Low-temperature synthesis of copper-filled carbon nanotubes in condensed medium

A.A. Didik, V.I. Kodolov, E.G. Volkova*, A.Yu. Volkov*
Basic Research – High Educational Centre of Chemical Physics and Mesoscopy, Udmurt Scientific Centre, Ural Division, Russian Academy of Sciences
222 Gorky str., Izhevsk, 426000, Udmurt Republic, Russia;
e-mail: didik@istu.udm.ru
*Institute of Metal Physics, Ural Division, RAS; Ekaterinburg

Carbon nanotubes first obtained by Iijima [1] are the objects of still growing interest due to their unique properties. Together with their application areas increase, they are being produced more and more effectively. In the given paper the multi-walled nanotubes with outer diameters 20-60 nm filled with metallic copper and copper (I) oxide are obtained from organic polymer – polyvinyl alcohol in the presence of copper chlorides using the carbonization process. Beside the nanotubes, copper nanoparticles with the diameters 5-20 nm covered with carbon shells are found in synthesis products. Depending on the method the initial mixture is prepared, the structures of nanotubes obtained differ considerably. While calcinating the gels obtained in the process of mixing water solutions of components with the following water evaporation, straight multi-wall nanotubes with the average diameters 30-40 nm and ~100 nm long are produced. The tubes have closed ends. When mechanical heterogeneous mixtures of components are used, strongly tangled spliced nanotubes in the form of “net” or “clews” are obtained. In this case the synthesis products can be observed as copper nanowires covered with carbon shell. The average wall thickness of the tubes is 5 nm. In both cases the synthesis products are introduced into the matrix of amorphous carbon present in the form of films. The nanotubes and nanoparticles are separated from the matrix under the ultrasonic field action.

The nanotubes formation mechanism under the conditions of the given synthesis differs from the dissolution mechanism – diffusion – carbon crystallization on metal catalyst particles proceeding in chemical vapor deposition – process, as well as from the surface diffusion mechanism. Under this synthesis temperature (250ºC), carbon diffusion via copper particles is unlikely. Apparently, copper embryos being formed during the carbonization process are nucleation centers on which carbon nanostructures grow. The presence of nanotubes together with nanoparticles can be explained by the insignificant copper affinity to carbon and its inability to form stable carbide phases. Due to this reason carbon does not completely cover nanoparticles but form tubular structures.

Oxidizers cause the nanotubes ends to open in the solution, defective regions are destroyed, thus resulting in the availability of copper inside the tube and which can be easily removed in this case. Hollow carbon nanotubes with open ends are obtained using this method. Empty nanotubes tangled in the form of “net” are perspective materials for the electrodes of electrolytic supercapacitors. The measurements carried out in acid solutions present high values of their electrochemical capacity. Inner channels in the nanotubes net provide the electrolyte access to the walls the defects in which form a developed structure of micropores leading to high electrochemical capacity values.

[1] S. Iijima Helical microtubules of graphitic carbon // Nature 354 (1991) 56.

Fig. 1

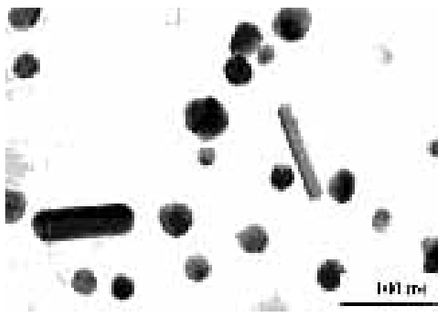

Fig. 2

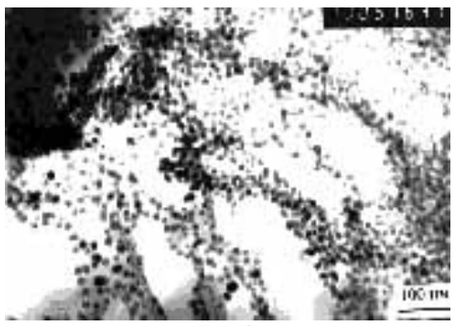

Fig. 3

Fig. 4