Abstract

Studies were focused on the new synthesis procedures of mesoporous silica and conductive polymer. Polypyrrole and coordination $C_{60}Pd$ polymers were applied as a polymeric competent of studied composites. Morphology spectroscopic and electrochemical properties of formed material were investigated.

In the theoretical part of the manuscript main mesoporous materials are described. The most attention was paid to silicas from the group of ordered mesoporous materials (OMS). In this part of the manuscript, the knowledge on the composites of mesoporous and polymeric materials is briefly described.

Scanning and transmission electron microscopy, infrared spectroscopy and X-ray photoelectron spectrometry were used to determine the morphology and composition of the obtained structures. Additionally, nitrogen adsorption-desorption isotherms and thermogravimetric curves were recorded. In electrochemical studies were used cyclic voltammetry and square wave voltammetry.

MCM-41 and MCM-48 silicas were used to create composites. Both materials were synthesized as spherical structures with a diameter of 400 to 800 nm. MCM-41 silica has a hexagonal arrangement of pores, while MCM-48 silica has pores of regular arrangement. The pore diameter range in both materials is 3 nm, and the specific surface area is 0.86 and 0.74 $m^2 \cdot g^{-1}$ for MCM-41 and MCM48, respectively.

The synthesis of composites with polypyrrole is based on the introduction of the pyrrole monomer into the silica pores and its subsequent polymerization with the use of iron (III) chloride. Results of the SEM, TEM, IR spectroscopy and nitrogen adsorption-desorption mesurments confirm the presence of the polymer inside the pores of silica. The structure of the silica remains intact during the polymerization process. Nevertheless, the polymer settles on the inner walls of the pores without completely filling them. The comparison of the change in the pore diameter and volume as well as the specific surface area of pure silicas and the synthesized composites shows that in the case of the polypyrrole@MCM-48 composite, the thickness of the polypyrrole layer deposited inside the pores is much greater than in the case of the polypyrrole@MCM-41 composite. Due to the presence of silica, the thermal stability polymeric component introduced to the silica pores increases compared to pure polymer.

The polypyrrole@MCM-41 and polypyrrole@MCM-48 composites also exhibit much greater reversibility of the redox processes under voltametric conditions compared to chemically synthesized polypyrrole. In addition, the oxidation and reduction peaks are characterized by a better defined shape as well as a high current response compared to pure

polymer. This is due to the increased surface area of the electroactive material through the use of mesoporous silica.

Removal of silica from the composites of polypyrrole@MCM-41 and polypyrrole@MCM-48 results in polymer nanostructures formation in the form of thin hairs clumped into larger agglomerates. The arrangement of the polypyrrole after removal of the silica reflects the pore structure of the silicas used in the synthesis of the composites. Polypyrrole structures have a large electroactive surface. Also in this case, a significant improvement in electrochemical properties compared to chemically synthesized polypyrrole is observed due to the large surface of electroactive material.

Due to incomplete filling of the silica pores with polypyrrole in the polypyrrole@MCM-48 composite it is possible to use this material for electrochemical dopamine detection. The use of a gold electrode coated with the polypyrrole@MCM-48 composite for dopamine detection causes almost 3-fold increase in the value of the dopamine oxidation peak compared to the pure electrode. Such behavior is related to the overlapping of the oxidation potentials of polypyrrole and dopamine, and mediation of electron transfer during to dopamine oxidation. The limit of detection for dopamine using cyclic chronovoltammetry is 2.5 μM and the range of linearity is from 10 μM to 1.2 mM. For square wave voltammetry, the detection limit is 0.7 μM and the range of linearity is 2 to 250 μM. The use of the polypyrrole@MCM-48 composite deposited on the surface of the gold electrode, enables the quantitative and qualitative determination of dopamine in the presence of interferents such as ascorbic acid and uric acid.

The synthesis of the composite of mesoporous silica with the "*n*" type conducting polymer is an important issue particularly for the charge storage devices production. The developed method of synthesis allows to obtain a composite of MCM-48 silica with $C_{60}Pd$ fullerene polymer. In this composite, the polymer is formed both inside and outside of the silica pores to form larger clusters. The use of silica increases the electrochemical stability of the polymer and improves its electrochemical properties compared to a pure polymer. In the $C_{60}Pd$@MCM-48 composite, the reduction and oxidation process is more reversible with the simultaneous increase in the reduction currents compared to pure chemically synthesized polymer.

22.04.2022 Izabela Łabiocka