Nanocomposites and nanomaterials

Frequency-controlled formation of nanoparticles, nanoalloys and core-shell objects in quasi-reversible redox systems

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Establishing the kinetic regularities of electrochemical processes in the heterogeneous redox systems during the formation of metallic nanoparticles is the key for obtaining nanostructured materials with the desired physico-chemical and functional properties. In present report, the formation of poly(diphenylamine) and poly(diphenylamine)-silver nanocomposite (PDPA-AgNPs) under cyclic VA and stationary conditions has been investigated and the frequency-controlled method for the formation of hybrid nanostructured materials has been proposed.

In the case of aniline derivatives, the formation of Ag NPs on a polymeric substrate via reduction of Ag^+ ions gradually transfers the polymers to oxidized state that allows to implement the electrochemically controlled NPs synthesis method. On a first phase, the polymeric 'template' film with the desired morphological parameters should be grown using the preferred method for a particular application. On the second phase, the metal-containing precursor should be added to the system. As a result of the redox reaction, the metal ions will be reduced to the metallic clusters and NPs while polymeric film will be gradually transferred to an oxidized state that will indicate end of cycle. Conductivity of the polymeric film facilitates the charge transfer toward a growing NPs seeds that also allows the distant molecules to indirectly take part in a surface redox reaction. Impulse external polarization should be applied to reduce film to the initial oxidation state and restart the redox cycle.

It should also be noted that electrokinetic phenomena have a significant contribution to the NPs formation process thus the optimal frequency, relaxation time and the impulse shape that ensures the desired NPs parameters should be determined experimentally. In case of aniline derivatives, the optical spectra of the sample may be used for automated frequency adjusting control system owe to electrochromism phenomenon. Splitting of the process into stages also allows one to obtain the mixed NPs, core-shell objects and nanoalloys embedded into polymeric matrices by replacing the metal-containing precursor between cycles.