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Icing and chemical pollution sensor based on carbon nanoparticles-based superhydrophobic coating

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Abstract. A method of using a section of a superhydrophobic coating based on xerogel made out of carbon nanotubes and carbon-like onions as an icing sensor was suggested. The obtained dependencies of the conductivity of the coating on the state of the environment are not linear, but unambiguous. They allow to track changes in the environmental conditions. The sensitivity of the coating to volatile substances adsorbed by the surface of the carbon nanoparticles was revealed. Selection ways of the influence of ice and pollutants were suggested. The coating area serves as a protective surface and a detector, and its dual purpose not only simplifies the anti-icing system, but also allows it to potentially work as a chemical sensor aimed at detecting contaminants. The dimensions of the sensitive areas are determined by the reliability of local data and the sensitivity of the surface resistance measurement circuit, and therefore can vary quite freely. Samples with an area from 10 to 0.5 square centimeter were used in the work.

Keywords: carbon nanotubes, anti-icing coatings, superhydrophobicity, icing

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Материалы конференции

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Датчик обледенения и химического загрязнения из сверхгидрофобного покрытия на основе углеродных наночастиц

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Аннотация. Предложен способ использования участка сверхгидрофобного покрытия на основе ксерогеля из углеродных нанотрубок и углерода луковичной структуры как датчика обледенения. Полученные зависимости проводимости покрытия от состояния окружающей среды не являются линейными, но однозначны и позволяют отследить изменение условий окружающей среды. Выявлена чувствительность покрытия к летучим веществам, сорбируемыми поверхностью углеродных наночастиц. Предложены пути селекции влияния льда и загрязнителей. Двойное назначение участка покрытия — защитная поверхность и датчик, не только упрощает антиобледенительную систему, но и потенциально способна работать как химический сенсор для определения загрязнений.

Размеры чувствительных площадок определяются достоверностью локальных данных и чувствительностью схемы измерения поверхностного сопротивления, а значит может варьироваться достаточно свободно. В работе использовались образцы площадью от 0.5 до 10 квадратных сантиметров.

Ключевые слова: углеродные нанотрубки, антиобледенительные покрытия, сверхгидрофобность, обледенение

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Introduction

Development of the North, work in areas with poor climatic conditions and the climate change itself require devising ways to protect structures, communication lines and equipment from corrosion, pollution and icing. One of the passive methods of protection that does not require energy is the use of hydrophobic and superhydrophobic coatings. Due to the small contact area of the droplet with the surface for such coatings heat exchange with the cold surface is greatly slowed down: the droplet has time to slide off the coating without having time to freeze [1].

In work [2], we proposed an anti-icing superhydrophobic coating based on carbon nanoparticles xerogel. The coating was presented as a two-layer coating - a heating layer of carbon nanotubes (CNTs) and a hydrophobic one of onion-like carbon (OLC). This combination allows you to save energy due to anti-icing properties at temperatures down to -10°C and de-ice the coating at lower temperatures, when the lotus effect is lost upon the icing of the surface.

During testing of the heating layer, the dependence of its electrophysical properties on the presence of volatile substances in the air, its humidity and temperature was noticed. This leads to the idea of using coating areas to determine environmental conditions and control the operation of the heating layer. The task of detecting icing is equivalent to the task of detecting a chemical substance (water and its vapors) in a certain range of conditions (temperature and humidity). The most common way to monitor icing processes is to measure the conductivity of the surface being iced.

In article [3], the authors grew carbon nanotubes on a silicon substrate using the chemical vapor deposition (CVD) method. The authors then functionalized the surface of the grown nanotubes to increase their sensitivity to ice formation. To do this, they used sulfonating agents such as concentrated sulfuric acid or a mixture of sulfuric acid and sulfuric anhydride. This made it possible to increase the sensitivity to ice formation. The resulting sensors were tested on a model aircraft in an ice chamber.

In article [4], the authors present a similar type of icing sensors. The principle of their manufacture is the same, however, CNTs were subjected to secondary functionalization. Initially, oxygen-containing functional groups were created on the surface of carbon nanotubes. Then sulfonating agents were used. This made it possible to increase the affinity of nanotubes for water and increase their sensitivity to ice formation. In [4], the authors also used the polymer polyvinyl-aminourea (PVI_m), which was chemically bonded to the surface of carbon nanotubes. Polymers such as polyethyleneimine (PEI), polyaminoimidazole (PAI), polyamine (PAM), polyacrylamide (PAAm) and others have been used.

In work [5], the authors describe the development of icing sensors based on carbon nanotubes with improved sensitivity and selectivity. Copper nanoparticles were deposited on CNTs. The sensors are highly sensitive and selective to the formation of ice on the surface, and also show a fast response to changes in temperature and humidity.

Materials and Methods

In the course of the work, carbon nanoparticles with known characteristics from the manufacturer were used (OLC [6], CNT–Nanotechcenter LLC [7]).

Taunit-M, if necessary, was subjected to oxidative functionalization in hydrogen peroxide to obtain -OH groups on their surface. To do this, 250 mg of purified CNTs were added to 250 ml of hydrogen peroxide (30%) heated to 100°C, and kept at atmospheric pressure at a temperature of 100 C in a water bath. The reaction lasted 120 minutes.

Coating samples were prepared according to the procedure in work [2]. The sputtering device consisted of a flask where nanoparticles were deagglomerated by the cavitation effect caused by an MEF 93.1 ultrasonic disperser with an effective power of 0.5 kW. Dispersion lasted about ten minutes, after which the resulting sol was fed into an airbrush mounted on a programmable coordinate device. By smoothly moving the airbrush over the sample, uniformity and homogeneity of the deposition of the sol with nanoparticles onto the sample were achieved.

Getinaks was used as a substrate. 2 mm thick tinned copper conductive tracks with an interval of 2 cm were glued on top of it. About 7-8 layers of coating were applied one after another as the previous one dried. The parameters for applying the hydrophobic layer were as follows: surface roughness, 28 μm ; concentration of nanoparticles in the dispersion suspension, 0.05 g of nanoparticles per 60 mL of hexane.

This is how the heating layer of the coating [2] was created on the basis of the Taunit CNT. To obtain a two-layer coating, an already obtained sample with a heating layer was coated with a hydrophobic layer of OLC. This layer was applied in exactly the same way as described above. Before the measurements, the samples were kept in a dry room for a week for a final drying. For measurements, the samples were placed under a sealed glass cap, which, in turn, was installed in an Espec PG-2J climate chamber (Japan). The electrical properties of the samples were measured using the Novocontrol Concept 80 dielectric spectrometer.

Results and Discussion

The dependence of the resistance of the coating from a single heating layer based on Taunit-M, Taunit-M with hydroxyl groups and from a two-layer sample consisting of a Taunit-M heating layer and a superhydrophobic layer (OLC) are shown in Fig. 1.

It is clear that the resistance of the proposed coating [2] is sensitive to humidity and temperature. The obtained dependencies are not linear, but are unambiguous and allow tracking changes in environmental conditions. Of particular note is the moment of intersection of the dependences in Fig. 1, *b*, which should correspond to the moment of formation of the conditions for the development of icing.

The main difficulty in using the proposed coating as a sensor is that the sensitivity of the resistance of carbon nanoobjects does not only apply to water in certain phases. Other volatile substances also change the resistance of carbon nanoobjects. For example, work [8] shows the sensitivity of CNTs to nitrogen dioxide and work [9], to ammonia. We measured the effect of ethanol and hexane vapor concentration on coating resistance at room temperature, the results are shown in Fig. 2. The data are normalized to the percolation network resistance in the absence of volatiles.

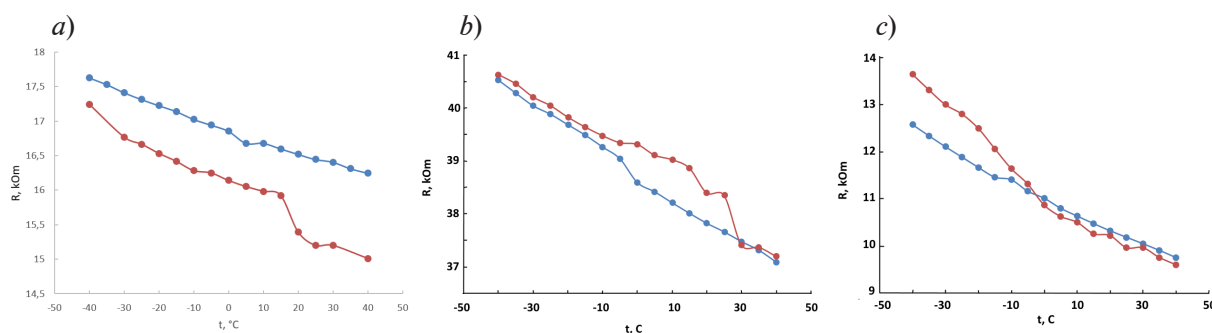


Fig. 1. Dependence of the resistance of the hydrophobic coating area depending on humidity and temperature: (a) is a heating layer based on the Taunit-M CNT, (b) a heating layer based on CNT-OH, (c) a two-layer coating of a heating layer and a superhydrophobic layer based on OLC. The data are normalized to sample readings at n.c. The red line is the sample at 5% humidity, the blue line is at 95% humidity

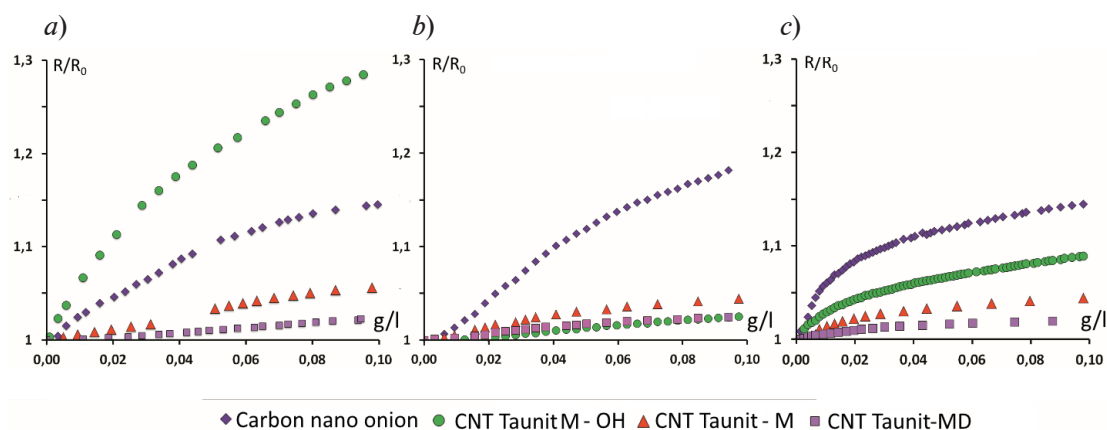


Fig. 2. Dependence of the resistance of the hydrophobic coating area (onion-like carbon (violet rhombuses), Taunit-M with hydroxyl groups (green circles), Taunit-M (red triangles) and Taunit-MD (pink squares) without functional groups) at different concentrations of volatile substances in the air.

Volatile substances: (a) hexane, (b) mixtures of ethanol and hexane in a ratio of 1: 1, (c) ethanol.

The values along the vertical axis are normalized for the resistance of the sample in clean air

It is clear that OLCs respond to an increase in the concentration of impurities in the atmosphere faster than non-functionalized CNTs. To change the resistance, a carbon nanoobject must be covered with a sorbed impurity so that the areas where the impurity affects the band structure of the nanoparticle are in contact and do not leave alternative paths for the movement of charge carriers. This assumption is indirectly confirmed by the higher sensitivity of Taunit-M over Taunit-MD.

It is interesting that CNT-OH react faster not only to polar impurities, but also to non-polar ones. We explain this by the fact that the functional groups play the role of protrusions that widen the gaps between individual CNTs during xerogel formation. As a result, the sorption of the impurity occurs faster due to facilitating the penetration of vapors into the CNT agglomerates. The reason for the decrease in the sensitivity of CNT-OH to a mixture of hexane and alcohol is not clear to us. One could assume that polar and nonpolar molecules interfere with each other's sorption.

The easiest way to organize the operation of the sensor is by comparing two sections of a two-layer coating - one that is protected from external moisture (inside the case) and an external one that is exposed to atmospheric influences and tracks the moment of intersection of the dependences in Fig. 1,b. Several approaches can be taken to avoid false positives that could cause volatiles in the air.

It is possible to protect the sensor area with a selective membrane that passes mainly water vapor. The downside of this method is that the coating area will no longer be superhydrophobic. Several additional sensitive sites from CNTs of other brands and functionalized CNTs could serve as an alternative. By processing the readings of additional areas, it is possible to determine the presence of contaminants and avoid false positives. However, this requires additional research.

The dimensions of the sensitive areas are determined by the reliability of local data and the sensitivity of the surface resistance measurement circuit, and therefore can vary quite freely. We used samples with areas ranging from 10 cm² to 0.5 cm².

Conclusion

The novelty of the proposed approach lies in the fact that the icing sensor can be organized on the basis of the existing technology for creating a superhydrophobic coating based on carbon nanoparticles. In the works listed in the review, the sensor was formed by growing a CNT percolation network by the CVD method on a substrate and connecting the contacts to it. This approach limits the available materials, as it requires the substrate to be heated to high temperatures. The technology we offer allows you to spray a coating on a wide range of substances - metals, plastics, polymers, wood. In fact, there is no need for the sensor as a separate part. The dual purpose of the coating area - a protective surface and a sensor, not only simplifies the anti-icing system, but also has the potential to work as a chemical sensor to detect contaminants.



The complexity of the practical application of this approach lies in the fact that the percolation networks of carbon nanoobjects are sensitive to the presence of air pollutants such as ammonia, alcohol vapor and gasoline. We assume that the presence of additional sections of sputtered nanotubes of other brands and types of functionalization (-OH, -COOH, -NH₂ groups) sensitive to volatile substances will make it possible to detect the presence of impurities in the atmosphere and subtract their effect on the conductivity of the coating. Undoubtedly, separate studies are needed for this. An alternative to this would be the search for a functional group that has a high selective sensitivity to ice formation, similar to work [5].

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