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Tuning the wetting angle of fluorinated polymer with modified nanodiamonds: towards new type of biosensors

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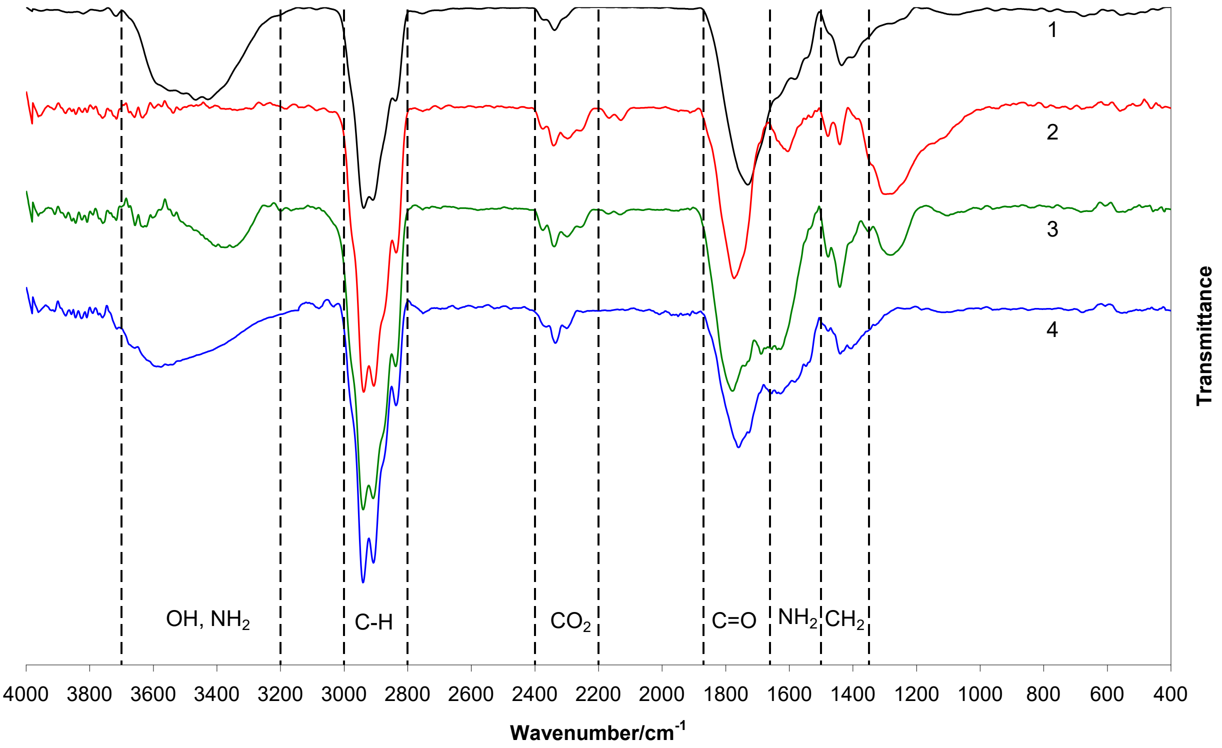
The sensor consisted of mesoporous SiO_2 microparticles (Merck silica gel 60) with adsorbed Pt(II) 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin (PtTFPP, Frontier Scientific, www.frontiersci.com), which was typically used for research and commercial oxygen analyzers. The particles were coated with a protective shell of fluorinated surfactant and distributed in fluorine containing polymer Fluoroplast 42 (HaloPolymer, www.halopolymer.ru), which protected the sensor from the influence of analyzed medium.

The surface properties of the sensor material were tuned using DNDs of three different modifications, namely aminated DND (DND_{amine}), chlorinated DND (DND_{chl}) and DND with mixed composition ($DND_{amine+chl}$). DND_{chl} was synthesized by heating DND of UDA-GO-SP brand (Sinta, Belarus, http://sinta.biz/produkt.html) in CCl_4–Ar mixture containing 3% CCl_4 at 400 °C for 5 h. DND_{amine} was obtained from DND_{chl} by heating in pure ammonia at 300 °C and 1 atm for 2 h. Partially converted product $DND_{amine+chl}$ was obtained similarly after 1 h reaction time in ammonia. For uniform application of DNDs on the surface of the material, their suspensions in glycerol were prepared, kept in an ultrasonic bath for 20 min and then immediately applied to the samples with following annealing at 160 °C for 12 h in an Ar atmosphere. For each type of modified DND, four different material types were prepared with total particle content on the surface of 2.3×10^{-4}, 3.1×10^{-4}, 3.8×10^{-4} and 4.6×10^{-4} g cm^{-2}.

To investigate biofouling, a pure culture of nonpathogenic facultative anaerobic organotrophic bacteria *Pseudomonas putida* strain K12 was used to study biofouling. The cultivation was carried out for 7 days in a liquid cultural media of the following composition: peptone - 4.0, yeast extract - 2.5, glucose - 1.0, NaCl - 1.0 g dm^{-3}. Optical visualization of biofilm was carried out by laser confocal scanning microscopy using a Leica SP5 microscope (Germany). Polysaccharide matrix was stained with lectin IV from wheat germ agglutinin (WGA) conjugated with Alexa Fluor 488 fluorescent dye (W11261 ThermoFisher, USA). Fluorescent dye SYTO 11 (S7573 ThermoFisher, USA) diluted 1:1000 in phosphate buffer was used for cell visualization. Images were obtained using an Ar laser with a wavelength of 488 nm (for detection of WGA fluorescence) and 594 nm (for detection of SYTO 11 dye). To detect undyed particles, the Nomarski contrast method was employed. The obtained images were analyzed using Imaris 7.0.0 software package (Bitplane, Switzerland) to calculate the percentage of area occupied by cells and polysaccharide matrix.



The presence of functional groups in DND samples after processing was evaluated by the IR spectra by comparing them with the spectrum of the initial UDA-GO-SP. Depending on the production method, the DND surface can contain different functional groups in different ratios[1]. A wide band of O–H stretching vibrations (3700–3200 cm^{-1}) is visible in the spectrum of the initial UDA-GO-SP; it may be either a group on of the DND surface, or a part of the carboxyl group. In addition, one can see typical valence (3000–2800 cm^{-1}) and torsion (maximum 1440 cm^{-1}) peaks of C–H vibrations, the band of CO_2 present in air (2400–2200 cm^{-1}), and C=O stretching vibrations of the carbonyl group (maximum ~1720 cm^{-1}), which is a part of the carboxyl group[2].

The peak of the OH group completely disappears in the DND$_{\text{chl}}$ spectrum; a new band of 1280 cm^{-1} appears and the shift of the C=O band is observed (maximum ~1780 cm^{-1}), which can

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[1] T. Burleson, N. Yusuf and A. Stanishevsky, *J. Achievements Materials Manufacturing Engineering*, 2009, **37** (2), 258.

[2] V.N. Mochalin, I. Neitzel, B.J.M. Etzold, A. Peterson, G. Palmese and Yu. Gogotsi, *ACS Nano*, 2011, **5** (9), 7494.

be explained by a change in the local environment, e.g., proximity to a Cl atom. In general, this allows us to suggest the formation of acid chloride groups on the surface (*R*-COCl). In DND_{amine} obtained from DND_{chl}, an intense peak that was initially absent is visible in the 1620–1670 cm^{-1} region, which corresponds to a slightly shifted band of secondary amides. This band is characteristic of all amides and occurs due to C=O stretching vibrations that are shifted to the high frequency region due to the proximity to the more electronegative N atom and to the low frequency region due to the resonance with the lone electron pair of the N atom and the hydrogen bond[2]. In addition, a peak again appears in the 3700–3200 cm^{-1} region, in this case, corresponding to N–H stretching vibrations; the intensity of the band at 1280 cm^{-1} is significantly reduced. For $DND_{amine+chl}$ particles, the intensity of the characteristic band of amides (1620–1670 cm^{-1}) is almost half as much, which indicates partial replacement of chlorine atoms by NH_2 groups, and the presence of both types of functional groups on the surface is observed.