PRELUDIUM 18

Synthesis, separation, chemical modifications and fluorescent properties of carbon quantum dots.

Popular Science Abstract

In times of pervasive consumerism when "more means better" and evidence of this theory is provided during using our smartphones, in world of science miniaturization or it would be better to say nano-turization is very fashionable. Nanomaterials offer properties such different from their macroscopic counterparts, scientist can not pull the plug on them due to longing of extracting their full potential.

In 2004, when knowledge about carbon nanomaterials was already well established and no one thought that anything could surprise us, carbon quantum dots (CQDs) appeared in the world. CQDs was discovered by accident. During the purification of carbon nanotubes (CNTs), it turned out that the "waste" was shining under the UV lamp. It is not known what led the scientist to check the properties of the sample under the lamp, but it is certain that he discovered a material with completely opposite properties compared to other carbon nanomaterials, which entranced scientist.

CQDs are a *quasi*-spherical carbon nanomaterials with a diameter less than 10 nm. CQDs consist of a carbon core and functional groups on their surface. They are biocompatible, non-toxic, soluble in water and can be obtained from any carbonaceous material. A feature that distinguishes CQDs on the background of their family is the occurrence of quantum confinement effect. After absorption of the photon, the CQDs show a fluorescence and emission wavelength depends on their size and composition.

Because materials with fluorescent properties have enormous application potential, especially in medical sciences, studies involving CQDs are particularly important. However it turns out, that as with other carbon nanomaterials, problems arise here. Although the CQDs are fluorescent materials, quantum yield (QY) is small. Because the material after the synthesis contains CQDs with different composition and size, the fluorescence bandwidth is wide. In addition, the emitted wavelength usually corresponds to blue light, and due a lot of functional groups on CQDs surface, the selectivity of reaction with organic compounds and biomolecules is low. The aim of my research is therefore to develop a method that will allow to obtain CQDs with controlled size and composition.

I decided to solve the above-mentioned problems by two-steps purification and functionalization process. Purification of CQDs using techniques based on size differences (gel chromatography) and functionalities (hydrophilicity gradient ultracentrifugation, hydrophilic interaction chromatography) will ensure better separation and purification than the techniques used so far, and thus reduce the bandwidth of the fluorescence band. The use of Ullmann-type reactions, known from organic chemistry, will allow for modification of the CQDs surface with practically unlimited number of compounds. Thus, modification will increase the selectivity of binding of CQDs in the cell and synthesis of family of CQDs with tunable colour emissions by a suitable selection of reagents.

To achieve my goals, I have developed a five-steps work plan:

1.Synthesis of CQDs via hydrothermal method.

2.Purification and separation of CQDs using size-exclusion chromatography (SEC) and hydrophilicity gradient ultracentrifugation and hydrophilic interaction liquid chromatography (HILIC).

3.Functionalization of CQDs of defined structure via Ullmann-type reactions.

4.Characterization of the modified CQDs using TEM, DLS, XPS, TGA, EDS, UV/Vis-PL, Raman, FT-IR, $^{1}H/^{13}C$ NMR spectroscopy and titration.

5.Analysis of the influence of the modification of CQDs on their fluorescence properties.

My research will allow for better control of the composition and size of CQDs as well as enriching the chemistry of CQDs. In addition, research will allow for clarification phenomenon of fluorescence of CQDs, and thus the modification of their properties depending on the needs. Not less important result of the proposal is that my studies will involve not only new functionalization methods, but also novel protocols of CQDs purification It is also worth noting that the developed purification and functionalization procedures may be used in the future for other carbon nanomaterials.