Carbon Nanotube-Based Ion Imprinted Polymers: Formation, Characterization and Electrochemical Properties

Karolina H. Markiewicz, Joanna Breczko, Agnieszka Z. Wilczewska

Institute of Chemistry, University of Bialystok, Ciolkowskiego 1K, 15-245 Bialystok, Poland k.markiewicz@uwb.edu.pl; j.luszczyn@uwb.edu.pl, agawilcz@uwb.edu.pl

Extended Abstract

Environment contamination by heavy metals cause serious health and ecological problems in many parts of the world [1]. Therefore, their accurate analytical determination is of great importance.

Chemical modification of electrodes is an effective way to improve sensitivity and selectivity of electrochemical sensors used for metal ions determination. Carbon nanotubes (CNTs) due to their high electrical conductivity can introduce strong electrocatalytic activity to electrochemical devices, and thus, have been successfully applied in the fabrication of electrochemical sensors for various applications [2]. Ion-imprinted polymers (IIPs) are macromolecules showing high selectivity toward target ion related to a memory effect resulting from the process of their preparation. Their other advantages are chemical stability, low cost, and easiness of preparation [3]. Carbon nanotubes functionalized with ion-imprinted polymers are promising materials for electrodes modification.

The aim of the study is formation of new selective materials based on carbon nanotubes and ion-imprinted polymers for modification of electrodes. The first stage of the project involved covalent functionalization of carbon nanotubes with dithiocarbonates, which are chain transfer agents in RAFT (reversible addition-fragmentation chain transfer) polymerization. Functionalization of CNTs with dithiocarbonates enables polymerization conducted directly from nanotube's surface. CNT-IIP hybrids were synthesized by polymerizing a mixture of dithiocarbonate-modified CNTs, template ions (Pd^{2+}), functional monomers and a crosslinker. Polymerizations were performed using commercially available monomers (*e.g.* acrylonitrile, acrylic acid) as well as synthesized ones *i.e.* carbamohydrazonothioate or thiourea-based molecules having high affinity to metal ions. In this way several CNT-IIP nanohybrids were obtained. The specific cavities complementary to the size and shape of the template ions were formed after their removal from the polymer network. The obtained materials were deposited on gold electrodes by solvent evaporation.

Raman spectroscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning and transmission electron microscopy were employed to confirm modifications and study chemical composition of the obtained materials. Electrochemical properties were analysed by cyclic voltammetry and electrochemical impedance spectroscopy.

Acknowledgments

The project was financially supported by the National Science Centre, Poland, grant no. 2014/13/N/ST5/01563 (KHM).

References

- [1] K. B. Chipasa, "Accumulation and fate of selected heavy metals in a biological wastewater treatment system," *Waste Manag.*, vol. 23, no. 2, pp. 135–143, 2003.
- [2] C. Gao, Z. Guo, J.-H. Liu, and X.-J. Huang, "The new age of carbon nanotubes: An updated review of functionalized carbon nanotubes in electrochemical sensors," *Nanoscale*, vol. 4, no. 6, pp. 1948, 2012.
- [3] C. Branger, W. Meouche, I. A. Margaillan, "Recent advances on ion-imprinted polymers," *React. Funct. Polym.*, vol. 73, no. 6, pp. 859–875, 2013.