Arendiazonium tosylates as new, available and convenient reagents for the formation of organic layers on carbon surfaces

Victor D. Filimonov¹, Pavel S. Postnikov¹, Marina E. Trusova¹, Nataly S. Surgutskaya¹, Ki-Whan Chi²

¹ Department of Organic Chemistry, National Research Tomsk Polytechnic University, Tomsk 634050, Russia, ² Department of Chemistry, University of Ulsan, Ulsan 680-749, Republic of Korea

Corresponding author (filimonov@tpu.ru)

Keywords: diazonium salts, carbon surfaces, covalent grafting

1 General Introduction

It has been well known that one of the most effective methods for the covalent surface modification of carbon, metal, and semiconductors is through the use of diazonium compounds. Commonly arenediazonium ions are chemically or electrochemically reduced into radicals that covalently attach to carbon, metal, and silicon surfaces, forming covalently bonded dense functional layers [1]. However, the usual arenediazonium salts are unstable and potentially hazardous or hard soluble in water and other common solvents.

Recently it was shown arenediazonium tosylates ArN₂⁺ TsO⁻ (ADT) are a novel class of available diazonium salts possess unprecedented stability and good solubility in water and common organic solvents [2].

2 Results and Discussion

We have found that ADT spontaneous react with various carbonize surfaces in water mediums lead to covalent grafting of different aryl groups on the surface (Scheme 1).

\[
\text{ArN}_2^+ \text{TsO}^- \xrightarrow{\text{water/rt/10 min}} \text{Ar} \text{Ar} \text{Ar} \text{Ar} + n \text{N}_2
\]

Ar = Ph, 4-C₆H₄NH₂, 4-C₆H₄NO₂, 4-C₆H₄CO₂H, 4-C₆H₄Bu, 4-C₆H₄C₆H₁₃, 4-C₆H₄I, 2,4,6-I₃C₆H₂

Scheme 1. Modification of carbon surfaces by arenediazonium tosylates of appropriate functional groups (COOH, NO₂, NH₂, etc.) on the surfaces.

Graphite, glassy carbon, carbon nanotubes, nanodiamonds, and metal nanoparticles coated by carbon shells M@C (M = Fe, Ni, Co, Ag) were successfully surface modified by ADT. The bonded organic layers are stable at storage and resistance with respect to treatment with water or organic solvents under the ultrasonic exposure.

The modified composite materials were analyzed by IR ATR spectroscopy which revealed the existence

To prove the covalent bond between the surface of nanoparticles and organic functional groups and determine the number of functional groups on the surface, we used an integrated method of DSC/TG analysis in argon atmosphere with mass-spectroscopy determinations of gaseous products. For the analysis we used carbon-coated Fe-nanoparticles (Fe@C) and nanoparticles, modified
by 4-carboxybenzenediazonium tosylate (Fe@C₆H₄COOH). The typical form of TG curves is presented in fig. 1.

**Fig. 1.** The TG curves of modified nanoparticles (Fe@C, Fe@C₆H₄COOH)

The thermal decomposition of nanoparticles Fe@C₆H₄COOH starts at lower temperatures (250 °C), then starting nanoparticles Fe@C. Also, on the TG curves we haven’t observed the thermal processes associated with phase transition of benzoic acid. Reduction of weight in the range from 250 °C to 450 °C is associated with CO₂ evolving, determinate by the mass-spectroscopic detection (fig. 2).

**Fig. 2.** The mass-spectra investigations of CO₂ (44 a.m.u.) evolving (Fe@C, Fe@C₆H₄COOH).

Release of CO₂ occurs due to decarboxylation of C₆H₄COOH functional groups covalently bound with the surface. The calculated quantity of functional groups C₆H₄COOH coated on the surface is 0.12 mmol/g.

In case of the modified Fe-nanoparticles coated by carbon (Fe@C₆H₄COOH and Fe@CCl₃H₂I) we have carried out also secondary chemical transformations of iodine atom and COOH functional group.

The polyvalent iodine derivatives are very useful reagents in organic synthesis [3]. But sometimes there are well known problems with separation these reagent from reaction mixtures and purification of target products. These problems can be solved by creating materials in which active iodoso groups are fixed on a nanosized magnetic platform and can be isolated from reaction mixtures by magnetic separation. For this purpose we oxidized modified nanoparticles Fe@CCl₃H₂I by peracetic acid in AcOH at room temperature for 24 hours according to scheme 2. The presence of I(OAc)₂ groups in the resulting material proved by strong absorption bands in the infrared spectrum at 1500-1750 cm⁻¹ (fig. 3).

**Fig. 3.** The IR ATR spectra of modified nanoparticles (Fe@C, Fe@CPhI, Fe@CPhI(AcO)₂)

The obtained material Fe@CPhI(AcO)₂ is the first example of polyvalent iodine reagent attached to magnetic nanosized support and can be used as magnetically separated reagent in organic synthesis.
Scheme 2. Synthesis of phenyliodoacetate groups on the magnetic nanoparticles surface

Chelating functional groups, covalently attached to the magnetic nanoparticles, can be used as magnetic separated catalyst in organic synthesis, as magnetically controlled diagnostically agent in medicine and in related fields of sciences. Also, chelating groups can be used for radioactive isotope immobilization. For this purpose, we have synthetized the chelator on the basis of iminodiacetic acid (IDA) on the nanoparticles surface (scheme 3).

Scheme 3. The synthesis of iminodiacetic groups on the nanoparticles surface

The synthesis was realized in three steps. After modification of Fe@C nanoparticles by 4-carboxybenzenediazonum tosylate, the carbodiimide activation of carboxy-groups on the surface was used. After activation the resulting material washed
by DMSO, EtOH (if DCC was used) or PBS buffer (if EDC was used). On the last stage the obtained material was treated with IDA solution. The IR ATR spectra of the resulting material (Fe@CC₆H₄-ID) shows the presence of characteristic absorption bands inherent in N(CH₂COOH)₂ structure (3200, 1650, 1220 cm⁻¹).

Obtained by this method nanoparticles Fe@CC₆H₄-IDA were used as magnetic support for immobilization of radioactive isotope Tc-99m. The immobilization was carried with Na₂TcO₄ solution after the reduction of Tc-99m with SnCl₂ in the presence of Fe@CC₆H₄-IDA. The result concentrations of Tc-99m was 1,12·10⁻⁹ g-at/g. The Tc-labeled nanoparticles can be the first example of potential radiopharmaceutical with magnetic controlled properties.

3. Conclusions

The developed procedures for covalent modification of carbonized surfaces with using arenediazonium tosylates offer the advantages of safety, simplicity, and efficiency. This method is presented as a promising tool for the achieving marketable composite biosensors, targeted drug-delivery systems and etc. of low-cost and mass-production possibilities.

Paramagnetic properties of the composite metal-carbon nano-conjugates open up many possibilities for using in catalysis, biomolecular chemistry, biotechnology, and medicine.

4. Standart procedure for covalent modification of metal nanoparticles coated by carbon shells

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 radiation at 22.2 kHz in 2 s). The suspension was held for 10 min with periodical agitation. The modified powders were separated using a magnet (the separation of Ag@C was performed by centrifuging) and washed twice with water, ethyl alcohol, and acetone.

References

