Abstract

Core-shell nanomaterials are interesting nanoscale structures that have many applications. Due to their small size and hybrid structure, consisting of a core and shell, they exhibit numerous advantages over other nanomaterials. The core is usually composed of nanoparticles with specific properties that dictates the end application of the material. The majority of such compounds consist of metal nanoparticles, e.g. silver, which exhibit plasmonic properties. However, various studies have indicated the toxicity of nanoparticles and their tendency to agglomerate, which limits control over their size. Coating nanoparticles with a suitable material can reduced such drawbacks, while enhancing the desired properties. Silica (SiO_2) is among the most commonly used material, due to its chemical neutrality and the prevention of agglomeration by nanoparticles in the core. Additionally, silica is easy to modify, which is allows for the production of new functionalised materials with unique properties.

The presented study involved the synthesis of core-shell nanomaterials with two different core components, including silver and titanium dioxide, which generated Ag@SiO_2 and TiO_2@SiO_2. The physicochemical properties of the core-shell structures based on silver and titanium dioxide were also characterised in detail. Moreover, the cytotoxicity of the silver-based nanomaterials against human skin cell lines, keratinocytes (HaCaT) and fibroblasts (HDF), was determined.

An important step in the study was the modification of the obtained materials by non-covalent and covalent attachment of fluorophores. The latter was used to form stable bonds between the core-shell nanomaterials and fluorophores, which proceeded *via* the activation of the silica surface through attachment aminopropyl groups.

The final stage of the work was the use of core-shell nanomaterials in the study of Metal-Enhanced Fluorescence (MEF) and Förster Resonance Energy Transfer (FRET). In this area, the fluorescence intensity spectra and the fluorescence intensity decay for the synthesised nanomaterials were measured.

Research on the characteristics of nanostructures allowed to determine that silver-based core-shell nanomaterials were more homogeneous than titanium dioxide-based structures. It was also shown that TiO_2-based structures tended to form aggregates that reduced potential modification. The synthesised Ag@SiO_2-type nanomaterials were superhydrophilic, which made them potential carriers in medicine or cosmetics. Importantly, this type of nanomaterials

exhibited low cytotoxicity against human keratinocytes and fibroblasts compared to the Ag NPs.

The study successfully developed a method for the determination of aminopropyl groups on the surface of the core-shell structures. This method made it was possible to determine the number of covalently attached fluorophores. Additionally, the procedure was applicable to all solid nanomaterials and was unique in the low amount of material required for the measurement, which is an important parameter for nanostructures.

The performed measurements of spectroscopic properties showed that the core-shell nanomaterials amplified the fluorescence signal of the tested molecules very well and can be used for the construction of plasmonic platforms. In addition, the FRET test system obtained after appropriate modification of the surface of the core-shell nanomaterials allowed for the verification of the previously obtained theoretical model for one-step excitation energy transfer on this type of nanostructures. The obtained compatibility of the experimental and theoretical results confirmed the usefulness of the theoretical model for determining the radii of nanostructures or the number of donor and acceptor molecules attached to them.

The results obtained in this Ph.D. thesis have considerably enriched the knowledge of the characteristics and toxicity of core-shell nanomaterials. In addition, their spectroscopic properties have been described, which is an introduction to research on their potential application aimed at creating new optical sensors.