reduced on thus-modified carbon-paper electrodes at potentials of around –0.5 V (vs. Ag/AgCl/Cl$^-$) in aqueous solutions. Unexpectedly, carbon-paper electrodes modified with the TiO$_2$/nano-Pt composites demonstrate a remarkable electrochemical activity toward the reduction of trinitrotoluene. A significant finding is that the two electrode processes—the reduction of TNT and of oxygen—are quite well separated in potential on the modified carbon-paper electrodes because of selective electrochemical activity of the TiO$_2$/nano-Pt and TiO$_2$/nano-Au composites. TiO$_2$/nano-Ru composites are found to be much less electrochemically active for the detection of TNT compared to the previous two. It was also established that the titanium dioxide support of TiO$_2$/nano-Pt composites plays a specific role for facilitating the TNT- and oxygen-reduction processes.

1. Introduction

An increased interest in the detection of explosive materials by means of various methods and techniques is seen nowadays as a consequence of recent efforts in the war against terrorism. The methods used for detection are gas- and liquid-chromatography, X-ray diffraction, neutron analysis, nuclear quadrupole resonance, etc., which may be indeed sensitive enough for detection. However, it is difficult to use some of these methods in practice because they require expensive and complicated equipment.[1,2] Electrochemical sensors (ESs) have several advantages in comparison with the above mentioned methods.[3–10] They are characterized by a reasonable sensitivity, low cost, and can be easily used for field detectors and remote control devices, due to the nature of the analytical signal. Limited sensitivity and specificity may be drawbacks of ESs. Various sensors for the detection of nitroaromatic compounds (NACs) have been developed so far. For instance, Wang and co-workers[3–6] have used bare carbon and boron-doped diamond-based sensors, which are compact, portable, stable, and not expensive, for the detection of NACs. Krausa et al.[7,8] developed an electrochemical sensor based on a bare gold electrode but its sensitivity was also not satisfactory. Chemically modified electrodes are, in general, successfully used in traces analysis.[9–11] Detection of traces of explosives using these electrodes is described in the literature.[12,13] By using Hg-film[12] and carbon/HgI$_2$[13] electrodes as the ES, the sensitivity of detection of NACs can be increased more than 4–5 times in comparison with the abovementioned techniques. However, these sensors are not environmentally friendly since they contain Hg. Recently, Hilmy[11] compared the electrochemical behavior of several NACs on bare glassy carbon, platinum, nickel, gold, and silver electrodes and established that Au, Ag, or Ag/Au electrodes are useful for the amperometric detection of NACs with a detection limit of about 70–110 ppb. At the same time, Pt and Ni bare electrodes displayed progressively reduced peaks with each cycle indicating the deactivation of the electrodes.[11] Using electrodes modified with nanoparticles of transition metals and precious metals, which have specific properties compared to that of the bulk materials, opens new ways for their application as electrochemical sensors and multifunctional reagents as well as in catalysis.[14–18]

We have found recently that modification of carbon with nanoparticles of noble metals is a promising approach for obtaining highly catalytically active electrodes for the detection of traces of aromatic compounds. The aim of this work was to

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study the electrochemical reduction of trinitrotoluene on carbon electrodes modified with catalytically active composites of mesoporous titanium dioxide (support) containing inserted/deposited nanoparticles of ruthenium, platinum, or gold. To the best of our knowledge, there are no reports in the literature on such types of modified electrodes and their application for the electrochemical detection of nitro-compounds.

2. Results and Discussion

Table 1 presents data on the active surface area and porosity measurements of the mesoporous TiO_2 and the composites containing ruthenium, platinum, or gold nanoparticles. It should be noted that fabrication and insertion/deposition of nanometer-sized metal powders into/on the TiO_2 nanoparticles take place simultaneously. The metal nanoparticles formed during the collapse of the ultrasonic bubbles near the solid particles (TiO_2) are deposited on their surfaces and into the pores of the TiO_2 nanoparticles. As a result, the metal nanoparticles of Ru, Pt, or Au are anchored to the TiO_2. As was expected, insertion/deposition of these metal particles into/on the TiO_2 particles via a sonochemical synthesis results in reducing the specific surface area, pore volume, and pore size of the TiO_2 due to a partial blocking of the pores. The changes in pore volume and pore size of the mesoporous TiO_2 due to insertion of the nanoparticles, are more noticeable for the TiO_2/nano-Ru composite, than for the TiO_2/nano-Pt and TiO_2/nano-Au samples (Table 1). This phenomenon could be assigned to the difference in metal–support interactions of titanium dioxide and the inserted metal. These interactions increase with the reactivity of the metals towards oxygen, and are stronger for Ru on TiO_2 than for both Pt and Au, which behave similarly on the mesoporous TiO_2.[19] Probably, strong metal–support interactions cause the incorporation of a substantial part of ruthenium nanoparticles into the pores of titanium dioxide resulting in their higher blocking compared to the platinum and gold nanoparticles.

Table 1. Specific surface area measured by gas adsorption using the BET method, pore volume and pore size of TiO_2 and its composites with ruthenium, platinum, and gold nanoparticles.

Composites [a]	Surface area [$m^2\,g^{-1}$]	Pore volume [$mL\,g^{-1}$]	Average pore size [Å]
TiO_2	850	0.47	25
6%Ru/TiO_2	273	0.13	15
6%Pt/TiO_2	280	0.20	18
6%Au/TiO_2	242	0.20	20

[a] All metal/TiO_2 composites contained about 6 % precious metal (w/w), resulting from the reagents ratio in the synthesis, which was established by EDAX measurements.

One of the advantages of the sonochemical method is that ultrasound irradiation results in producing homogeneous coatings by highly dispersed nanoparticles having a narrow size distribution. It should also be emphasized that the physical parameters (surface area, pore volume, and pore size) of TiO_2/nano-metal composites when the metal is platinum or gold, are supposed to be stable under various reaction conditions due to a relatively low sensitivity of platinum and gold to bulk oxidation.[20]

A typical high-resolution scanning electron microscopy (HRSEM) image of the modified carbon paper impregnated with TiO_2/nano-Pt composites (see Experimental section) is shown in Figure 1, which demonstrates a snowflake-like morphology with quite uniform distribution of the composites on the carbon paper. The inset in this figure exhibits several nanometer-sized TiO_2/nano-Pt composites spread on a single fiber of the carbon paper. It was found from energy-dispersive X-ray analysis (EDX) that an average loading of these composites is 7.5 µg of Pt per 1 cm^2 of the geometric area of the carbon paper (i.e., 6.3 mg of TiO_2 and 380 µg of Pt per 1 g of carbon paper).

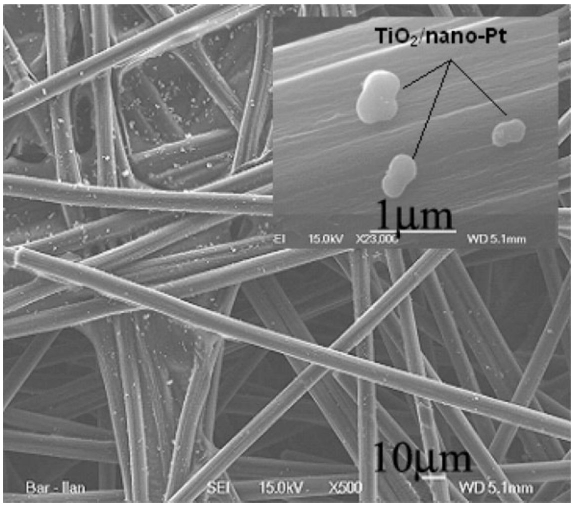


Figure 1. HRSEM image of a typical sample of modified carbon paper impregnated with nanometer-sized TiO_2/nano-Pt composites. The inset shows several nanometer-sized TiO_2/nano-Pt composites spread on a single fiber of the carbon paper.

Figure 2a–c presents high-resolution transmission electron microscopy (HRTEM) images of the TiO_2 composites (an average size of 200 nm) with inserted/deposited nanoparticles (2.5 nm) of ruthenium, gold, and platinum, respectively. These particles are inserted into pores of the TiO_2 substrates and are also uniformly deposited on them.

Figure 3 presents cyclic voltammograms of the bare carbon-paper electrodes in a reference (background) solution and in solutions containing various concentrations of TNT (indicated). Figures 4, 5, and 6 show CVs of the carbon-paper electrodes modified with TiO_2/nano-Ru, TiO_2/nano-Au, and TiO_2/nano-Pt composites, respectively. In the reference solution and in TNT solutions of various concentrations, the CVs of the carbon-paper electrode are characterized by a broad peak at –0.75 V, which can be ascribed to the reduction of trace oxygen. As seen in these figures, the TNT (at various concentrations) is reduced at potentials around –0.5 V.

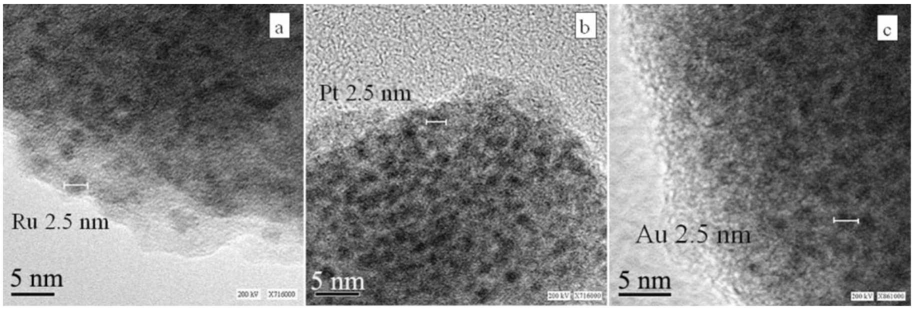


Figure 2. HRTEM images of sonochemically synthesized composites of mesoporous, nanometer-sized TiO_2 particles, containing inserted in/deposited on nanoparticles of noble metals (6 %, w/w): a) TiO_2-nano-Ru; b) TiO_2-nano-Pt, c) TiO_2-nano-Au. The scale bar is 5 nm and appears on each image. An average size of the metal nanoparticles is marked in the images.

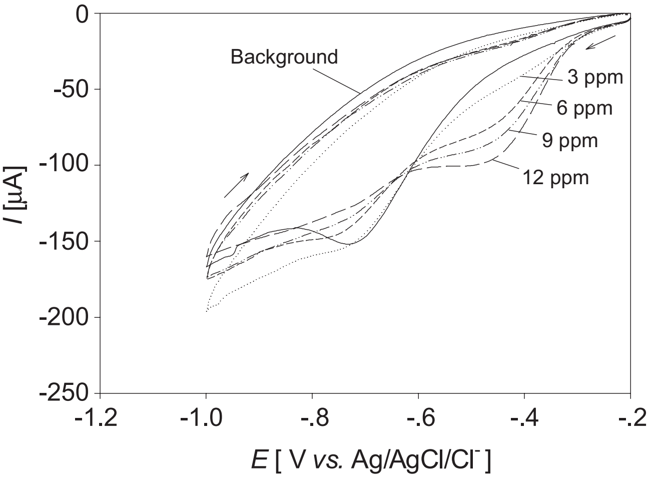


Figure 3. Cyclic voltammograms (CVs) obtained from the bare carbon-paper electrode in a background solution and in solutions containing various concentrations of the TNT, as indicated. A background solution contained ethanol and ethylene glycol (1:1, by volume) and 0.1 M KCl; the water content was 30 %, pH 9. The potential scan rate was 10 mV s^{-1} and an Ag/AgCl/3.5 M KCl reference electrode was used.

The CVs of the carbon-paper electrode modified with TiO_2/nano-Ru composites (Fig. 4) exhibit a broad peak around –0.7 V, which may relate to a superposition of the electrochemical reduction of trace oxygen and the TNT. Note that the peak current, in this case, depends only slightly on the concentration of the nitro-compound (even at higher concentrations of the TNT). For carbon-paper electrodes modified with the TiO_2/nano-Au composites (Fig. 5), the above two processes, namely those of the TNT and of the oxygen reduction, are well separated: the electrochemical reduction of the TNT is seen at a potential of about –0.5 V and oxygen reduction takes place at around –0.75 V. This figure also shows that the higher the concentration of the TNT, the more intensive are the peak currents developed with these modified carbon-paper electrodes. From this figure, the sensitivity for determination of the TNT in solution is estimated as 10 µA ppm^{-1}.

An important finding of this work is unexpected and pronounced electrochemical activity of the TiO_2 composites containing nanoparticles of platinum. The peak currents related to the electrochemical reduction of TNT at potentials around –0.50 V to –0.55 V, are proportionally dependent on the concentration of the nitro-aromatic compound in solution (Fig. 6). On carbon-paper electrodes modified with TiO_2/nano-Pt composites, the electrochemical reduction of oxygen takes place at ca. –0.8 V. Removal of trace oxygen from solution (by purging pure argon through it) results in a diminishing of the above peak at –0.8 V, as clearly seen in Figure 6, dashed line. When the electrochemical cell was opened to the air again, the oxygen reduction peak emerged and was present in further CV measurements in air. The sensitivity of the TNT reduction process with TiO_2/nano-Pt composites is estimated as 40 µA ppm^{-1}, which is much higher than that obtained with TiO_2/nano-Au modified electrodes. In control experiments of carbon paper electrodes modified only with nano-Pt particles or with TiO_2, containing no Pt, the sensitivity for TNT reduction is much smaller compared to electrodes modified with TiO_2/nano-Pt composites (see Fig. 7).

It should also be noted that the reduction of TNT on the carbon-paper electrodes modified with TiO_2/nano-Pt composites is probably a multistep process, which includes several consecutive stages. There is some data in the literature regarding mechanisms of the electrochemical reduction of nitro-aromatic compounds.[21] It is suggested that in aqueous solutions electrochemical reduction results in the formation of hydroxylamine derivatives, which can be further reduced to the amine derivative (at higher potentials). Also, oxidation of the hydroxyl-

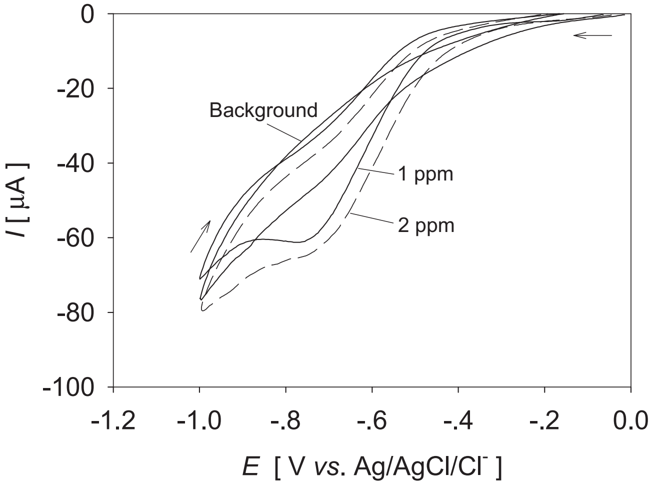


Figure 4. CVs obtained from a carbon-paper electrode, modified with TiO_2/nano-Ru particles in a background solution and in solutions containing 1 and 2 ppm of the TNT, as indicated. The background solution contained ethanol and ethylene glycol (1:1, v/v) and 0.1 M KCl; the water content was 30 %, pH 9. The potential scan rate was 10 mV s^{-1} and an Ag/AgCl/3.5 M KCl reference electrode was used.

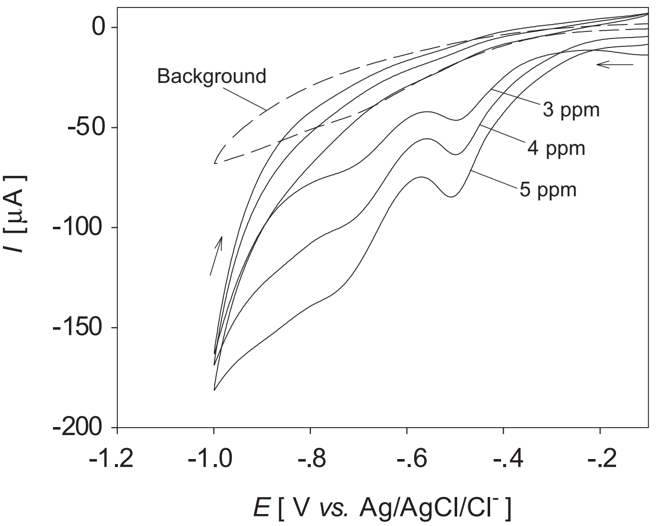


Figure 5. CVs recorded from a carbon-paper electrode, modified with TiO_2/nano-Au particles in a background solution and in solutions containing various concentrations of TNT, as indicated. The background solution contained ethanol and ethylene glycol (1:1, by volume) and 0.1 M KCl; the water content was 30 %, pH 9. The potential scan rate was 10 mV s^{-1} and an Ag/AgCl/3.5 M KCl reference electrode was used.

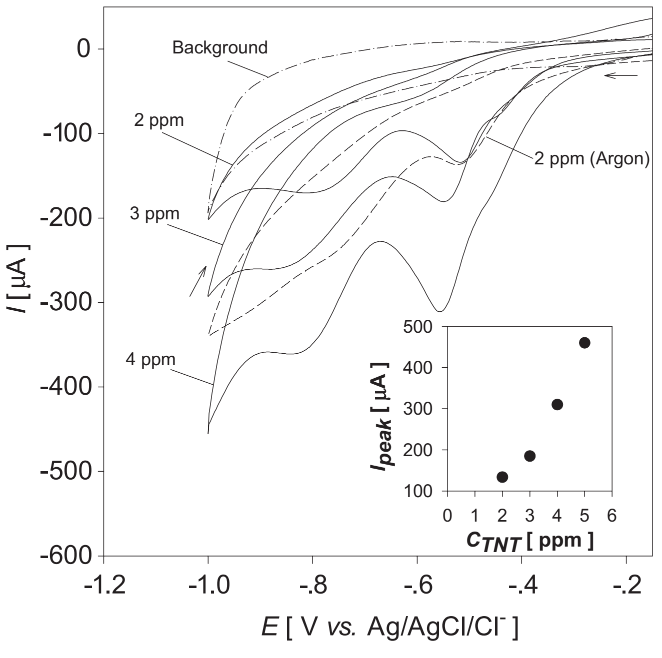


Figure 6. CVs recorded from a carbon-paper electrode, modified with TiO_2/nano-Pt particles in solutions containing various concentrations of the TNT, as indicated. A CV obtained in a background solution is also presented. The background solution contained ethanol and ethylene glycol (1:1, v/v) and 0.1 M KCl; the water content was 30 %, pH 9. The dashed line is a CV obtained from the solution containing 2 ppm of TNT, purged with pure argon for 15 min prior to the measurements, in order to remove all traces of oxygen (as a result, the oxygen reduction peak diminishes). The potential scan rate was 10 mV s^{-1} and an Ag/AgCl/3.5 M KCl reference electrode was used. The inset shows a typical dependence of the CV peak currents (around –0.55 V) on the TNT concentration.

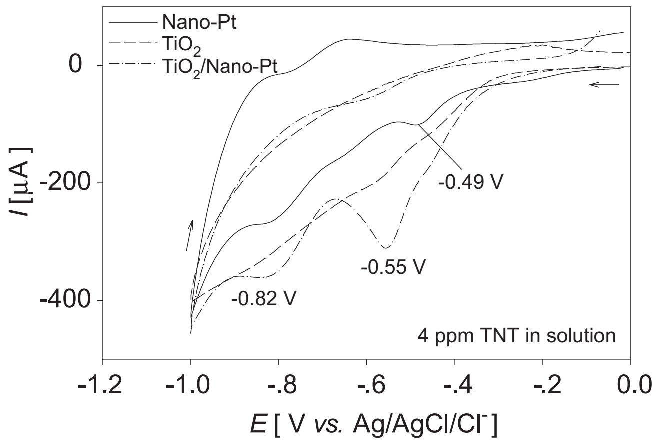
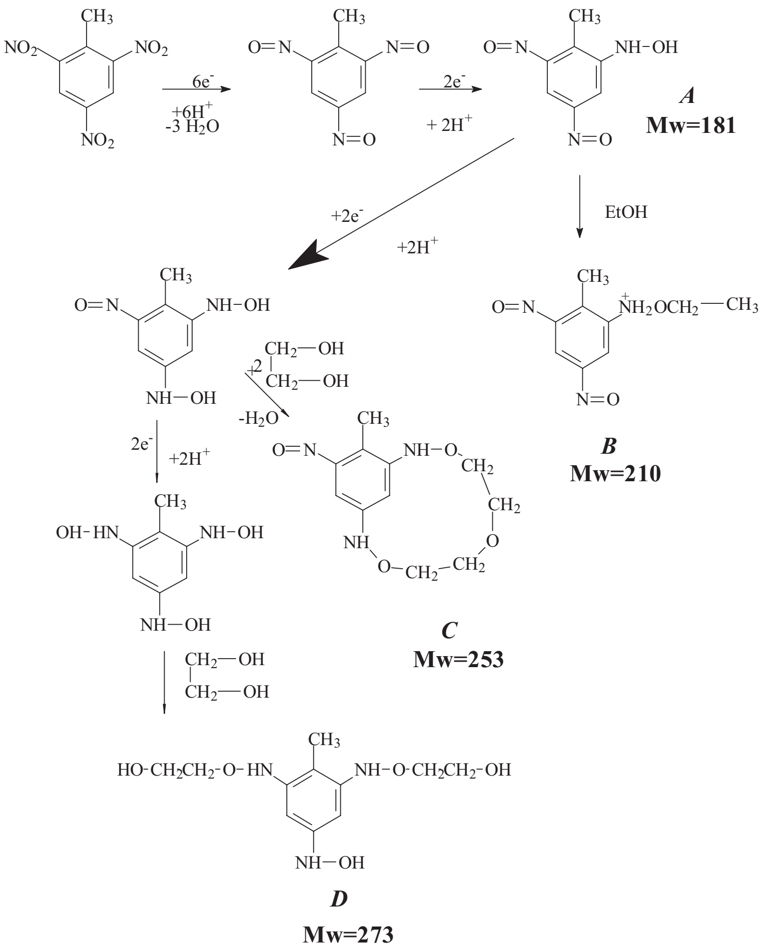


Figure 7. CVs obtained from carbon-paper electrodes modified with nano-Pt particles, embedded by sonication, and with TiO_2 particles comprising no Pt nanoparticles (as indicated) in a solution containing 4 ppm of TNT. The potential scan rate was 10 mV s^{-1} and an Ag/AgCl/3.5 M KCl reference electrode was used.

amine derivative may lead to the production of the nitroso derivative, which can then be reduced in a second cycle. It was proposed, for instance, that on a mercury-dropping electrode, the electrochemical process of reducing nitro-aromatic compounds consists of diffusion and adsorption of molecules, electron transfer, and formation of a radical anion which undergoes fast protonation.[22a]

On the basis of the results obtained in the present work we assume that the reduction process of TNT on the modified TiO_2/nano-Pt electrodes can be described by the following scheme. First, nitro groups of TNT are reduced to 2,4,6-trinitroso-toluene and then a hydroxylamine derivative **A** ($M_w = 181$), as indicated in Scheme 1, can be formed through three two-electron transfers. These processes correspond to a shoulder at –0.45 V and to the main reduction peak at –0.55 V in the CVs (Fig. 6). We assume also that in the protic electrolyte solution, hydroxylamine derivatives may react with one and/or two molecules of ethylene glycol of the background solution thus producing compounds **C** and **D** ($M_w = 253$ and $M_w = 273$, respectively). In addition, a compound **B** ($M_w = 210$) can be formed by reaction of the hydroxylamine derivatives with ethanol in solution, which is a mixture of ethylene glycol and ethanol, 1:1 by volume. A rigorous analysis by mass spectrometry (MS) of the solution remaining after the TNT reduction on a modified TiO_2/nano-Pt electrode revealed the presence of a compound with $m/Z = 253$ (the major peak of the spectrum), which corresponds to compound **C**. The presence of compounds with $m/Z = 181$, $m/Z = 210$, and $m/Z = 273$ (minor peaks), which correspond to compounds **A**, **B**, and **D**, respectively, was also observed. The proposed Scheme 1 is similar, on the whole, to that described in the literature for the TNT reduction on SiO_2-modified electrodes.[22b]

The electrochemical steps in the above Scheme 1 may not involve simultaneous reduction of all nitro groups, but rather can



Scheme 1. A scheme of the TNT reduction processes on the modified TiO_2/nano-Pt electrodes.

be stepwise, as may be evident by the broad reduction peak that does not reflect a single multielectron transfer event.

As seen in Figure 8, when the potential was limited cathodically to –0.60 V (i.e., the reduction process was limited to the first step), anodic potential scans demonstrate an oxidation peak which corresponds to the cathodic peak around –0.55 V. The wide peak-potential separation, the small charge involved in the anodic process compared to that of the cathodic process, and the behavior of these parameters on the potential scan rate, indicate that the electroreduction of TNT in these systems is highly irreversible. This irreversibility is due to the fact that the overall reduction process involves a series of reactions, part of which includes strong interactions of the reduction products with solvent molecules, as suggested by Scheme 1 based on our solution analysis. In any event, a detailed mechanistic study of the full electroreduction process of TNT is much beyond the scope of this work, which was focused on development of a sensor for TNT detection by relatively easy electrochemical measurements.

We emphasize that the results obtained with the TiO_2/nano-Pt composites could not be expected beforehand. Fortunately, the potential for hydrogen reduction on the highly dispersed platinum electrodes is much lower (more negative) than the potential of the TNT reduction. Thereby, this process of hydrogen reduction does not interfere at all with the reduction of TNT. Hence, the use of carbon electrodes modified with Pt nanoparticles, provides promising applications of this highly catalytically active functional material for new electrochemical sensors working in a wide range of cathodic potentials. It should be emphasized that the high sensitivity is obtained only by the combination of porous TiO_2 and Pt nanoparticles in modified carbon-paper electrodes. A similar phenomenon of an improved catalytic activity of rhodium on TiO_2 supports for the partial oxidation of methane has been recently described in the literature.[23]

3. Conclusions

In this work, we carried out a comparative study on the behavior of newly developed carbon-paper electrodes modified with TiO_2/nano-Ru, TiO_2/nano-Au, and TiO_2/nano-Pt composites, for the electrochemical detection of TNT. An unexpected high sensitivity for TNT electroreduction on carbon-paper electrodes modified with TiO_2/Pt nanoparticles was discovered. This finding can be successfully used in a new generation of electrochemical sensors, in particularly for the detection of traces of explosives (TNT), providing a reasonable sensitivity of the electrochemical reaction. In general, TiO_2/nano-Au and TiO_2/nano-Pt composites may be considered as promising electrocatalysts for a variety of electrochemical applications as well. The inertness of Au and Pt to massive oxidation processes may play an important role in their catalytic activity. It was interesting to find out that in the absence of a TiO_2 support, the platinum nanoparticles embedded in porous carbon exhibit less electrochemical activity for the TNT reduction process, compared to the TiO_2/nano-Pt composites. Hence, the TiO_2 substrate may play a specific role in enhancing the electrocatalytic activity of the platinum or gold nanoparticles. This issue deserves a further study.

4. Experimental

For the electrochemical reduction of TNT we used three-electrode cylindrical cells, comprising a carbon-paper working electrode (CPE), glassy carbon counter electrode, and Ag/AgCl/3.5 M KCl reference electrode. The geometric area of the working electrode was $0.3\ cm^2$. Typically, the electrochemical cells contained ca. $5\ cm^3$ of a solution. Carbon paper B-2 and glassy carbon SU-2000 were received from E-TEK Inc., USA and NEZ (Novocherkassk, Russia), respectively. The specific surface area of the carbon paper was $1.4\ m^2\,g^{-1}$ as measured by gas adsorption (Gemini 2375 analyzer from Micromeritics Inc., the BET model), and its bulk porosity was around 75 % [24]. The reference background solution was comprised of ethanol and ethylene glycol (1:1, v/v) and 0.1 M KCl; the water content was 30 %,

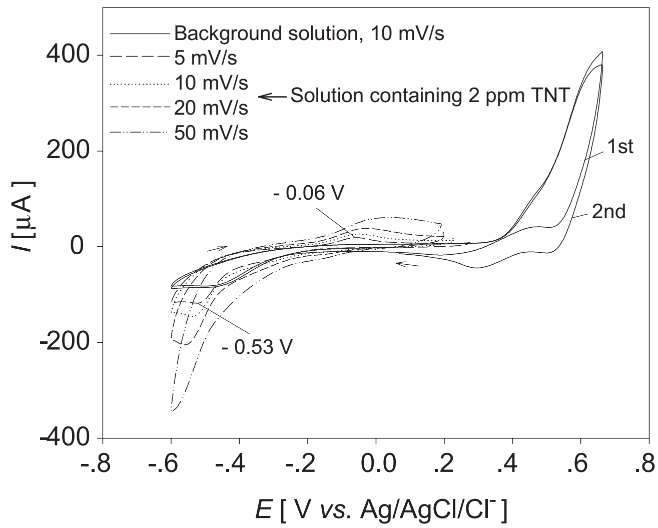


Figure 8. CVs recorded from a carbon-paper electrode, modified with TiO_2/nano-Pt particles in a background solution and in a solution containing 2 ppm of TNT, in the potential range –0.6 V to +0.6 V, at various scan rates. The background solution contained ethanol and ethylene glycol (1:1, v/v) and 0.1 M KCl; the water content was 30 %, pH 9. An Ag/AgCl/3.5 M KCl reference electrode was used.

pH 9. The concentration of 2,4,6-trinitrotoluene in solution varied in the range of 1–15 ppm. The electrochemical experiments by cyclic voltammetry were performed using a computerized multichannel potentiostat/galvanostat BTU-1470 from Solartron Analytical, driven by a CorrWare program (Scribner Associates, Inc.). CPEs were modified with composites containing ruthenium, platinum, or gold nanometer-sized particles (an average size around 2.5 nm) inserted in/deposited on the mesoporous TiO_2 anatase particles (around 200 nm in diameter). These composites were synthesized sonochemically as described elsewhere [20,25]. The insertion/deposition of metal nanoparticles (Ru, Pt, and Au) into/on TiO_2 was carried out by ultrasonic irradiation. For instance, TiO_2/nano-Ru composites were prepared as follows (using $RuCl_3$ as a precursor): 1 g of TiO_2 was added to 100 mL of 0.01 M $RuCl_3$ solution in ethylene glycol to form ca. 6 % (by weight) of the ruthenium on the TiO_2. The pH of this solution was adjusted to a value around pH 6 by dropwise addition of NaOH (10 % aqueous solution) and testing with a pH paper. A gas mixture containing 95 % Ar and 5 % H_2 was purged through the reaction solution for 1 h to remove all traces of oxygen. Then sonication was performed for 1 h under the same gas flow (Ti horn, 20 kHz, 100 $W\,cm^{-2}$ at 60 % efficiency). The sonication cell was placed in a water cooling bath (25–30 °C). The product was separated by centrifugation, washed three times with ethanol, and dried in vacuum overnight. The TiO_2/nano-Pt and TiO_2/nano-Au composites were prepared similarly in ethanol, using 0.01 M solutions of H_2PtCl_6 and $HAuCl_4$ as precursors, respectively. The content of noble metal in the TiO_2/metal composites was controlled by energy-dispersive X-ray analysis (EDX) using a JEOL-JSM 840 electron scanning microscope. The active surface area of nanometer-sized TiO_2 and of the corresponding composites was measured using a Micromeritics (Gemini 2375) analyzer and calculated using the Brunauer–Emmett–Teller (BET) model. Pore-size distribution was estimated according to the Barret–Joyner–Halenda model using the Halsey equation [26], and the pore volume was determined at the point $P/P_0 = 0.9947$. HRTEM images of as-prepared nanometer-sized metal composites were obtained using a JEOL-3010 electron microscope (300 kV accelerating voltage). Mass-spectrometric studies of solutions remaining after the TNT reduction, were carried out with a VG-AutoSpec Micromass mass spectrometer DCI (United Kingdom), and direct chemical ionization in methane was performed for molecular weight confirmation.

Modification of the carbon paper was carried out as follows: A small amount of a TiO_2/nano-metal composite (around 30–50 mg) was put in a glass vial containing 2–3 mL of a background solution [10] and was stirred in an ultrasonic bath, for 5–10 min. Several pieces of carbon paper were then immersed in the suspension thus obtained, stirred for several minutes, and then left unstirred overnight for impregnation. A typical HRSEM image of the carbon paper impregnated with TiO_2/nano-Pt composites is shown in Figure 1, which demonstrates a snowflake-like morphology with quite uniform distribution of the composites on the carbon paper. The inset in this figure exhibits several nanometer-sized TiO_2/nano-Pt composites spread on a single fiber of the carbon paper. It was found from EDX measurements that an average loading of these composites is 7.5 μg of Pt per 1 cm^2 of the geometric area of the carbon paper (i.e., 6.3 mg of TiO_2 and 380 μg of Pt per 1 g of carbon paper).

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