

Aryldiazonium Tosylates as New Efficient Agents for Covalent Grafting of Aromatic Groups on Carbon Coatings of Metal Nanoparticles

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Abstract—The possibility of the spontaneous covalent modification of the surface of metal nanoparticles coated by carbon by arylldiazonium tosylates was demonstrated for the first time.

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More and more attention is being focused on the application of nanosized materials in medicine, biotechnologies, and other branches of science and technology [1–3]. It is necessary to add certain properties to the surfaces of nanoparticles, which can be achieved by modifying their surfaces with various organic functional groups [4–6]. As a result, it becomes possible to obtain the immobilization of various biomolecules on the surface of nanoparticles [7, 8], the stability of colloidal solutions of the particles [9], or an affinity to certain receptors [10].

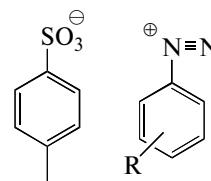
Recently, it has been revealed that a certain class of organic compounds, arylldiazonium chlorides $\text{ArN}_2^+ \text{Cl}^-$, is capable of interacting with the surfaces of certain nanoparticles coated by carbon layers when a nitrogen molecule is evolved and when the covalent bonding of aryl (Ar) radicals with the surface occurs [11]. However, these reagents are characterized by several significant disadvantages related to their low stability and explosion hazard, and this requires a special operation environment (a decreased temperature, fine pH adjustment, etc.). Relatively stable diazonium salts are known (aryldiazonium tetrafluoroborates $\text{ArN}_2^+ \text{BF}_4^-$); however, their application is restricted by their low solubility in water and in organic solvents.

We have recently obtained a new type of stable diazonium salts: arylldiazonium tosylates $\text{ArN}_2^+ \text{OTs}^-$ (ADT) [12]. ADTs are characterized by numerous valuable advantages in comparison with the known diazonium salts: high solubility in water and organic solvents, high storage stability, and explosion safety (confirmed by the data of differential scanning calorimetry). We have demonstrated that ADTs react spontaneously with the surfaces of graphite voltammetric electrodes, providing the covalent bonding of

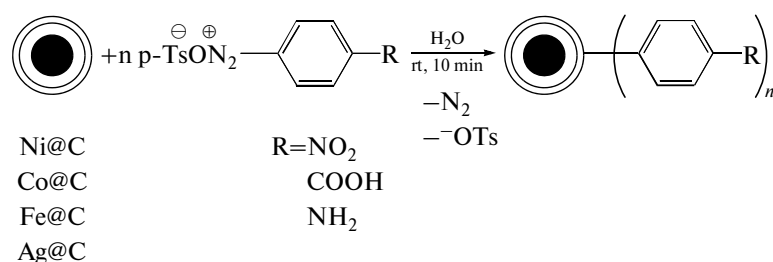
Ar radicals with the surface and increasing the sensitivity of electrodes in a voltammetric analysis of certain organic substances [13]. In this work we demonstrate the possibilities of applying ADTs (I–III) to modify the nanoparticle surfaces for the first time.

Nanoparticles of various metals (iron, nickel, cobalt, and silver) with carbon coatings were studied as nanocomposites. The nanocomposites were obtained by gas-phase synthesis, which has been described in details elsewhere [14]. In our modified method, the evaporator is droplet of liquid metal (Fe, Ni, Co, Ag) that is highly overheated by inductive currents and suspended and flushed by the flow of inert argon gas containing hydrocarbons. Metal clusters Fe, Ni, Co, and Ag, evaporating from the surface of the liquid metal, serve as centers of the nucleation and growth of the carbon phase resulting from the pyrolysis of hydrocarbon. The nanocomposites which formed in the bulk of the inert gas are, as a rule, spherically symmetric metal nanoparticles encapsulated in carbon. Detailed data on the structure of the nanocomposites, for instance, on the basis of nickel encapsulated in carbon (Ni@C) are presented elsewhere [14].

It was found that the ADTs react spontaneously with the aforementioned nanoparticles in aqueous suspensions at room temperature according to the general scheme (Scheme 2).



Scheme 1. The structure of arylldiazonium tosylates ($\text{R} = \text{NO}_2$ (I), NH_2 (II), COOH (III)).



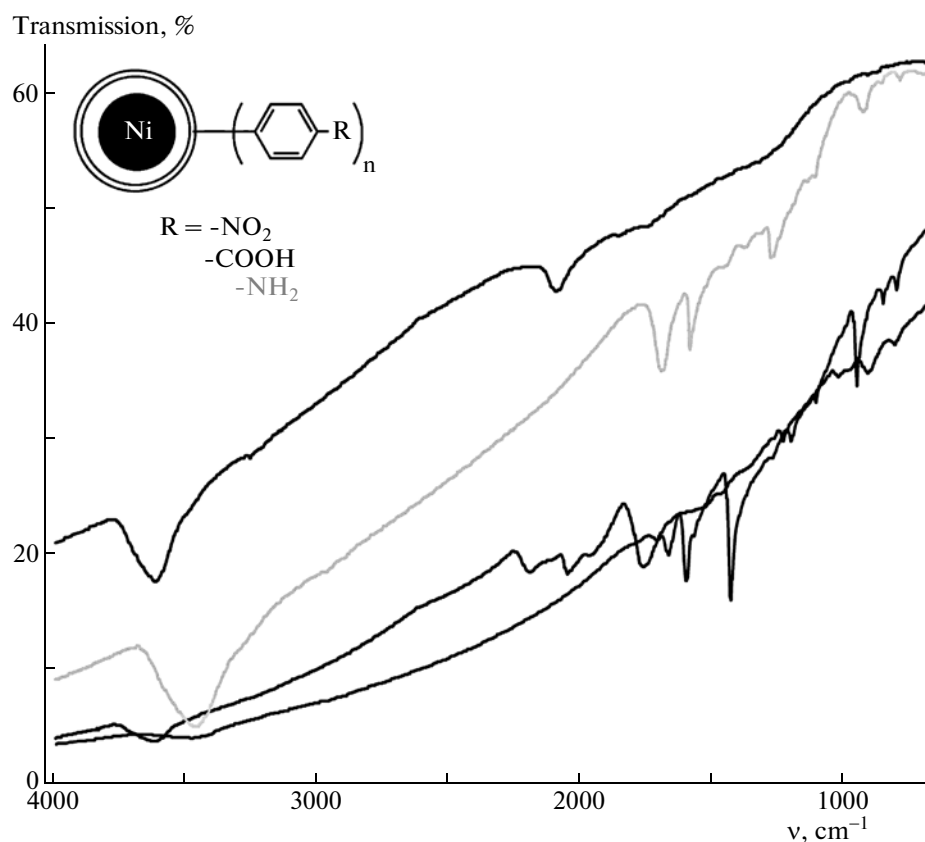
Scheme 2. Covalent functionalization of nanomaterials by arenediazonium tosylates (I–III).

Upon the addition of aqueous solutions of ADT (I–III) to a preliminarily prepared suspension of nanoparticles, nitrogen intensively evolves, evidencing the decomposition of diazonium salt. After the termination of the gas evolution, the modified nanoparticles were magnetically separated (for the case of the modified Ag@C particles, the separation was performed by centrifugation). The decomposition products of ADT were removed by the double washing of the obtained materials with distilled water, ethanol, and acetone until organic products in the wash solutions disappeared (thin-layer chromatography). The modified nanoparticles were analyzed by IR-spectroscopy, which revealed the existence of appropriate functional groups (COOH, NO₂, NH₂) on the surfaces

(characteristic bands of bond vibrations are given in Table 1).

The characteristic bond oscillation of benzene rings in the range of 650–1100 cm⁻¹ was also observed in all cases. The spectral characteristics illustrated in the figure coincide completely with the spectra of the nanoparticles modified by aryldiazonium chlorides [11].

The method is of a sufficiently general character: the modifications are applied only to the nanoparticles coated by carbon (Ni@C, Co@C, Fe@C, Ag@C), irrespectively of the composition of the metal cores. The reaction run was equally efficient for the whole set of ADT, and no effect from the substitutes (-NO₂; -COOH; -NH₂) on the process behavior was observed. It should be noted that this method makes it



IR-spectra of Ni@C nanoparticles modified by ADT (I–III).

Characteristic frequencies of bond vibrations in the structure of modified nanoparticles

R	Nanomaterial	ν , cm^{-1}
-COOH	Fe@C	1601, 3441
	Ag@C	1630, 3434
	Co@C	1594, 3434
	Ni@C	1601, 3444
-NH ₂	Fe@C	1625, 3426
	Ag@C	1633, 3436
	Co@C	1617, 3440
	Ni@C	1618, 3441
-NO ₂	Fe@C	1346, 1521, 1628
	Ag@C	1336, 1463, 1743
	Co@C	1347, 1520, 1632
	Ni@C	1346, 1519, 1634

possible to graft reactive groups on the surface of nanoparticles. In particular, amine- and carboxy-groups make it possible to immobilize various biomolecules or pharmaceutical drugs on the surface of nanoparticles.

When the surface of nanoparticles is modified by 4-carboxyphenyldiazonium tosylate, the products obtained in an aqueous medium resulted in a sufficiently stable suspension. No noticeable sedimentation of nanoparticles was observed even after storage for a week.

Therefore, we developed a new and simple method for the covalent modification of the surfaces of metal nanoparticles (Ni@C, Co@C, Fe@C, Ag@C) coated by carbon by applying aryldiazonium tosylates. This method makes it possible to obtain organic reactive groups on the surface of nanosized materials which are potentially suitable for the covalent immobilization of various biomolecules.

EXPERIMENTAL

Ethyl alcohol and acetone of the "chemically pure" grade without purification were used. The IR-spectra were recorded by a Nicolet 5700 FT-IR spectrometer in KBr tablets.

STANDARD PROCEDURE OF COVALENT MODIFICATION OF NANOSIZED POWDERS COATED BY CARBON

A solution of ADT (0.01 mol) in 5 ml of distilled water was added to 0.03 g of carbon-coated nanoparticles (Ni@C, Co@C, Fe@C, Ag@C) that had been preliminarily dispersed in 5 ml of distilled water (ultrasonic irradiation at 22.2 kHz in 2 s). The reacted mass was held for 10 min with periodical shaking. The modified powders were separated using a magnet (the sep-

aration of Ag@C was performed by centrifugation) and washed twice with water, ethyl alcohol, and acetone. The characteristic frequencies of bond vibrations of organic residues on the surface of the obtained products are given in Table 1.

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