Hydrogen storage in irradiated low dimensional structures

Obolensky M.A., Basteev A.V., Bazyma L.A.

National Aerospace University "Kharkov Aviation Institute", 61070 Kharkov, Ukraine

Low dimensional periodic structures such as carbon nanotubes are looking perspective from point of view of the mass, volume, cost, safety, and efficiency requirements for vehicular hydrogen storage systems. Carbon nanotube (CNT) aggregates have been suggested as candidates for hydrogen storage due to their adsorbing characteristics, high surface area, and nanoscale dimensions. The two-dimensional substance $NbSe_2H_x$ has been studied lately [1]. Currently, it is important to continue searching for ways to increase the storage level at temperatures close to room temperature.

The high level H_2 molecule-binding energy is achieved both at elevated pressures and on the CNT bundles defect sites. The goal of paper is testing of CNT bundles hydrogen sorption capabilities increasing. The approach for this task solving consists in generation of defect sites in CNT and two-dimensional crystals $NbSe_2$ structures due to γ-irradiation treatment. The experiments have been performed using set-up [2]. In experiments two types of samples were tested both irradiated by γ-rays and non-irradiated and two temperature levels – the room temperature (293K) and liquid nitrogen temperature (78K).

The γ-irradiation in Co^{60} source with γ-quantum energy 1.17 MeV and total exposure 10^5 R was provided. The equilibrium temperature in the Co^{60} γ-channel was at the level of 325K (about 18 J/mole). After the irradiation procedure the irradiated samples were tested concerning the hydrogen absorption capability and comparative analysis was done. It has been showed that $NbSe_2$, CNT are sustainable for irradiation. The increasing (~15 percent) of hydrogen sorption-desorption capability for carbon nanotubes after irradiation treatment was demonstrated. Low temperature procedure of hydrogen storing showed the 2.9-3.5 mass percent of hydrogen. The increasing of hydrogen storing in $NbSe_2$ has not been observed.

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Carbon nanotubes in electronics and sensor devices

Bobrinetskiy I.I., Nevolin V.K.

Moscow Institute of Electronic Technology (Technical University), 124498 Zelenograd, Russia

The discovery of carbon nanotubes entailed large-scale investigations of their properties in the tasks of electronics, sensor techniques, composite structures, and probe microscopy. The most promising trends are the fields of using carbon nanotubes as functional devices for transistors, sensor systems, and temperature and moisture detectors.

We have realized principles and methodic of carbon nanotube integration in electronic devices, such as: varistors, FETs, logic gates and chemical sensors. In this work the precipitation of carbon nanotubes on wafers was performed using deferent deposition techniques based on carbon nanotubes solution covering. Carbon nanotubes were preliminarily diluted in 10 mL of 2-propanol for several hours in an ultrasonic bath. Then, a 3 inch silicon wafer with predefined metallic pattern placed in Petri dish was attached to voltage sources limiting electrodes. After that the solution was filled up into the Petri dish and voltage was applied. The duration of electrophoresis is 5-7 s.

We have investigated carbon nanotubes in electronics and sensors devices.

The carbon nanotubes ammonia sensor prototype had the following features:

- ammonia sensitivity range 25 - 300 *ppm*;
- output signal: ~ 15 nA/*ppm*;
- time response (room temperature): 150 sek;
- heater: no;
- power consumption: less then $3 \cdot 10^{-3}$ Watt;
- weight: 5 g;
- chip size : 6×6×2 mm;
- nanotube channel length: 2 μm;
- nanotube bundle diameter: 10 nm.

Using dielectrophoresis allows us to position nanotubes when they need to be fixed on electrically unconnected regions or to produce a complex three-dimensional scheme [1]. The last results show the perspectiveness of dielectrophoresis usage during the controlled and simultaneous precipitation of nanotubes on wafers containing the matrix of single-type crystals [2].

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Higher yield growth of multiwall carbon nanotubes at Fe-based catalysts

Mordkovich V.Z.*[*,+], Karaeva A.R.*, Zaglyadova S.V.*,
Maslov I.A.*, Don A.K.*

**United Research and Development Centre,119333, Moscow, Russia*
[+]ONEXIM group,123104 Tverskoy blrd 13, Moscow, Russia

The one of the most perspective fields of applications of short carbon nanotubes (CNTs) is filling various composites based on polymer, metal or ceramic matrix for improvement they properties such as strength, modulus, wear resistance, fire resistance, heat and electricity conduction etc. The chief problem for realization of unique properties of CNTs as filler is their high cost and low yields reached at present time. The yields of lower than 300 g/g, which were typical for earlier catalytic growth works reported before 2003 are no longer interesting for future development. The future of higher-yield CNT growth is related to satisfaction of three major requirements, i.e. (a) yield higher than 1000 g/g; (b) impurities of non-CNT as low as possible for easier purification; and (c) cheaper catalyst.

This work is dedicated to formulation of growth conditions for higher yield CNT growth on relatively simple and cheap Fe/Al_2O_3 catalysts. It is necessary to note that the Fe/Al_2O_3 catalysts of seemingly identical composition are reported to give wildly varying CNT yields. We are set to confirm that it is possible to reach reproducible, high yields of high quality CNT on these catalysts. The catalysts were prepared by impregnation of Al_2O_3 powder supports with aqueous or ethanol solutions of $Fe(NO_3)_3 \cdot 9H_2O$ to provide 1, 5, 10 or 20% Fe content in the support. The impregnated supports were then dried and fired. The supports were prepared by thermal treatment of boehmite AlO(OH). Depending on the temperature of the treatment we received γ-Al_2O_3 or δ-Al_2O_3 or θ-Al_2O_3 or α-Al_2O_3, which was confirmed by X-ray diffraction. The catalysts were additionally exposed by continuous wave laser annealing (Nd:YAG laser with $\lambda=1.064$ μm) before loading the catalyst into reactor. The laser power density of 10 to 100 W/cm^2 was used.

All the prepared catalysts were activated by hydrogen at 600°C and then the catalytic growth of CNT was carried out in a reaction gas mixture flow at the temperature from 650°C to 950°C. The reaction gas mixtures contained CH_4, H_2, N_2, benzene or toluene in various ratios. The reaction time was varied from 0.5 hr to 3 hr in order to confirm additionally the reproducibility. Experiments with all the catalysts led to formation of black powders of short CNT. The best results were reached for the catalyst 10 % Fe/δ-Al_2O_3 prepared with the use of ethanol solution of $Fe(NO_3)_3 \cdot 9H_2O$. The yield of 19100 g/g_{Fe} was reached at 650°C in 3-hour experiment with the use of benzene-saturated hydrogen gas (saturation temperature 20°C) as a precursor. The use of the laser annealing promotes the increase of CNT yield by 20-30%. Characterization by TEM, TGA and XRD showed that the product is dominated by short multiwall CNT with relatively narrow size distribution (20-50 nm diameter. 500-600 nm length) and nearly cylindrical layer stacking. No non-CNT carbon was observed. Carbon content was 97 to 98% weight; TGA manifested a single peak of CNT oxidation at 615°C.

The results witness very high yield of carbon nanotubes suitable as filler material for composites. The absence of non-CNT carbon in the product of catalytic growth makes final purification much easier.

Development and study of new modified fullerene coatings for the singlet oxygen generation

Kiselev V.M., Kislyakov I.M., Pavlova A.L.

Institute for Laser Physics, SIC Vavilov SOI, 199034 St.Petersburg, Russia

Results of development studies of new types of fullerene coatings designed for their application in solid-phase generators of singlet oxygen are presented. The purpose of the study was a search for the optimal composition of solid-phase fullerene-containing coatings and determination of an influence of modifying additives to fullerene on the singlet oxygen generation efficiency at an optical pumping light irradiation of the coatings. These additives should assure, on the one hand, a high mechanical strength of the coatings at the solid adhesion to the substrate, and on the other hand, the maintenance of a developed porous coating structure providing the optimal conditions for the singlet oxygen output from the coatings into the gas phase. Efficiency of the singlet oxygen production was detected by intensity and time duration of the singlet oxygen luminescence at the wavelength 1268 nm. It was shown that at certain factors satisfaction the operating parameters of the singlet oxygen generators with an application of the developed and studied coatings are succeeded in remarkable improvement.

MWCNT/poly(phenylene-*iso*-phtalamide) nanocomposite membranes for pervaporation of organic mixtures

Penkova A.V.[1], Toikka A.M.[1], Pientka Z.[2], Polotskaya G.A.[3]

[1] *St.-Petersburg State University, Chemical Department, St.-Petersburg, Russia*
[2] *Institute of Macromolecular Chemistry A S C R, Prague, Czech Republic*
[3] *Institute of Macromolecular Compounds R A S, St.-Petersburg, Russia*

Pervaporation is the modern process of membrane technology that allows separating azeotropic mixtures by evaporation through membrane. In the present work pervaporation was used for separating methanol and methyl-*tert*-butyl ether (MTBE) mixture that is characterized by azeotropic point containing 14.3 wt.% methanol and 85.7 wt.% MTBE at 20°C and 760 mmHg. The task of MTBE purification from methanol impurities after its synthesis is very important because MTBE finds application as an anti-knock additive to gasoline for increasing octane number.

The pervaporation efficiency depends on the correct selection of membrane material. The available membrane materials are needed in improvement of their physico-mechanical and transport properties. One of the ways for solving this problem is modification of membrane materials by nanoscale fillers. The aim of the present work is modification of poly(phenylene-*iso*-phtalamide) (PA) by multi-walled carbon nanotubes (MWCNT) Taunit®, preparation of homogeneous membranes from this nanocomposite, and study on their transport properties in separation of methanol/MTBE mixture.

Pervaporation of methanol/MTBE was studied in a wide range of feed mixture compositions using both nonmodified and modified (by 2 and 5 wt% MWCNT) membranes. It was shown that the selectivity and permeability for membrane containing 2 wt.% MWCNT have the highest values with respect to methanol as compare to conventional PA membrane and membrane containing 5 wt.% MWCNT. Study of membrane swelling in methanol took it possible to calculate Flory-Huggins parameters and coefficients of methanol diffusion in membrane that were involved in analysis of transport properties. To explain obtained results, membrane structure was studied by scanning electron microscopy, Raman and IR spectroscopy. It was established that MWCNT/PA nanocomposite membranes is effective in purification of MTBE from methanol impurities.

This work was supported by Russian Foundation for Basic Research (grant 09-03-00812).

Nanocomposites based on carbon materials and polyaniline for various applications

Sapurina I.Yu., Stejskal J.

Institute of Macromolecular Compounds RAS, 199004 St.-Petersburg, Russia
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

Polyaniline (PANI) is an organic polymer, which exhibits electronic conductivity of a semiconductor type in the range 10–10–102 S cm–1, and proton conductivity up to 102 S cm–1. It has a redox activity and good thermal and environmental stability. The nanocomposites of carbonaceous materials and PANI can be obtained in a single reaction step by the oxidation of aniline in the presence of carbon nanotubes, nanofibres, various types of graphites, and carbon black. The objects in such composites have a core–shell structure, where the carbon template is encapsulated in a nanolayer of PANI. The content of PANI can be widely varied, as well as the coating thickness. The coatings are uniform and have a good adhesion to the carbon surface.

It has been demonstrated that the morphology of a composite material, its surface area and porosity are determined basically by the carbon template. The properties of PANI in the composite can reversibly be changed by controlling the degree of oxidation and protonation and, consequently, the properties of the whole composite change. The protonation of PANI with various acids enables the conversion of hydrophobic carbon substrate to hydrophilic PANI-coated carbon and may improve the compatibility with other polymer materials due to the presence of functional nitrogen-containing groups in PANI. The materials with a wide range of properties can be prepared in this way, by selecting a carbon of suitable morphology, and by controlling the type, content, and thickness of PANI coating.

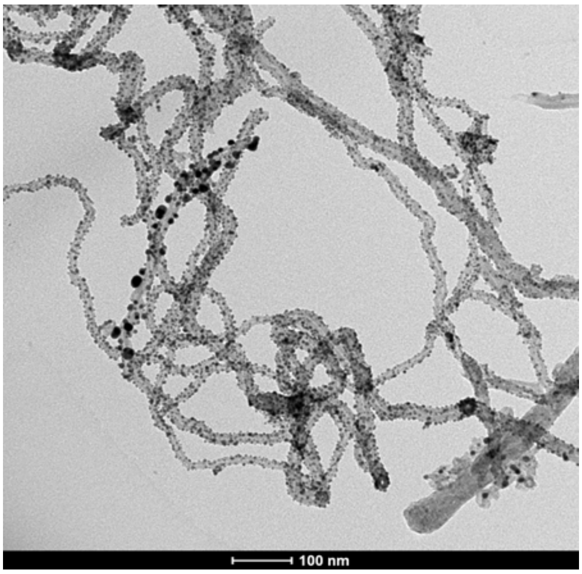

Figure. Multi-wall carbon nanotubes coated with PANI and decorated with platinum nanoparticles.

The nanocomposites are well suited for the various applications, such as redox-active electrodes in batteries and supercapacitors, dispersed phase in electro- and magnetorheology, low-temperature emitters of electrons, active elements in sensors, low-density electromagnetic-interference shielding, etc. The present study demonstrates following means of the application of a conducting polymer, PANI, along with various allotropic forms of carbon.

(1) Composites of PANI with carbon black have been used as substrates for the deposition of catalytically active noble metals – platinum, palladium, rhodium, ruthenium, and gold – followed by the application in hetero-geneous catalysis. (2) The composites with graphite have been used as components in the coatings for corrosion protection of metals. (3) The composites of PANI with carbon nanotubes have a good compatibility with epoxy resins. Such composites may exhibit improved mechanical properties and good conductivity.

Newcatalytic systems based on nanodiamonds for CO oxidation

Vershinin N.N.[1,2] , Efimov O.N.[1], Bakaev V.A.[1], Korobov I.I.[1],
Gusev A.L.[3], Aleksenskiy A.E.[4], Vul' A.Ya.[4],

[1]Institute of Problems of Chemical Phisics, 142432 Chernogolovka, Russia
[2]JSC "VEAL Sensor", 142432 Chernogolovka, Russia
[3]Scientific Technical Centre "TATA", 607183 Sarov,Nizhny Novgorod, Russia
[4]Ioffe Physical- Technical Institute, 194021 St.-Petersburg, Russia

Carbon monoxide is one of most dangerous air contaminants in accommodation space (kitchens, passenger compartments, garages, etc.). A brief analysis of properties of CO oxidation catalysts comprising platinum metal and gold clusters on oxide supports nanocarbon materials is reported in [1]. We were the first to find [2,3,4] that the use of detonation nanodiamonds (DND)as platinum metals and gold carriers allows one to develop efficient CO oxidation catalysts operating at room temperature. The catalysts show the following physical-chemical characteristics:

1. Characteristic size of active metal cluster - 5×5×0.7 nm;
2. Active metal - Pt, Pd, Rh, Ru, Au and their alloys;
3. Specific surface of active metal cluster - 100…200 m^2/g;
4. Content of surface atoms of active metal - 20…30%.

High activity of newly developed catalysts in CO oxidation reactions (GHSV=2…5· 10^6 h^{-1} at 20°C and CO conversion level is 90%) is die to small size and localization of metallic clusters on high-purity DND surface (average size of ND particles is 5 nm). Nanodiamonds were prepared at Ioffe Physico-Technical Institute [5,6]. Using these catalysts JSC "VEAL Sensor", IPCP RAS and Scientific Technical Centre "TATA" developed new mini solid-state gas sensors to CO, which demonstrate high selectivity, and efficient catalytic systems for CO oxidation at 0…100 ppm and -10…50°C. Figure 1 shows the dependence of relative oxidation rate for CO on active metal content in catalyst. Figure 2 shows CO sensors.

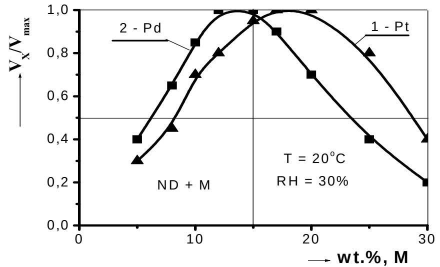

Figure 1

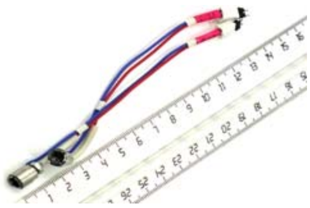

Figure 2

The work was supported by Federal Science and Innovation Agency (SC N02.513.12.3022).

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