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ORIGINAL PAPER

Electrochemical synthesis and characterization of TiO_2-polyaniline composite layers

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Abstract The electrochemical formation of TiO_2-polyaniline (PANI) composite layers was studied by anodic polymerization of aniline in the presence of TiO_2 nanoparticles. The composite layers were investigated for their electrochemical, photoelectrochemical, and surface morphological characteristics. It was found that thick composite layers showed no photoresponse, whereas thin layers, prepared by a few potentiodynamic scans, have small photocurrents almost independent of the layer thickness. Due to the small photocurrents of the composite single-layers, bi-layered structures consisting of a first pristine PANI layer followed by an outer TiO_2-PANI composite layer were also studied. The bi-layered structures were found to have up to threefold larger photocurrents than the composite single layers. The TiO_2-PANI composite layers were additionally modified by deposition of platinum particles using galvanostatic electroreduction or photoreduction in the presence of hexachloroplatinate anions.

Keywords TiO_2 · Polyaniline · Composite layers · Photoelectrochemical response · Platinum photoreduction

1 Introduction

Conducting polymer materials are often used as a matrix for dispersing a variety of metal and metal oxide particles with the final aim of producing polymer-based composites with improved mechanical, electrical or photoelectrical properties. Various attempts have been made to incorporate TiO_2 nanoparticles in conducting polymer materials with the aim of obtaining composites with high conductivity [1], high piezoresistivity [2], high photoconductivity [3], improved battery storage characteristics [4] and corrosion protection properties [5] or for light image formation [6]. Most of the work in the field [1–3, 7–11] was performed by using chemical approaches for the synthesis of composite polyaniline (PANI) and polythiophene-based materials. Electrochemical synthesis has been used in a few studies, i.e., in the case of TiO_2/PANI [1, 6, 12] and TiO_2/polypyrrole [5, 13, 14].

The first attempt at electrochemical synthesis of the TiO_2/PANI composite was performed by electropolymerization of aniline in the presence of TiO_2 nanoparticles [6]. In a later work a more complicated multistep procedure involving polymerization of aniline and subsequent electrodeposition of TiO_2 is suggested [12]. In both cases there is scant information on the characteristics of the obtained composite layers. The first aim of the present work is an extensive study of the electrochemical, photoelectrochemical, and surface morphological characteristics of TiO_2/PANI composite layers obtained through electrochemical polymerization of aniline in the presence of TiO_2 nanoparticles. In the course of our work the investigation was extended to the electrochemical formation of bi-layered structures consisting of a first pristine PANI layer and a subsequent composite TiO_2/PANI layer. In the present study, we report on the photoelectrochemical behavior of both single- and bi-layer structures.

A further aim of our investigation relates to the possibility of modifying TiO_2/PANI composite layers with platinum particles. It is known that Pt/PANI composites have been studied in view of possible electrocatalytic applications, e.g., for oxidation of methanol [15, 16] and

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ethylene glycol [17, 18] or reduction of oxygen [19]. On the other hand Pt- modified TiO_2 layers have been successfully used for methanol electro-oxidation [20]. Thus the second aim of our study was to deposit platinum particles on the TiO_2/PANI composite layers by means of two approaches—photoreduction and galvanostatic electroreduction in solution containing hexachloroplatinate anions.

2 Experimental part

All experiments were performed in a three electrode set-up using platinum plates as counter electrodes and acid mercury/mercury sulfate reference electrodes (MSE). The working electrodes were graphite or stainless steel plates with surface area of about 2 cm^2. The stainless steel plates were pre-treated using a three component etching bath consisting of 13 v/v% HCl, 9 v/v% HNO_3, and 4 v/v% H_2SO_4. This procedure provided a reproducible surface roughness of the stainless steel surface. Platinum plates, ITO and reticulated vitreous carbon were also tested as working electrodes. A computerized potentiostat/galvanostat (PAR 263A) was used for the electrochemical measurements.

The synthesis of PANI layers was performed by potentiodynamic cycling between +0.42 and –0.63 V at 100 mV s^{-1} in aqueous solutions of 0.5 M H_2SO_4 and aniline—0.3 M for the composite single- and 0.1 M for the composite bi-layers. The incorporation of TiO_2 particles occurred in the course of polymerization, in the presence of 60 g l^{-1} of TiO_2 powder (P25, Degussa, Parsippany, NJ, USA) in the aniline solution under constant stirring. The thickness of the composite layers was controlled through the number of voltammetric scans. Two types of layer were produced: (1) TiO_2-PANI single-layers were produced by starting the electropolymerization in the TiO_2 particle containing solution; (2) PANI/TiO_2-PANI bi-layers were produced by starting the polymerization in TiO_2 free solution and synthesizing a first pristine PANI layer and then transferring it to the TiO_2 containing solution for further growth of a second TiO_2-PANI layer. The thickness of the bi-layer structures was modified by varying the thickness of the first PANI layer and keeping the number of scans used for producing the outer TiO_2-PANI composite layer constant.

After synthesis the voltammetric behavior of the composite layers was investigated in supporting electrolyte (0.5 M H_2SO_4) by scanning the potential between +0.32 and –0.66 V at 10 mV s^{-1}. The redox charge obtained by integrating the voltammetric curve was used as an indirect measure of the thickness of the polymer layer. In a test experiment the thickness of a composite layer deposited on stainless steel was measured in SEM by making a scratch on the surface layer. For this particular specimen an average thickness of 33 μm corresponded to a redox charge of 350 mC cm^{-2} and a very high surface roughness (morphology features with height between 25 and 50 μm) was observed. On the other hand SEM on TiO_2-PANI-coated graphite substrates with composite layers produced through a few (3–15) potentiodynamic scans showed incomplete coverage of the underlying substrate by the polymer layer. For this reason in the text we have always specified the redox charge of the deposited composites instead of the polymer layer thickness.

Photoelectrochemical measurements were performed in a specially designed home made photoelectrochemical cell with a quartz window using an 8 W UV xenon lamp (Philips, Mumbai, India). The spectrum of the UV lamp, measured by means of a monochromator Bentham M300 with two diffraction grids and photoelectrical detector DH-2, covered the wavelength range between 350 and 420 nm and exhibited maximal spectral intensity at 370 nm. The average specific power density, amounting to 4.6 mW cm^{-2}, was determined in air using a power-meter Scientech Vector S310. The TiO_2-PANI coated electrodes were located in the electrochemical cell at a distance of 1.0 cm from the quartz window.

Platinum deposition was carried out in aqueous solution of 5 mM H_2PtCl_6 and 1 M HCl using two different approaches; (1) photoreduction (the pH value was adjusted to pH 4) and (2) galvanostatic electroreduction at $j = -0.11$ mA cm^{-2}. In the case of platinum photoreduction the specimens were irradiated for 1 h.

Scanning electron micrographs were obtained at JSM 5300 (Jeol, Peabody, MA, USA) and JSM 6340F (Jeol). EDX analysis was performed by means of a Superprobe 733 instrument (Jeol). Quantitative results on the amounts of Ti are not communicated because only the chemical elements C and Ti are detectable in the TiO_2-PANI composite specimens. Since the amount of C was determined with inadequate accuracy there is no sound reference point for calculating the real Ti atomic percentage.

3 Results and discussion

3.1 Formation and characterization of TiO_2-PANI composite layers

The potentiodynamic polymerization of aniline in the presence of TiO_2 nanoparticles proceeded without inhibition for all working electrodes studied. After synthesis the PANI layers obtained in the absence and presence of TiO_2 nanoparticles exhibited similar voltammetric behavior (Fig. 1). The main PANI oxidation/reduction peaks are due to the reversible leucomeraldine to emeraldine transition,

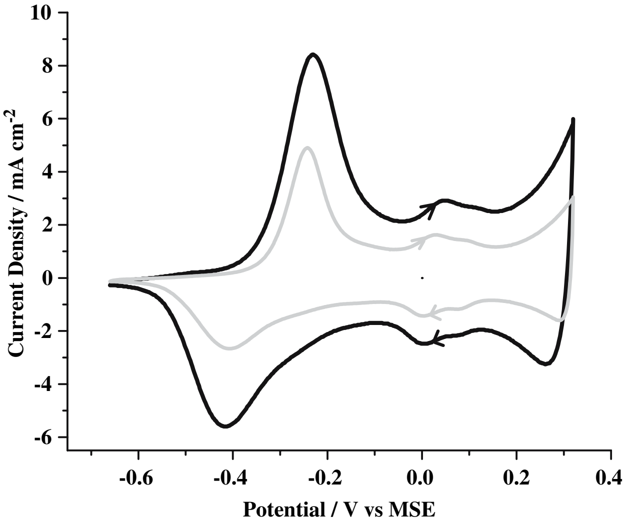

Fig. 1 Voltammetric curves measured in 0.5 M H_2SO_4 on PANI layers obtained after polymerization through 25 cycles on graphite substrates in absence (*gray line*) and presence (*black line*) of TiO_2 particles in the polymerization solution (q_{redox} = 238 mC cm^{-2} for PANI and q_{redox} = 116 mC cm^{-2} for TiO_2-PANI)

which is accompanied by uptake/release of anionic species and water from/out of the polymer composite structure. It is evident that these processes are not impeded by the presence of TiO_2 nanoparticles in the polymer structure. It was found that for one and the same number of polymerization scans the PANI coating obtained in the presence of TiO_2 nanoparticles has a much higher redox charge in comparison to the pristine PANI layer.

Figure 2a–c show the surface morphology of thick TiO_2-PANI layers synthesized on stainless steel and graphite substrates. The layers synthesized on stainless steel substrate show much rougher surface structure in comparison to the homogeneous and flat surface of the composite layer obtained on graphite. Figure 2b shows a cross-section of the TiO_2-PANI composite deposited on stainless steel. EDX-analysis performed on both type of specimen shows the availability of large amounts of Ti distributed evenly over the polymer surface.

The photoelectrochemical response of the synthesized TiO_2-PANI layers was studied at low scan rates under intermittent UV-light illumination. Hardly measurable photocurrents were detected for composite layers with redox charge exceeding 250 mC cm^{-2}. This is most probably due to the large intrinsic capacitive currents of the polymer layer, concealing the photocurrents, and the possible inhibition of the transport of the photogenerated electrons in the bulk of the thick composite layer. In fact only TiO_2 particles located at the surface of the polymer material may take part in the photoprocess. Marked photoelectrochemical response was observed by reducing the thickness of the composite layers, the best result being obtained with layers synthesized by only a few potentiodynamic cycles (Fig. 3). In the course of measurements performed at constant potential at intermittent light (Fig. 4) a stable photoresponse was observed. At one and the same redox charge of the TiO_2-PANI composites the photocurrents measured using stainless steel substrates for the deposition were lower than those using graphite substrates. For this reason graphite substrates were used in our further

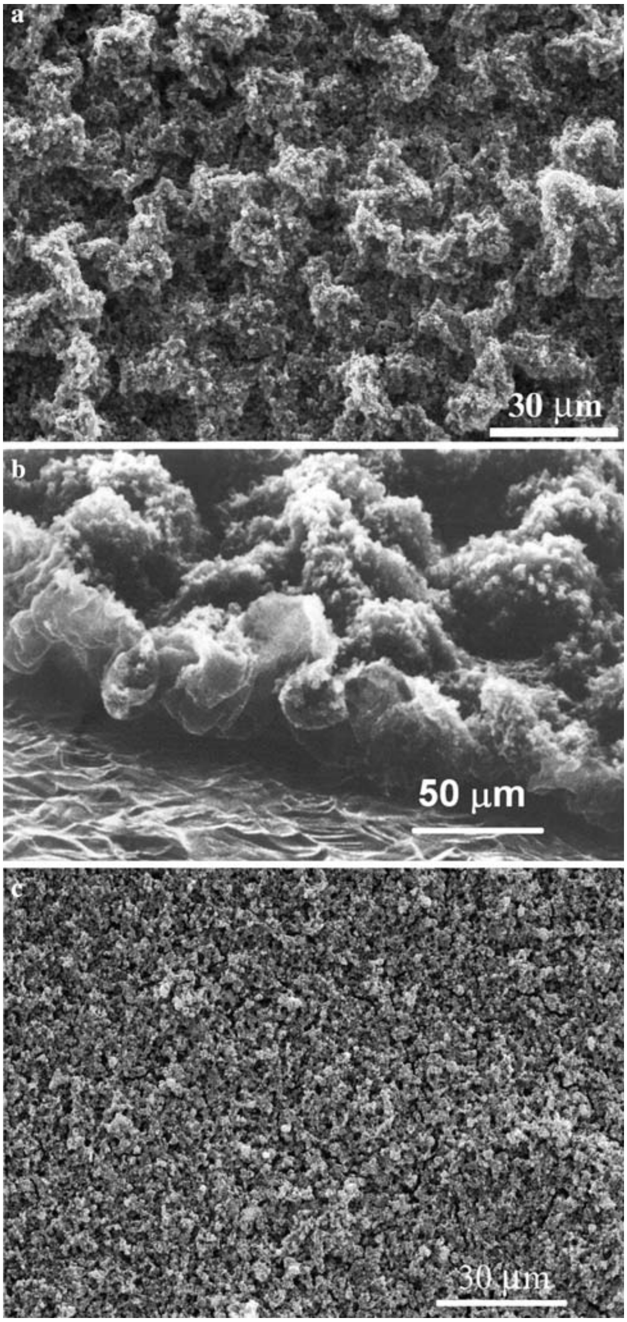

Fig. 2 SEM images of thick TiO_2/PANI composites deposited on (**a**), (**b**) stainless steel and (**c**) graphite. The values of q_{redox} are (**a**) 90 mC cm^{-2}, (**b**) 330 mC cm^{-2}, and (**c**) 870 mC cm^{-2}

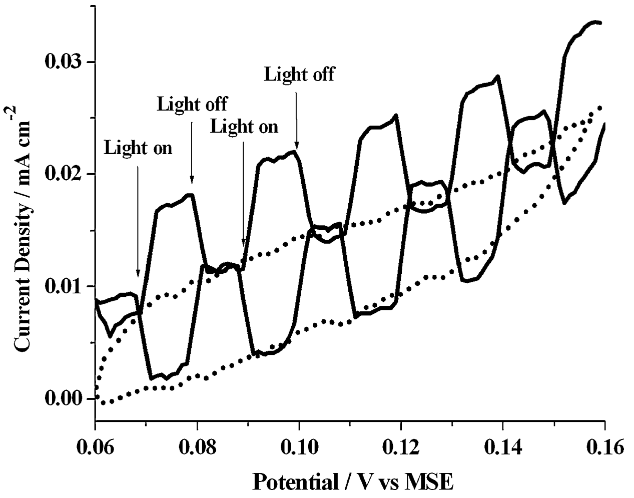

Fig. 3 Photoelectrochemical response (*solid line*) under intermittent light measured on a thin TiO_2-PANI layer, synthesized through five potentiodynamic cycles on a non-polished graphite substrate. The *dotted line* shows the reference measurement in the dark. $v = 1$ mV s^{-1}

experiments. For these substrates the amplitude of the photocurrent was found to depend markedly on the substrate pre-treatment (Fig. 4). No substantial dependence of the photoresponse on the redox charge of thin composite layers (with redox charge below 250 mC cm^{-2}) deposited on graphite was observed. It was established that TiO_2-PANI composite layers obtained by a few (3–15) potentiodynamic scans in the polymerization solution do not completely cover the underlying substrate (Fig. 5). In such a situation the roughness of the substrate is of major importance for the initial stage of the composite layer formation and thus for the exposed composite surface.

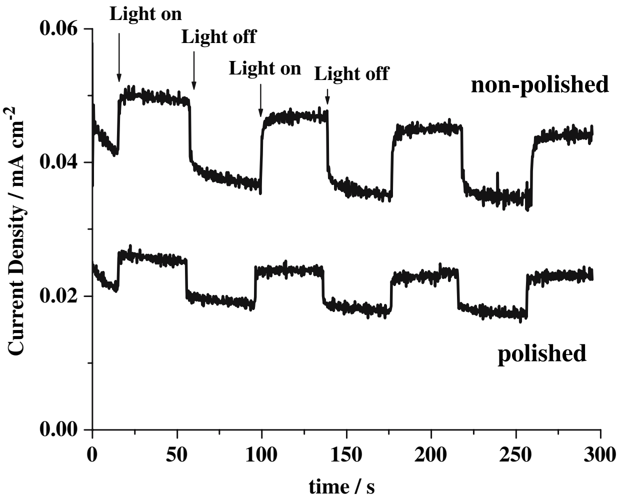

Fig. 4 Phototelectrochemical response measured at $E = 0.2$ V versus MSE on thin TiO_2-PANI layers deposited on polished and non-polished graphite substrate

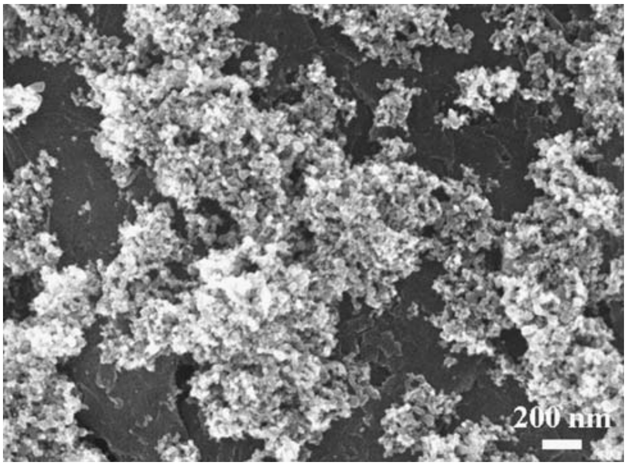

Fig. 5 SEM image of the TiO_2-PANI composite synthesized on graphite by three potentiodynamic scans. $q_{redox} = 36$ mC cm^{-2}

The results presented so far show that, although the growth of compact TiO_2-PANI composite layers proceeds without inhibition, the photoelectrochemical activity is due only to the surface layers of the composite structure deposited through few potentiodynamic scans. Thus, it seemed reasonable to try combining the high conductivity of the pristine polymer favoring transport of photogenerated electrons through the polymer structure and the surface induced photoelectroactivity due to the presence of TiO_2 particles only in the surface composite layer. This was the reason to investigate further the formation of bi-layered structures consisting of a first compact PANI layer completely covering the underlying substrate and a second thin surface layer of the TiO_2-PANI composite.

3.2 Bi-layer PANI/TiO_2-PANI structures

The bi-layered PANI/TiO_2-PANI structures were synthesized in a two step procedure: (1) polymerization in TiO_2-free solution by means of a varying number of potentiodynamic scans and (2) polymerization in the TiO_2 containing solution by making five additional scans. The redox charge of the first pristine layer and the final bi-layered structure were measured in sulfuric acid solution. The results for the redox charges obtained for various layers (Fig. 6) show that the growth of the composite layer during the five additional scans in the TiO_2 containing solution is accelerated in comparison to the growth of the pristine PANI layer. This result is in line with the already established enhancement of the redox charge in the course of the TiO_2-PANI single-layer growth. Bearing in mind that, for the bi-layered structures, this effect is observed by applying only five cycles in the TiO_2 containing polymerization solution it should

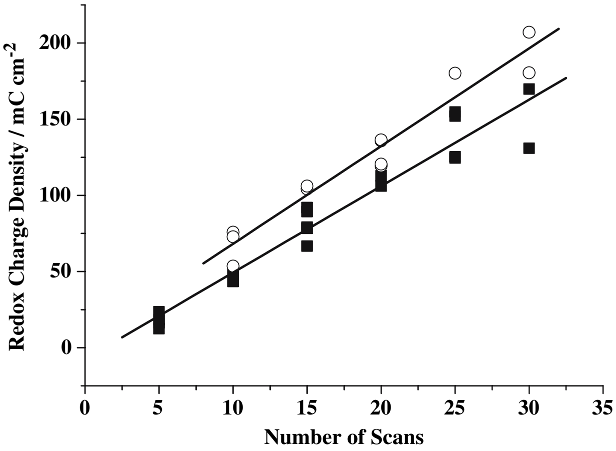

Fig. 6 Dependence of the reduction charge of single- (■) and bi- (○) layered structures on the total number of polymerization scans obtained on graphite substrates. In the case of the bi-layers the outer composite TiO_2-PANI layer is obtained always by five potentiodynamic scans

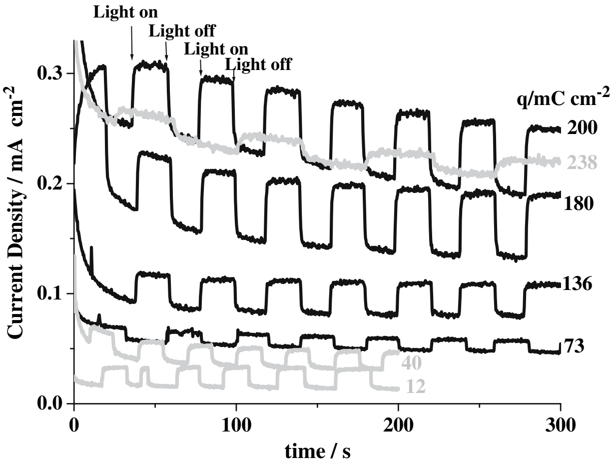

Fig. 7 Photoelectrochemical response measured at $E = 0.2$ V versus MSE on single (*gray lines*) and bi-(*black lines*) layered composite structures with different redox charges obtained on graphite substrates

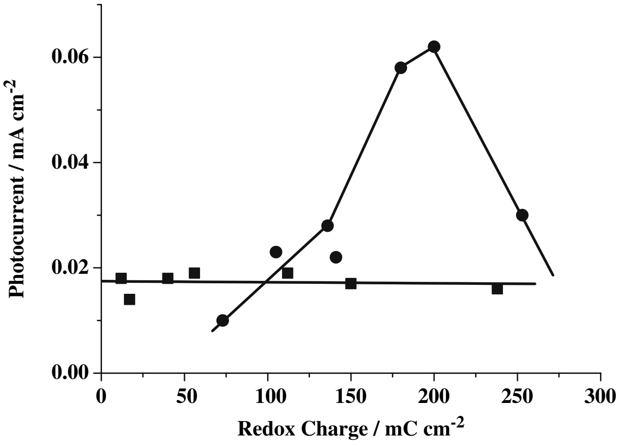

Fig. 8 Amplitudes of the photocurrent in dependence of the redox charge of single (■) and bi-(●) layered composite TiO_2-PANI structures obtained on graphite substrates

be attributed to a much more favorable growth of the polymer chains in the presence of the TiO_2 particles. A possible reason for the enhanced PANI growth may be the influence of the TiO_2 nanoparticles on the polymer chain conformation and/or charge compensation finally resulting in a different, more open, and ramified growth morphology. It is worth noting that at low pH values, such as those used for polymerization of PANI, the TiO_2 particles have positive surface charge which will interact with the positive charges distributed along the oxidized polymer chains. Thus charge compensation and, in general, charge distribution in the composite structure should be different in comparison to the pristine PANI structure and should affect the polymer growth morphology.

Photoelectrochemical measurements at intermittent light were performed at constant potential for the various bi-layered structures. The measurements are presented together with data obtained at single TiO_2-PANI composite layers in Fig. 7. It is evident that the bi-layered structures have, in general, larger photocurrents than the single layered ones. The data for the photocurrent amplitudes summarized in Fig. 8 show a maximum in the thickness dependence at a redox charge of 200 mC cm^{-2}. It is difficult to give an unambiguous explanation for the presence of such a maximum in the thickness dependence of the photoresponse. With increasing average thickness of the polymer structure the layer becomes compact and affords the most favorable conditions for transfer of the photogenerated electrons with an additional effect of increasing the real surface area of the polymer structure and thus the surface involved in the photoresponse. However extreme thickening of the PANI layer may result in decreased conductivity, an effect driving the photoresponse in the opposite direction.

3.3 Platinum particles deposition

Platinum particle deposition was studied at both TiO_2-PANI single- and PANI/TiO_2-PANI bi-layer structures using two approaches—galvanostatic electroreduction and photoreduction. Large amounts of platinum were detected on the surface in both cases by EDX analysis. The microscopic picture was, however, very different: several hundred nm sized particles, evenly distributed over the surface, were observed in the electroreduction case (Fig. 9). The Pt particles in the photoreduction case were at least an order of magnitude smaller and could not be well

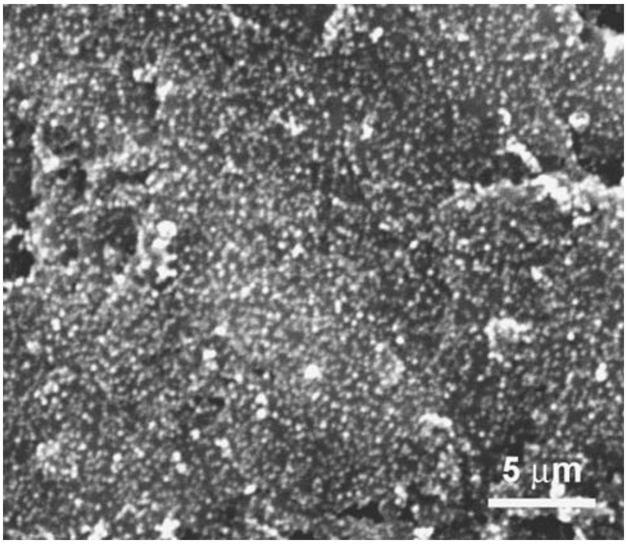

Fig. 9 SEM of platinum modified TiO_2-PANI composite bi-layer obtained through galvanostatic reduction. $q_{redox} = 38$ mC cm^{-2} graphite substrate is used

resolved. Evidence for the presence of platinum in this case was obtained by comparing the voltammetric response of the TiO_2-PANI layers before and after Pt deposition (Fig. 10a). The hydrogen evolution current rise characteristic for platinum was found in the voltammogram. At the same time a decrease in the redox charge of the composite TiO_2-PANI layer was observed. Despite the loss in electroactivity the photoresponse of the Pt modified TiO_2-PANI layer remained unaffected (Fig. 11). It is worth noting that photodeposition of platinum was observed after UV irradiation of PANI layers in the presence of hexachloroplatinate and ascorbate ions, the latter playing the role of hole scavenger [21]. This was the reason for performing a reference experiment of UV irradiation of a pristine (free of TiO_2) PANI layer in the presence of hexachloroplatinate without ascorbate ions. As a result photodeposition of platinum was observed, again accompanied by roughly the same decrease in electroactivity of the PANI layer (Fig. 10b). EDX analysis also confirmed the presence of platinum in this case. Thus it became clear that the photodeposition of platinum is not due to the involvement of the TiO_2 particles in the photoreduction process and PANI alone plays the role of photocatalyst for the reduction of hexachloroplatinate ions.

4 Conclusions

The polymerization of aniline in TiO_2 nanoparticles containing solution occurs without inhibition and results in enhanced growth of the polymer structure. This effect is probably related to the influence of the charged TiO_2 nanoparticles on the polymer chain conformation and on the ionic charge compensation in the polymer structure. Photoelectrochemical response is observed only for composite layers with redox charge below 250 mC cm^{-2}. This is due to the large intrinsic capacitive currents of the polymer material combined with loss of transfer efficiency for the photogenerated electrons in the bulk of thick composite layers. It is shown that either thin TiO_2-PANI composite layers or bi-layered structures consisting of a first pristine PANI layer followed by a very thin TiO_2-PANI composite layer may be employed for photoelectrochemical applications. Depending on the thickness of the first pristine PANI layer the by-layered structures show up to threefold higher photoelectric currents than the composite single-layers.

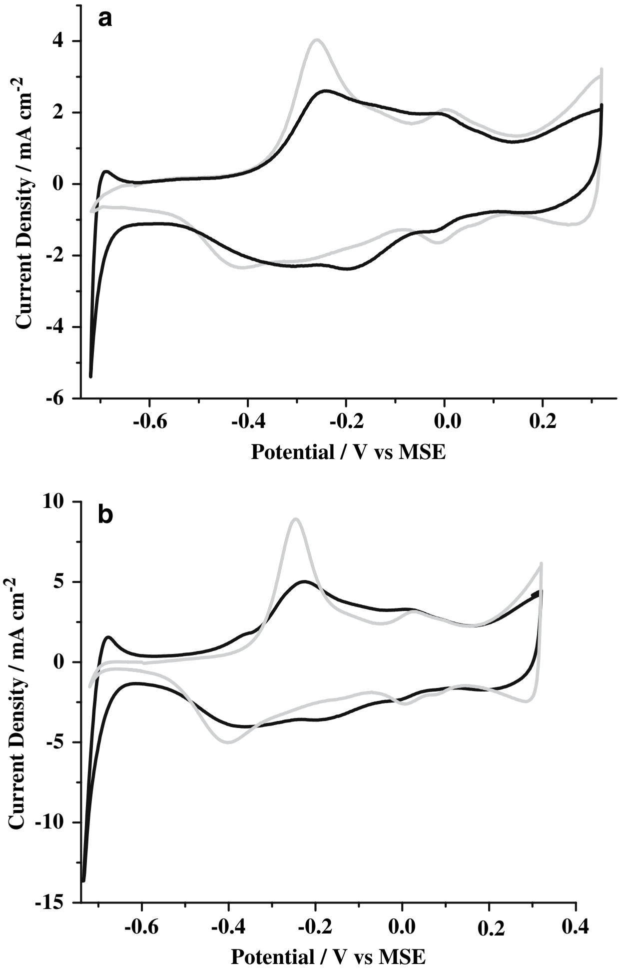

Fig. 10 Voltammetric curves measured in 0.5 M H_2SO_4 on: (**a**) TiO_2-PANI composite layer and (**b**) pristine PANI layer before (*gray line*) and after (*black line*) platinum deposition performed through photoreduction ($q_{redox} = 82$ mC cm^{-2} for (**a**) and $q_{redox} = 118$ mC cm^{-2} for (**b**)) (graphite substrates are used)

It is important to note that in all cases the irradiation with UV light of pristine PANI and TiO_2-PANI composite

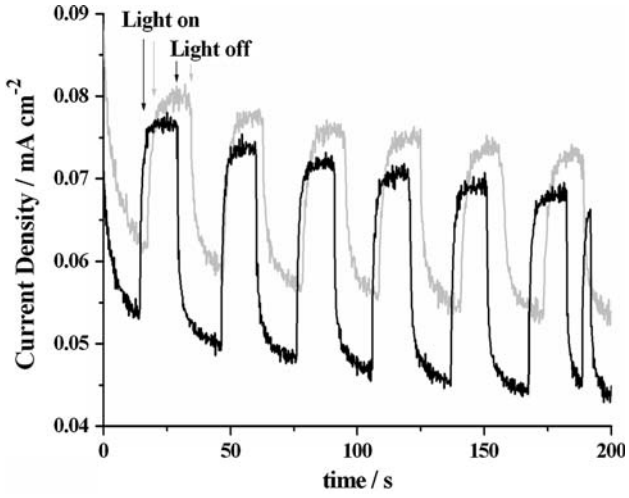

Fig. 11 Phototelectrochemical response measured at $E = 0.2$ V versus MSE on TiO_2/PANI layer (**a**) before (*gray lines*) and (**b**) after (*black line*) photoreduction of platinum (graphite substrates are used)

layers results in a decrease in the redox electroactivity of the PANI material. Despite the loss of electroactivity it seems that the PANI structure provides sufficient conductivity and thus the photoelectrochemical response observed at TiO_2-PANI and platinum modified TiO_2-PANI composite layers remains unaffected. Finally combining photoreduction of hexachloroplatinate and TiO_2-PANI composite layers offers a way of producing conducting polymer-based platinum catalytic material with both electrocatalytic (e.g., for methanol oxidation) and photoelectrical activity.

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