PROPERTIES OF COPPER-MODIFIED GRAPHENE OXIDE NANOCOMPOSITES FOR BIOMEDICAL APPLICATIONS

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Two feasible methods were developed for the preparation of $CuS/Cu_2O/CuO$ -GO or CuO-GO nanocomposites in the use of the ultrasonic nanotechnology (20 kHz) and oxidized graphene nanomaterial. The $CuS/Cu_2O/CuO$ -GO nanocomposites have a submicron size (~ 490 nm) with small spherical nanostructures (~ 30 nm) on their surface. In contrast, CuO-GO nanocomposites exhibit a distinct cone-like morphology (~ 20 nm) in the graphene network. The XRD studies reveal the crystalline phases of CuS, Cu_2O and CuO in the first type of graphene nanomaterial, and distinct reflexes of the CuO phase in the second type of nanocomposite.

Nanomedicine offers beneficial approaches based on objects at the nanoscale aiming at an increase of the drug surface area by reducing its size and modifying its surface to facilitate more rapid dissolution and absorption by a target tissue [1]. Moreover, it provides techniques for safe handling and methods for minimizing toxicity of nanoscale carriers for the *in vivo* application [2]. These nanoscale carriers can significantly improve the bioavailability of drug and decrease the dose of administration, thereby enhancing its therapeutic efficacy with lower side effects. The pharmacological properties of drugs can be enhanced through the bonding with Cu(II)-complexes via the Cu-O and Cu-Cu complexation. Importantly, the copper carboxylates drugs constitute an important element of anti-inflammatory and anticancer agents, some of which are a part of several commercially available drugs [3].

Graphene oxide (GO) can be used as a nanoscale carrier for a drug due to its high surface area, biocompatibility and a very rich surface chemistry offering a wide choice for the smart design of effective drug delivery platform [4]. GO can remain for a long time in a body and have good biocompatibility, but size, shape, agglomeration state and toxicity (presence of contaminants) can cause undesired inflammation. Appropriate GO purification and modification can increase the efficacy of drug loading in GO and optimize adsorption/desorption kinetics at minimal toxicity. Immobilization with drug molecules can regulate GO dispersal in water or in the cell culture media, reduce its cell/tissue toxicity and induce accumulation to the target cells and tissues. Drug release from GO can be activated by the pH gradient naturally present in the cells/tissues through the distortion of the interactions between the drug and GO nanocomposite.

Ultrasonic nanotechnology is an efficient tool to construct multifarious nanomaterials, and it derives from acoustic cavitation, which is the formation, growth and implosive collapse of gaseous bubbles [5]. Nowadays little is known about the sonochemical formation mechanism of copper-GO nanocomposites and much less about their interaction with the anti-inflammatory drug as aspirin or diclofenac via ultrasound. This work aims at the development of new sonochemical method for the preparation of two different types of new nanocomposites based on graphene oxide that is modified by CuS/Cu₂O/CuO nanostructures or individual CuO nanoparticles. The morphology of GO and CuO nanoparticles as well as CuS/Cu₂O/CuO-GO or CuO-GO nanocomposites is shown in Figure 1 in the use of SEM technique. SEM images reveal smooth planes of GO with a submicron size (Figure 1A), small spherical nanostructures (~ 30 nm) in the carbon network structure (~ 490 nm) of CuS/Cu₂O/CuO-GO nanocomposites (Figure 1B), CuO nanoparticles (~ 65 nm) (Figure 1C) and submicron CuO-GO nanocomposites with cone-like nanostructures (~ 20 nm) (Figure 1D).

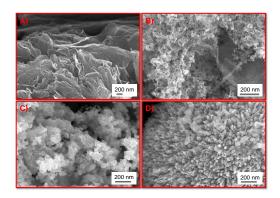


Figure 1 – representative SEM images of (a) graphene oxide prepared by a modified Hummer's method, (b) sonochemically formed CuS/Cu₂O/CuO-graphene oxide nanocomposite, (c) CuO nanoparticles prepared by a wet chemical precipitation method and (d) ultrasonically formed CuO-graphene oxide nanocomposites.

The crystalline structure of $CuS/Cu_2O/CuO$ -GO and CuO-GO nanocomposites is shown in Figure 2 in comparison to the GO nanoparticles. The XRD patterns reveal characteristic reflexes of graphene and GO and CuS, Cu_2O and CuO planes (Figure 2A) as well as distinct CuO crystalline phase on the GO network (Figure 2B).

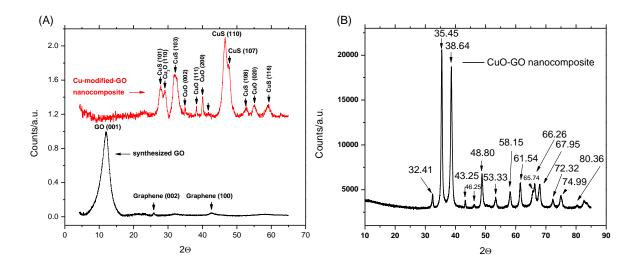


Figure 2 – X-Ray powder diffraction patterns of a) graphene oxide nanoparticles and CuS/Cu₂O/CuO-GO nanocomposite and b) CuO-GO nanocomposites that were synthesized in the use of the ultrasonic nanotechnology (20 kHz, 18W/cm²).

In conclusion, two different methods have been developed for the formation of new CuS/Cu₂O/CuO-GO and CuO-GO nanocomposites in the use of the ultrasonic nanotechnology via acoustic cavitation. The first one is based on the sonochemical synthesis of three types of copper compounds involving CuS phase and the second one is introduced by the ultrasonic binding of pre-formed CuO nanoparticles with the GO nanomaterial. At present both types of copper-GO nanocomposites are being studied for their interaction with aspirin and diclofenac in the use of ultrasound.

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УЛЬТРАЗВУКОВАЯ НАНОТЕХНОЛОГИЯ ДЛЯ ПОЛУЧЕНИЯ МАГНЕТИТА В МАТРИЦЕ ОКИСЛЕННОГО ГРАФЕНА

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Разработан новый ультразвуковой метод для формирования суперпарамагнитного материала на основе оксида графена и магнетита с целью его применения в качестве магнитно-углеродной матрицы для носителя органических веществ. Новый магнитный нанокомпозит был синтезирован в водной фазе при воздействии ультразвука с частотой 20 кГц. Проведены исследования морфологии, состава и структуры нового нанокомпозитного материала. Установлено, что полученный