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Fabrication and characterization of composite TiO_2 nanotubes/ boron-doped diamond electrodes towards enhanced supercapacitors

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Abstract

The composite TiO_2 nanotubes / boron-doped diamond electrodes were deposited using Microwave Plasma Enhanced Chemical Vapor Deposition resulting in the improved electrochemical performance. This composite electrode can deliver high specific capacitance of 7.46 $mFcm^{-2}$ comparing to BDD deposited onto flat Ti plate (0.11 $mFcm^{-2}$).The morphology and composition of composite electrode were characterized by scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) techniques. According to XPS and Raman analysis, structure of TiO_2 was greatly changed during Chemical Vapor Deposition process: formation of Ti^{3+} sites, partial anatase to rutile transformation and titanium carbide phase formation. This effect is attributed to the simultaneous presence of activated hydrogen and carbon in the plasma leading to enhanced dehydration of NTs (nanotubes) followed by carbon bonding. The enhanced capacitive effect of TiO_2 NT / BDD could be recognized as: (1) the unique synergistic morphology of NTs and BDD providing more efficient conducting pathway for the diffusion of ions and (2) partial decomposition of NTs and transformation towards to TiC and Ti_2O_3 fractions. Finally, highly ordered titania nanotubes produced *via* simply, quick and controllable method – anodization, could act as promising substrate for conductive BDD layer deposition and further application of such composites for supercapacitor construction.

Keywords: Microwave Plasma Enhanced Chemical Vapor Deposition, Boron-Doped Diamond, Titania Nanotube, Supercapacitors

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1. Introduction

In recent years, various efforts have been made towards development of electrode materials especially including extended surface area [1–4] and usage of metal oxides [5] or organic compounds [6] together in order to form composite structures with unique electrochemical features. Among these oxide materials, TiO_2 nanotubes are the most attractive candidates which can be prepared by a simple electrochemical anodization The titania nanotubes provide a large specific surface area, a direct pathway of charge transport but the specific capacitances are generally limited to less than 1 $mFcm^{-2}$ without intentional doping or treatment. Lu e*t al*. [7] and Li *et al.* [8]

reported that hydrogenated TiO_2 obtained by heating in hydrogen atmosphere resulted in an improvement of specific capacitance up to 3.24 $mFcm^{-2}$. Furthermore, Wang and Leshuk *et al.* [9,10] received also hydrogenated TiO_2 under hydrogen plasma treatment characterized with similar electrochemical behaviour. Several groups reported results on composite structures based on carbon / TiO_2 nanotubes multilayer. Chen and Dwivedi *et al.* [11,12] showed synthesis of diamond-like carbon (DLC) nanorods onto TiO_2/Ti nanotubes and DLC films on nanostructured titanium. Zanin *et al.* [13,14] reported electrochemically active (DLC) electrodes featuring high specific surface area prepared by microwave plasma enhanced chemical vapor deposition (MWPECVD) onto multiwall carbon nanotubes. Yuan *et al.* [15,16] proposed a direct deposition of titania nanotubes onto boron-doped diamond (BDD) films. Moreover, Gao *et al.*[17] showed Multiwall nanotubes-TiO_2 composite electrode with specific capacitance up to 4.4 mF cm^{-2} for 10 mg ml^{-1} of APS in 1 M H_2SO_4 and long-term cycle stability. Dash *et al.* [18] fabricated titanium carbide derived nanoporous carbon by thermo-chemical etching of titanium carbide. Those electrodes showed specific up to 130 F g^{-1} in organic electrolyte.

The advantage of using diamond in supercapacitor applications were recently reported by several authors [13,19,20]. They demonstrate that deposition of diamond on porous substrate significantly increases specific capacitance on different substrates like Si, Ti or carbon nanotubes. Moreover, the combining diamond with porous or structured substrate can occurs with nanopores and mesopores that significantly increase capacitance investigated by Chmiola *et al.* [21,22]. Gao et al. reported various bottom-up grown diamond nanostructures like diamond-coated Si nanowires [23] or SiO_2 spheres [24], which could deliver capacitance of 105 $\mu F/cm^2$ and 0.598 mF cm^{-2}, respectively. Moreover, they proved that diamond based materials show the potential to work as pseudocapacitor electrode without organic electrolyte [24] offering simultaneously the high specific capacitance, low cost, non-toxicity and the high conductivity.

In this paper, we show the formation of TiO_2 nanotubes (NTs) / BDD structure and resolve the potential origin of capacitive effect. The electrode material dedicated for supercapacitor application based on TiO_2 nanotubes over-grown by thin boron-doped diamond film in MWPECVD deposition process was presented. In our previous work, we concluded that the BDD over-grown titania NTs can provide high specific capacitance increase resulting in 2.10, 4.79, and 7.46 mF cm^{-2} at a scan rate of 10 mV s^{-1} for the [B]/[C] ratio of 2, 5 and 10k, respectively [25]. Nevertheless, the precise explanation of improved electrochemical performance of composite TiO_2 NTs / BDD has not yet been resolved and reported.

The surface analysis was employed to investigate structure and its potential influence on the increase of capacitance. The scanning electron microscopy (SEM) was applied to investigate evolution of surface morphology. Cross-sectional studies of composition of electrode was investigated by means of Raman spectroscopy and the electrode composition was analyzed by means of X-ray photoelectron spectroscopy (XPS).

Figure 1

Figure 1. Formation scheme of composite TiO_2 nanotubes / boron-doped diamond electrode.

2. Experimental details

The fabrication process of TiO_2 nanotubes and diamond film synthesis can be found elsewhere [25]. Titania nanotube arrays were formed by anodization of 0.5 mm thick titanium foils (1 x 1 cm, ASTM Grade 1, 99.5%, Spinex, Poland).The boron-doped diamond was synthesized in an MWPECVD system (SEKI Technotron AX5400S, Japan) on titanium/titania nanotubes (NT) substrates (see Fig. 1).The diborane (B_2H_6) was used as dopant precursor, and [B]/[C] ratio of boron level in the gas phase was 2000, 5000 and 10 000 ppm. The growth time was 1 h, producing microcrystalline film of ca. 400 nm thickness.

The surface morphology and molecular structure of the electrode surface was analyzed using SEM (EVO-40, Zeiss, Germany) and Raman spectroscopy (InVia, Renishaw, UK), respectively. The SEM photographs were taken under high vacuum conditions. Beam accelerating voltage was kept at 20kV. The Raman spectra were recorded at room temperature using micro-Raman system with 514 nm argon ion laser as excitation. Spectra were recorded in the range of 120 – 3300 cm^{-1}.

Electrochemical measurements of prepared electrode materials were performed by the potentiostat-galvanostat system AutoLab PGStat302N in a three-electrode assembly at 295 K. Ti metal plate covered with pure nanotubes, BDD layer or composite material TiO_2/BDD with different [B]/[C] ratio stayed as a working electrode. The counter electrode consisted of Pt gauze and reference electrode was: Ag/AgCl/0.1 M KCl. Electrodes with a geometrical surface area of 1 cm^2 were tested by cyclic voltammetry in deareated solutions: 0.1 M $NaNO_3$ without and with 1 mM $K_3Fe(CN)_6$. Prior to taking electrochemical measurement, a pretreatment was performed holding electrode at -0.1 V for 60 s.

The high-resolution photoelectron spectroscopy (ThermoFisher Scientific, Escalab 250Xi, UK) was used to determine chemical binding properties of the surface, utilizing monochromatic Al-Kα source with spot diameter of 650 μm. High-resolution spectra were recorded in CAE mode, at energy step size of 0.1 eV at a pass energy of 10 eV and dwell time 50 ms. Charge neutralization was implemented by means of a flood gun. In order to normalize spectroscopic measurements, X axis (BE) was calibrated for peak characteristics of neutral carbon 1s (BE = 284.6 eV). Data analysis was performed using Avantage v.5 software provided by the manufacturer.

3. Results and discussion

3.1. Composition and surface morphology of TiO_2 NT/BDDelectrode

Structure of composite electrode (SEM, Raman): As it is presented in Figure 1, the electrode is expected to have the multilayer structure consisting of layer of titania nanotubes covered in MWPECVD process with layer of boron doped diamonds. The morphology of composite electrode was investigated using SEM. To visualise the internal structure of electrode the top BDD layer was partially removed what is presented in Figure 2a. The BDD layer (R1) forms a fully encapsulated film of total thickness of 400 nm and average diamond diameter of 250 nm. The polycrystalline BDD exhibits columnar growth. Thus, such films have highly tailorable microstructure and intergrain porosity [26]. Under BDD film the regular structure of TiO_2 NTs can be observed – Figure 2a (R2). The nanotubular architecture is not affected by BDD growth process and keep their pristine shape [25]. On the cross sectional SEM image (Fig. 2b) it can be observed that TiO_2 NTs layer is overgrown with semi-spherical nanostructures. Such a TiO_2 NTs /BDD composite have been subjected to a detailed analysis using Raman spectroscopy, giving information about molecular composition of the interface between TiO2 NTs and diamond overlayer. Additionally, XPS was utilized to identify semi-spherical nanostructures across TiO_2 NTs and explain origin of these carbonous inclusions.

Figure 2

Figure 2. SEM image of composite BDD-TiO_2 NTs electrode (left image): (a) top view of electrode with partially removed BDD layer and (b) cross section image showing top BBD layer and titania nanotubes overgrown with semispherical nanostructures; (c) Raman spectra recorded for top BDD layer (R1) and TiO_2 NTs layer (R2).

Figure 3

Figure 3. Raman spectra recorded for TiO_2 NTs processed in carbon free plasma (a) and diamond deposition process (b).

Raman spectra recorded for top BDD layer (R1) and TiO_2 NTs layer uncovered by mechanical removing of BDD film (R2) are presented in Figure 2c. Raman spectrum of BDD film (R1) is characterised with bands typical for BDD structures [27]. Raman spectra (R1) presented in Figure 2c is standard for BDD deposited on the titanium based substrates. Similar spectra were recently reported by other authors in electrochemical field [28,29]. Relatively low quality of BDDs deposited on titanium base substrates is mostly caused by low quality of substrate surface (no polishing), thermal stresses (different thermal expansions coefficients) as well as preferable growth of graphitic phase on non-diamond materials.

In the deeper layer of titania NTs only carbon structures characterised with bands D (1353 cm^{-1}) and G (1600 cm^{-1}) typical for sp^2-type bonded carbon can be identified. It allows to conclude that semi-spherical nanostructures observed in the SEM image are composed of carbon. The width and intensity of Raman bands suggest the disordered nature of these carbon forms. The absence of anatase bands (143.7, 396.6, 518.6 and 637.7 cm^{-1}) observed for pristine titania NTs indicates transformation of primary crystalline structure of nanotubular layer into another structure characterised with intense Raman bands located near 243 and 331 cm^{-1}. These signals are found to be typical for Ti_2O_3. [30]. The Raman spectrum also exhibits broad signals centred around ~289 and 450 cm^{-1}, corresponding to Ti–O vibration modes in the titania framework [31,32]. The wide bands located at 420 and 605 cm^{-1} indicates the presence of TiC inside NTs structure.

Table 1. Raman bands positions for un-processed and plasma processed TiO_2 NTs.

Table 1

The comparison of Raman spectra recorded for carbon overgrown titania NTs present in composite electrode and titania NTs processed in carbon free H_2 plasma (Fig. 3, Tab. 1) allows to observe the shifts in Raman band positions attributed to internal stress in the structure induced by lattice defects generated by TiO_2 and TiC inclusions.

Composite electrode composition (XPS): Figure 4 presents high-resolution C1s spectra carried out for thin BDD film grown on TiO2 NTs at two different [B]/[C] ratios (2k and 10k). For both analyzed BDD electrodes, XPS spectra contains four main peak components. For the purpose of peak deconvolution during analysis, all the C-C peaks were constrained in the FWHM range between 0.8 and 1.2 and C-O peak in the FWHM range between 1.0 and 1.5. Peaks had a form of Lorentz/Gaussian mix sum of 10:40. Peak background type used was Smart, as implemented in Avantage software.

Figure 4

Figure 4. The high-resolution C1s spectra carried out for thin BDD film grown on TiO_2 NTs with 2k and 10k [B]/[C] ratio.

The main C1s peak was noted at 284.4 ± 0.2 eV and corresponds to hydrogen terminated boron doped diamond (HT-BDD). Its location can shift for different dopant levels [33]. However, it remains within ± 0.2 eV range for both 2k and 10k BDD samples. The second peak is shifted at +0.8 eV and corresponds to oxygen terminated boron doped diamond (OT-BDD). The third peak is observed at +1.2 eV shifts and is related with the presence of oxidized carbon atoms C-OH and C-OC. Finally, a small peak was observed for 283.4 eV, which should be interpreted as sp^2 hybridized carbon. Its presence is over two times higher in the case of BDD electrode with 10k [B]/[C], which results from higher disorder of diamond structure with higher boron dopant level. Such interpretation is in agreement with previously published results [34,35].

Table 2. Percentage contribution (in at.%) of each C1s peak for BDD grown on TiO_2 NTs with 2k and 10k [B]/[C] ratio.

Table 2

High-resolution XPS spectra of Ti2p peaks of TiO_2 NT reference sample consists mostly of a mixture of anatase (17.2 at.%) and rutile (12.2 at.%), Ti2p3 BE of those is 459.1 eV and 458.6 eV respectively [36]. Third Ti2p3 component corresponds to Ti_2O_3 and can be observed at BE of 457.2 eV[37].

As a result of BDD deposition on the top of TiO_2 NTs, fourth component was found on Ti2p high-resolution spectra. It originates from TiO, which was confirmed by both position (455.3 eV) as well as an energy separation value between Ti2p3 and Ti2p1 peaks [38]. The BDD deposition or exposition to hydrogen rich microwave plasma changes the structure of TiO_2 NTs significantly and results in decrease in the oxygen stoichiometry. Higher amount of Ti^{3+} and Ti^{2+} can be observed, together with a significant drop of Ti^{4+} and oxygen in so treated TiO_2 NT substrate.

Furthermore, the cross-sectional XPS spectrum recorded at the composite electrode reveals another peak, at considerably lower energy (454.6 eV), corresponding to TiC [39]. Presence of TiC arrangement was also confirmed via Raman analysis (see Fig. 2 and 3) and by cross-sectional SEM observations - semi-spherical nanostructures across TiO_2 NTs (see Fig. 2B).

3.2. Electrochemical characterization of TiO_2/BDDelectrode

Cyclic voltammetry performed in ferricyanide solution was used to investigate the difference in electrochemical properties between composite material and its pure counterparts, because such redox system is characterized with kinetics highly dependent on density of electronic states near the formal potential (E_f). As it can be seen in Figure 5, typical redox behavior is observed for BDD modified samples. For pure titania any redox peaks is never observed because E_f overlaps bandgap energy of TiO_2 nanotubes [40]. The replacement of titanium flat plate by TiO_2 nanotube arrays as a support for BDD deposition results in charging character of registered cyclic voltammetry (CV) curves. The voltammograms were registered also at different scan rates and the relation *j vs*. $(V/s)^{-0.5}$ was depicted in Figure 5b. According to given plots, clear linear relation shows that oxidation process is under diffusion control. Same linear dependence but with opposite slope was also observed for reduction peak current. The value of double layer capacitance calculated on the CV obtained in purely 0.1M $NaNO_3$. The specific areal capacitance of TiO_2/BDD composites equals 2.10, 4.79, 7.46 mF cm^{-2} for the respective [B]/[C] ratios of 2k, 5k and 10k at a scan rate of 10 mV/s, whereas for the pure BDD film, the value of double-layer capacitance reached only 0.11 mF/cm^{-2} [25]. Such small capacitance value reported for Ti plate covered by BDD layer [41] or pure titania nanotubes [42,43] is typical for these electrode materials. The increase in charging current displayed on CV curves can be caused by two main factors: (a) specific architecture of titania nanotube that increase remarkably real surface area available for BDD growth and each tube could act as a straight path for charge movement [20]; (b) transformation of crystalline phase and chemical composition of titania during BDD deposition *via* MWPECVD processing. Concerning (a), highly enlarged surface area provides improved boundary density comparing to simple metal plate [44]. Therefore, expanded electrode/electrolyte interface for TiO_2/BDD materials is ready for charge accumulation exhibited as a capacitive current [13]. On the other hand, according to detailed XPS and Raman analysis described above, structure of TiO_2 was greatly changed during MWPECVD process: formation of Ti^{3+} sites, partial transformation from anatase to rutile crystalline phase a and titanium carbide formation. According to literature, the mixture of anatase and rutile phase [45], oxygen non-stoichiometry [46] as well as appearance of Ti-C

[47] greatly improve electrical properties observed here as huge capacitive current. Thus, highly ordered titania nanotubes produced *via* simply, quick and controllable method – anodization, could act as promising substrate for conductive BDD layer deposition and its further application for supercapacitor construction.

Figure 5

Figure 5. Cyclic voltammetry curves: (a) the composite electrodes TiO_2NTs /BDD-10k, pure titania and BDD layer immersed in 0.1 M $NaNO_3$ (ν = 50 mV/s), (b)The plots of peak currents versus the square root of the scan rate for different BDD covered electrodes.

4. Conclusions

The fabrication and characterization of composite TiO_2 nanotubes / boron-doped diamond electrodes grown in MWPECVD was investigated in details. The BDD overlayer fully encapsulates-TiO_2NTs exhibiting typical columnar growth character. Thus, obtained electrode has highly tailorable microstructure and intergrain porosity. The architecture of NTs are not affected by BDD growth process and keep their pristine shape. The XPS and Raman analyses reveal that structure of TiO_2 is changed during MWPECVD process: formation of Ti^{3+} sites, partial transformation from anatase to rutile crystalline phase and titanium carbide formation. Furthermore, the cross-sectional SEM images display that TiO_2 NTs are overgrown with semi-spherical nanostructures. These effects are attributed to the simultaneous presence of activated hydrogen and carbon in the plasma leading to enhanced dehydration of NTs followed by carbon bonding. The electrochemical studies showed the strong effect of enhanced specific areal capacitance of TiO_2/BDD up to 7.46 mF cm^{-2} for the highest [B]/[C] ratio at a scan rate of 10 mV/s, whereas the pure BDD reached only 0.11 mF/cm^{-2}.

Summarizing, highly ordered titania NTs produced *via* simply and controllable method – anodization, could act as promising substrate for conductive BDD layer deposition and its further application for supercapacitor and energy storage devices.

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List of figure and table captions:

Figure 1. Formation scheme of composite TiO_2 nanotubes / boron-doped diamond electrode.

Figure 2. SEM image of composite BDD-TiO_2 NTs electrode (left image): (a) top view of electrode with partially removed BDD layer and (b) cross section image showing top BBD layer and titania nanotubes overgrown with semispherical nanostructures; (c) Raman spectra recorded for top BDD layer (R1) and TiO_2 NTs layer (R2).

Figure 3. Raman spectra recorded for TiO_2 NTs processed in carbon free plasma (a) and diamond deposition process (b).

Figure 4. The high-resolution C1s spectra carried out for thin BDD film grown on TiO_2 NTs with 2k and 10k [B]/[C] ratio.

Figure 5. Cyclic voltammetry curves: (a) the composite electrodes TiO_2NTs /BDD-10k, pure titania and BDD layer immersed in 0.1 M $NaNO_3$ (ν = 50 mV/s), (b)The plots of peak currents versus the square root of the scan rate for different BDD covered electrodes.

Table 1. Raman bands positions for un-processed and plasma processed TiO_2 NTs.

Table 2. Percentage contribution (in at.%), binding energy of core levels (in eV) and FWHM (in eV) of each C1s peak for BDD grown on TiO_2 NTs with 2k and 10k [B]/[C] ratio.