Biocatalytic Approach as Alternative to Chemical Synthesis of Polyaniline/Carbon Nanotube Composite with Enhanced Electrochemical Properties

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Electronic Supplementary Information

1. General remarks

Aniline (Labtech, Russia) was distilled under reduced pressure before using. Aniline dimer (N-phenyl-1,4-phenylenediamine), ABTS – (2,2'-aminobis-(3-ethylbenzothiazoline-6-sulfonic acid) (Aldrich), Na_2HPO_4, citric acid anhydrious (Riedel-de Haen, Germany) were used without further purification. Flexible graphite foil (thickness 0.2 mm) was purchased from (Unichimtek, Russia). Multi-walled carbon nanotubes "Taunit M" (NanoTechCentre Ltd, Russia) were used after treatment with hot 70% nitric acid (MWCNTs). A laccase from the fungus *Trametes hirsuta* (Wulfen) Pilát CF-28 was purified to homogeneity as described previously [Gorshina E.S. et al. Appl. Biochem. Microbiol. 2006, 42(6), 558-563]. The laccase activity was measured spectrophotometrically using 1 mM ABTS as chromogenic substrate ($\lambda = 420$ nm, ε=36000 $M^{-1}cm^{-1}$) at 24°C in 0.1 M Na-citrate-phosphate buffer, pH 4.5. One unit of activity is defined as the amount of laccase oxidizing 1μm of substrate per min. The specific activity of the enzyme preparation was about 158 U/mg of protein.

Cyclic voltammetry measurements of PANI/MWCNT composite were performed using a BAS CV-50W voltammetric analyzer (Bioanalytical System, USA). An electrochemical cell with a commercial Ag|AgCl electrode (Bioanalytical System, USA) as reference electrode and

platinum sheet as counter electrode were used for an electrochemical investigation. Flexible graphite foil covered with a precise amount of PANI/MWCNT composite served as working electrode. Electrochemical measurements of PANI/MWCNT composites were carried out with electrodes immersed in 1 M H_2SO_4 aqueous electrolyte.

The morphology of PANI/MWCNT composites was examined by transmission electron microscopy (TEM, LEO 912 AB OMEGA, Carl Zeiss). FTIR spectra were recorded using KBr pellets on a FTIR spectrometer (IRPrestige Fourier, Shimadzu, Japan). Four-point conductivity measurements were carried out with a Loresta GP (Mitsubishi, Japan).

The specific capacitance (C_s) of the composites was calculated from the cyclic voltammetric measurements. In the case of non-rectangular shape, the CV curves were integrated for specific capacitance calculation. The formula $Cs = \frac{\int IdE}{v\Delta Em}$ was used, where ΔE is the potential range, v is the potential scan rate, m is the mass of electroactive material.

2. Adsorption of AD on MWCNTs was monitored by UV-vis spectroscopy. 5 mg of acid treated MWCNTs was incubated in 5 ml of 1M AD solution. The maximum adsorption of AD was registered in 60 min (Figure S1).

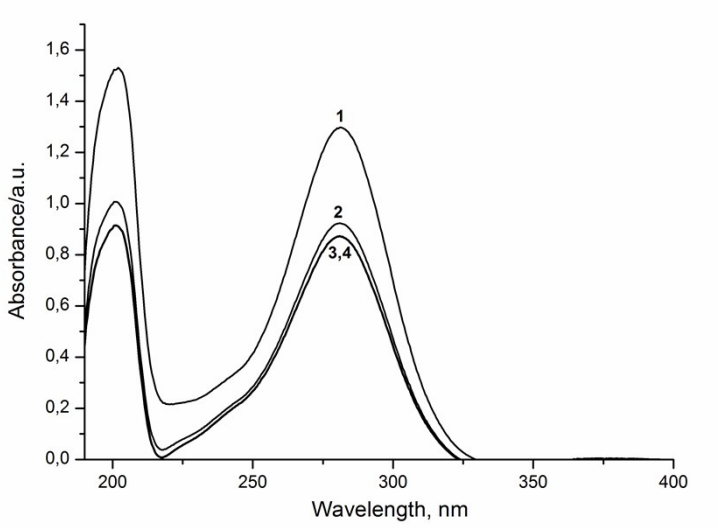

Fig. S1. Adsorption of aniline dimer onto acid treated MWCNTs.
Adsorption time: (1) – 0 min; (2) – 30 min; (3) – 60 min; (4) – 120 min

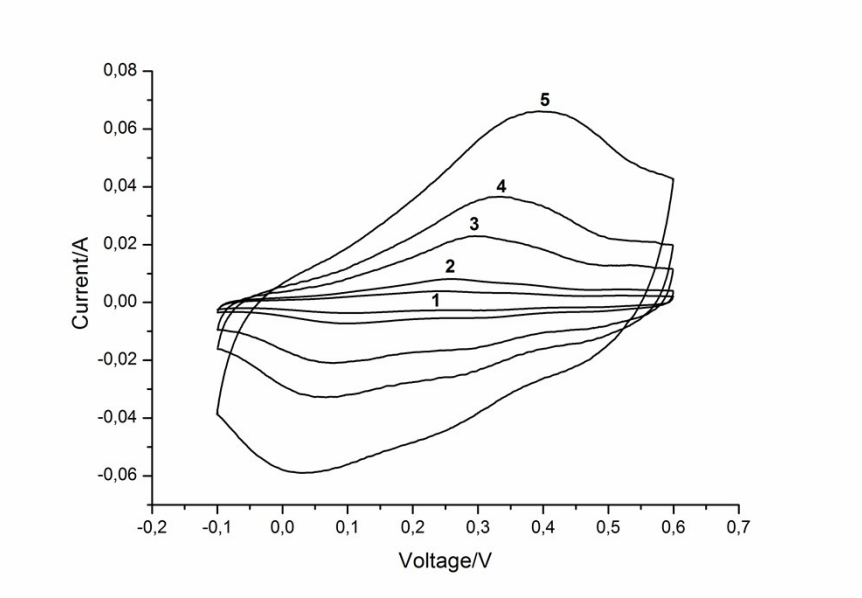

Fig. S2. Cyclic voltammograms of PANI/MWCNT composite fabricated after AD preadsorption on MWCNTs at various scan rates: (1) 5 mV/s; (2) – 10 mV/s; (3) – 30 mV/s; (4) – 50 mV/s; (5) – 100 mV/s.

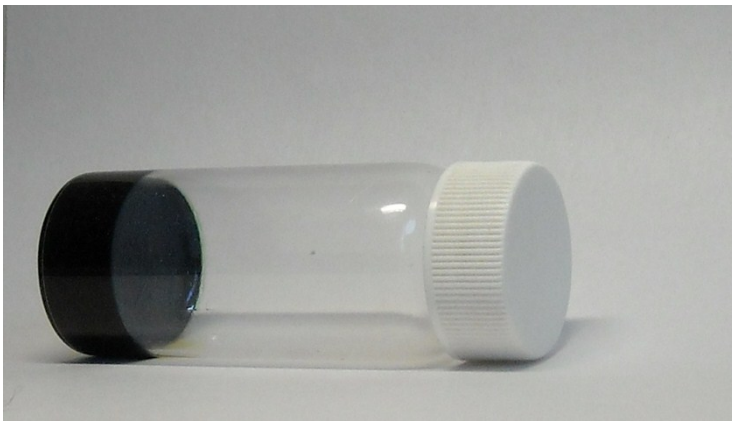

Fig. S3. PANI/MWCNT hydrogel synthesized by laccase-catalyzed method.