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THE CHLORINATED SYNTHETIC DIAMOND SURFACE INTERACTION WITH C-NUCLEOPHILES

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Abstract

Several reactions of C-nucleophiles with the chlorinated surface of two types of diamond were implemented. Detonating nanodiamond "UDA-SF" and synthetic diamond "DALAN" have been employed in the above procedures. The incorporation of butyl and nitrile groups has been achieved. However the incorporating of phenyl groups via reaction with PhLi is still a problem. For the first time NMR-H1 spectroscopy of suspension was used for elucidating structure of grafting compound was proposed.

Keywords: nanodiamonds; grafting compounds; surface chemistry; chemical functionalization.

[*Engineering of Biomaterials*, 56-57,(2006),16-19]

Introduction

There is an escalating interest in diamond chemistry to

nanoscale diamonds in recent years [1]. It is due to several reasons. The first is that nanodiamonds (ND) became commercially available only in last ten years [2]. The second and obviously the most significant ones are their unique properties which combine mechanical, termic, radio and chemical stability of diamond as well as lability of functional cover of surface. The latter is determined by large value of specific surface area in ND. In various patterns of NDs specific surface area is about 300 m²/g or less whereas in the case of natural or synthetic diamonds powders the value of specific surface area usually is about several metres per gram. Such large value of specific surface area of NDs substantially increases possibilities of their further chemical modification and moreover enlarges the field of potential application of diamond materials. Among the most attractive utilizations of NDs are biomedical applications (nanoparticles for drug carry in vivo) and development of new chromatographic materials, especially for HPLC.

Also stable hydro- and organosoles of NDs are required for many technological applications. Therefore the problem of chemical modification of ND particle surface is of current importance. Besides modification of ND surface is attractive as a technique for unification of surface chemical state.

Notwithstanding the fact that NDs is a promising material the number of works concerning chemical modification of its surface is rather modest [3,4,5]. Therefore investigations on controlled chemical creation of grafting compounds on the ND's surface are of fundamental and technological importance.

Experimental

In the present work two types of diamond were employed: detonation nanodiamond "UDA-SF" and synthetic diamond powder "DALAN". "UDA-SF" is typical nanodiamond with the size of aggregates no more than 0.04 μm and specific surface area 245 m²/g (BET measurement). Synthetic diamond powder "Dalan" used represents itself a polydisperse powder with the size of particles from 5 nm up to 10 microns with a specific surface area of 22 m²/g (BET measurement).

Chemical state of diamond particles was characterized using Fourier-transform spectroscopy (IR200 Thermo Nicolet), NMR-H1 - spectroscopy (Bruker-Avance-400).

Results and discussions

It is necessary to mention that in native state the surface of diamond powder is covered by different oxygen containing groups (for ex. alcohol, carboxyl, carbonyl and others that is firmly confirmed by infrared spectra [6,7]), i.e. the surface is polyfunctional. And this fact complicates any further chemical reactions on the diamond surface due to nonselectivity of their passing. Consequently the polyfunctionality arises the problem of unification of diamond surface in order to make reactions that are carried out on it to be selective.

The most common procedure of unification, and moreover the only one, consists in hydrogen stream treatment of diamond at 1073 or 1173 K for 4 or 5 hours. These conditions are sufficient to modify the diamond surface in a way of hydride group's layer formation (Scheme, FIG.1).

It should be noted that specific surface area of diamond powder is slightly affected by this treatment as determined by BET analysis. So, after such treatment we obtained a fully hydrogenated diamond surface that is confirmed by IR-spectra presented (FIG.2).

As we can see from spectra, after such treatment stretch-

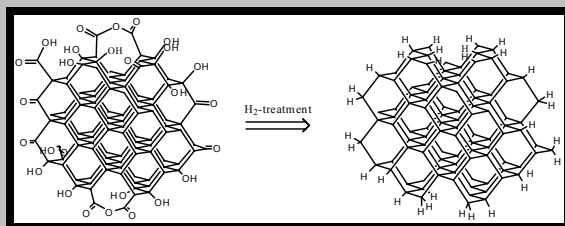


FIG. 1. Scheme. Reduction of diamond surface.

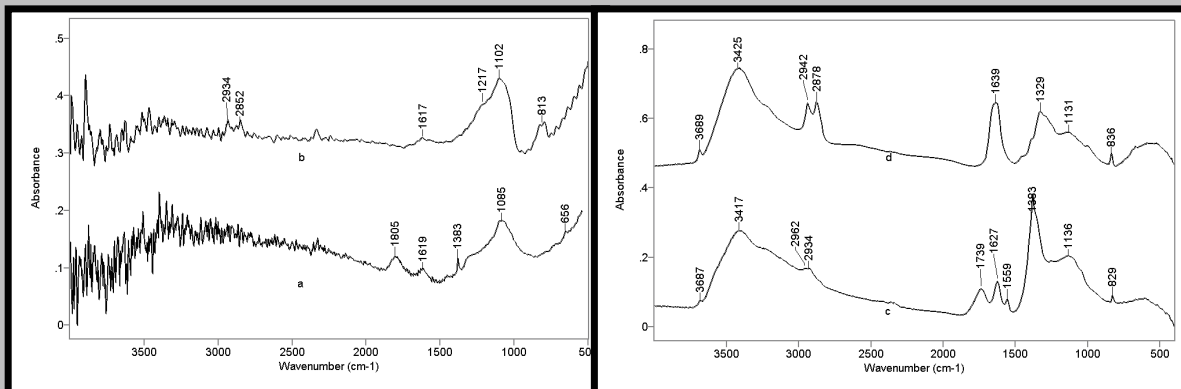


FIG. 2. FTIR spectra: a, c - pristine "DALAN" and "UDA-SF", b, d - the same diamonds after hydrogen stream treatment at 800°C for 5 h.

ing vibration related to C=O-group disappeared whereas two stretching vibrations of CH - bonds appeared. In the case of "UDA-SF" (FIG.3 spectra c and d) very strong adsorption of hydroxyl groups (3400-3500 cm^{-1}) is present even after hydrogen treatment.

By the way with the loss of polyfunctionality of the diamond surface we also have lost its reaction capacity within the formation of the CH-bonds on the surface.

In order to activate the surface in terms of electrophile center creation it was subjected to chlorination. Chlorination was performed in two ways. In case of "DALAN" chlorination was carried out by treating sample with sulfurylchloride in the presence of azobisisobutyronitrile (AIBN) in benzene in Ar ambient at 50-60°C. Photochemical chlorination by molecular chlorine dissolved in carbon tetrachloride was employed in case of "UDA-SF". As it was found by elemental analysis this treatment resulted in the ultimate chlorinated diamond surface formation. It is worth to point out that further treatment of "DALAN" with sulfurylchloride is yielded in sulfonylchloride group's layer

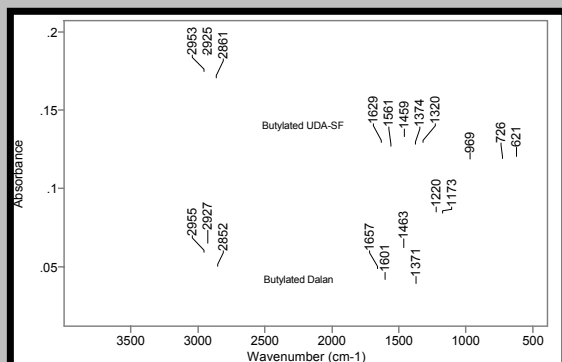


FIG. 3. FTIR spectra of butylated samples of "DALAN" and "UDA-SF".

formation.

Speaking of chlorinated diamond powder one should always keeps in mind that "fully chlorinated" doesn't mean that all surface bonded hydrogen atoms are substituted by chlorine. It only means that no further chlorination is possible under described conditions and that is due to steric hindrance or repulsion between chlorine atoms on the surface.

Further reactions of chlorinated of both types of diamonds were carried out after an exhaustive vacuum evaporation of the reaction mixture. The chlorinated diamond powder was then treated with n-BuLi (2.5M solution in hexane). The

butylation was carried out by stirring the suspension at 25°C for 24 h under an argon atmosphere. It should be noted that initially reaction mixture was subjected to ultrasonic treatment (50 Wh, 35±10% KHz) for 1.5 hours. The reaction was then terminated by adding water to the solution. The powder was then repeatedly washed with acetone, ether and water to remove LiCl and other organic by-products, and was dried in vacuum (<1 mm Hg.) for several hours and then characterized by FTIR spectroscopy.

This makes it possible to incorporate n-butyl groups onto the diamond surface which clearly seen from IR-spectra presented (FIG.3).

As it can be obviously seen from spectra presented the new vibrations appeared in the region of 3000-2800 and 1500-1300 reciprocal centimeters that are related to stretching and bending vibrations in alkyl chains, i.e. in butyl groups bonded to the diamond surface. Also frequencies assigned to stretching and bending vibrations of alcohol groups appeared too.

IR spectroscopy supplies us only with qualitative data. We can only see appearance or disappearance of certain bands in spectrum but very little can be gathered about the structure of grafted substance. In order to precisely determine the structure of surface groups we have proposed a simple technique utilizing NMR-H1 spectroscopy. We have collected NMR-H1 spectrum of suspension of n-Bu-UDA-SF in CDCl_3 (FIG.4). And it clearly indicates the presence of n-Bu group on the diamond surface.

Reaction of phenyl lithium (1.2M solution in Et_2O) with chlorinated diamond surface of "DALAN" was carried out in the same manner as with butyl lithium. FTIR spectra presented below (FIG.5).

But unfortunately the interpretation of IR-spectra of phenylated diamond surface isn't so vivid as with butylated diamond surface. For instance none of CH-bond stretching vibrations can be observed in spectra whereas bending vibrations (1488 and 1431 cm^{-1} , 1504 and 1434 cm^{-1}) are present. Thus in this case direct evidence of Ph-group grafting on to the diamond from IR-spectra cannot be obtained. In order to prove phenyl groups bonding to the diamond surface we treated phenylated diamond "Dalán" with nitrating mixture (hydrogenated diamond was also treated in the same way for comparison). In the case of phenylated diamond a

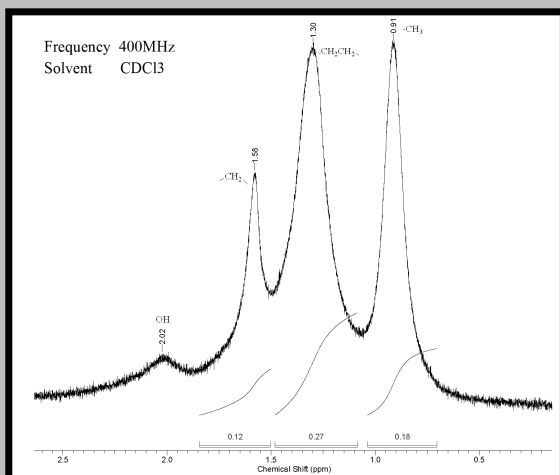


FIG. 4. Utilization of NMR-H1 spectroscopy of modified diamond suspension for elucidation structure of grafting compounds (by ex. of butylated UDA-SF).

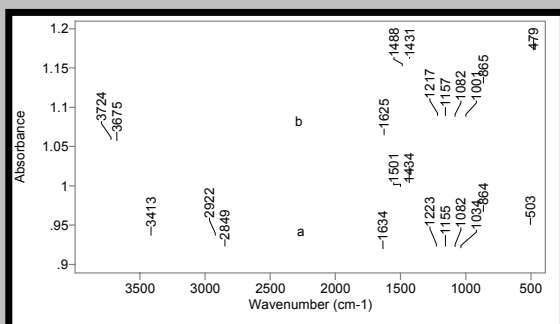


FIG. 5. FTIR spectra of phenylated „DALAN”: a - sample was treated with SO_2Cl_2 for 22 hours and then treated with PhL obtained via exchange reaction $n\text{-BuLi}+\text{PhBr}$ in Et_2O ; b - sample was treated with SO_2Cl_2 for 8 hours and then treated with PhLi obtained via reaction of met. Li with PhBr in Et_2O .

new adsorption at 1536 and 1347 cm^{-1} has appeared and these are due to antisymmetrical and symmetrical vibrations in NO_2 -group in $-\text{C}_6\text{H}_4\text{-NO}_2$ -fragments formed during nitration (FIG.6). No adsorption at 1536 and 1347 cm^{-1} was found in the case of hydrogenated diamond.

Thus we get an indirect evidence of incorporation of phenyl groups onto the diamond surface.

Our attempts to incorporate phenyl groups onto the "UDA-SF" surface via reaction with PhLi obviously have failed. On FIG.7 one can see FTIR spectra for the pristine, hydrogen treated and subjected to phenylation "UDA-SF". Phenylation was performed by adding a solution of PhLi in Et_2O (obtained via exchange reaction: $n\text{-BuLi} + \text{PhBr}$) to photochemically chlorinated for 24 hours "UDA-SF". FTIR spectra of treated sample clearly indicates that no phenyl groups are incorporated onto the surface at appreciable concentration. The only result of such treatment is only additional hydroxylation of diamond surface.

Nitrile group on the diamond surface is very attractive due to various possible ways of its trans-formation. So as to incorporate cyanide groups onto the surface of "DALAN" and "UDA-SF" a solution of sodium cyanide in anhydrous dimethylsulfoxide was added to chlorinated diamond powder. The reaction was carried out by stirring the suspension

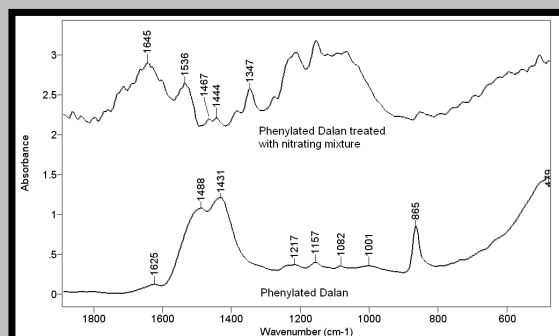


FIG. 6. FTIR spectra of phenylated „DALAN” and the same sample subjected to nitration by mixture of HNO_3 and H_2SO_4 .

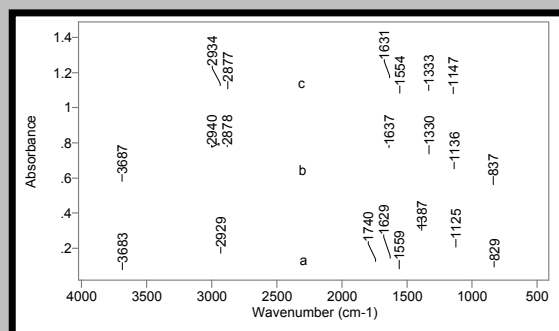


FIG. 7. FTIR spectra: a-pristine UDA-SF, b-hydrogen treated, c-phenylated”.

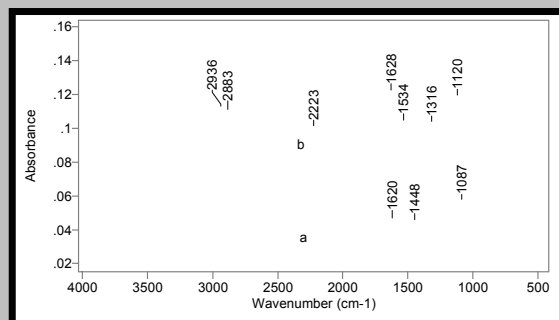


FIG. 8. FTIR spectra: a-NC-DALAN, b-NC-UDA-SF.

at room temperature for 24 h. The powder was then filtered, repeatedly washed with water and acetone, dried and characterized by FTIR spectroscopy (FIG.8). In both cases FTIR spectra showed strong disappearance of the CH-bond stretching vibrations but only in "UDA-SF"s spectrum new frequency ascribed to CN-group vibrations have appeared at 2223 cm^{-1} . The most evident reason explaining this fact is low concentration of nitrile groups on the surface of "DALAN" which has comparatively small specific surface area (22 m^2/g).

Conclusion

Reactions of several C-nucleophiles with chlorinated diamond surface were investigated and new modified diamonds with n-butyl and nitrile groups were obtained. For the first time NMR-H1 spectroscopy of suspension was proposed to elucidate structure of grafting compounds that can be helpful for fast and precise determination of organic functional groups on the surface.

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GROWTH OF CELLS ON CARBON COATINGS MANUFACTURED IN NEW MW/RF REACTOR

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Abstract

Due to unique physico-chemical properties and good biocompatibility are carbon layers considered to be promising material for wide field of biomedical applications. In this study, carbon films were manufactured in microwave and radio frequency plasma reactor using dual frequency method (MW/RF PCVD - microwave and radio frequency plasma chemical deposition). Four various processes of deposition were used for preparation layers on substrates of medical stainless steel AISI 316 L. On samples of all four processes, growth and adhesion of cells were observed.

[Engineering of Biomaterials, 56-57,(2006),19-21]

Experimental details

Materials and deposition procedure

In the present study we have studied carbon coatings (NCD) prepared in microwave and radio frequency plasma reactor using dual frequency method MW/RF PCVD - mi-

crowave and radio frequency plasma chemical vapour deposition. Parameters of the deposition were optimised to get uniform films on the stainless steel AISI 316L. Stainless steel substrates used in the present study were shaped as 2,5 mm thick circular discs with diameter of 8 mm. Substrates were machined, electropolished, ultrasonically cleaned in methanol and dried. Prior to NCD deposition, the surface were cleaned in an argon inert plasma in the vacuum chamber for 10 minutes. [1] Four various processes of deposition were used TAB. 1. In present paper, coated samples were named after number of deposition process, uncoated were just AISI 316L.

Cells and cultures conditions

Coated and uncoated samples were sterilized in steam autoclave by temperature 120°C for 20 minutes, immersed in tissue water. All samples were placed into polystyrene multidishes (Costar, 24 wells, diameter 15 mm) and seeded with human osteosarcoma cell line MG 63 and Dulbecco medium at the initial density 30 000 cells/well. Glass coverslips and the polystyrene dish as control materials were used. Cells were cultured for one, three and seven days in the temperature of 37°C in atmosphere containing 5% of CO₂. On day one and three after seeding, the cells were rinsed in phosphate-buffered saline (PBS), fixed with 70% cold ethanol (-20°C, 5 min), vizualized by propidium iodide (5µg/ml, 5min). Their morphology was evaluated and documented using epifluorescence microscope IX 50 equipped with a digital camera DP 70 (Olympus, Japan). Fluorescent cell linker kit PHK 26 RED and propidium iodide for better vizual representation, were used. The number of adhering MG 63 cells was counted in 10-16 randomly selected mi-

PROCESS	Methane [%]	Bias [V]	Power [W]	Pressure [Pa]	Time [min]
1.	30	400	150	10-60	6
2.	30	500	250	10-30	3
3.	20	600	250	10-25	4
4.	15	700	250	10-30	5

TABLE 1. Parameters of deposition processes.

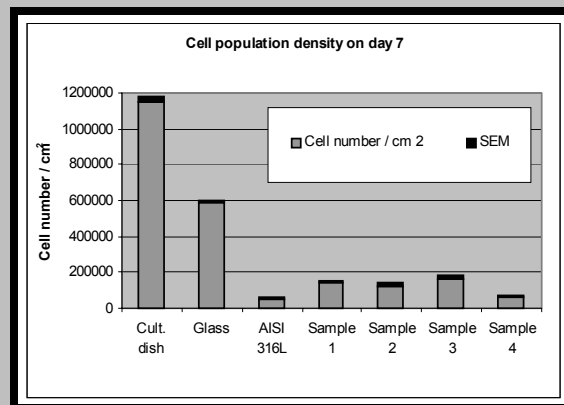


FIG. 1. Number of initially adhered osteoblast-like MG 63 cells on tissue culture polystyrene (Cult.dish), on glass coverslips (Glass), uncoated sample AISI 316 L, Sample 1, 2, 3, 4 on day 7 after seeding. Average \pm SEM from 10-16 measurements, statistical significance in comparison with values obtained on culture dish.

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