Doctoral Dissertation

"Gold Nanoparticles as Components of Advanced Hybrid Materials Employing Light to Control the Course of Chemical Processes"

mgr inż. Nina Tarnowicz-Staniak

Summary

Scientific research on advanced materials is required for the overall development of humankind. New material designs enable exploration of previously unattainable experimental scenarios and phenomena. Thus, the overall understanding of the world is broadened and new things become possible.

The presented dissertation is interdisciplinary and combines fields of chemical sciences and materials science. This work aims at the preparation of advanced materials able to employ light to control the course of chemical processes. Light is one of the best stimuli to control the behaviour of materials, because it is ultrafast, fully tunable, and can trigger phenomena with high spatio-temporal resolution. Since plasmonic nanostructures, such as gold nanoparticles (AuNPs), provide both catalytical surfaces and strong interactions with light, they became a central component of the materials proposed in this dissertation. Moreover, to investigate influence of optical properties of nanostructures, anisotropic nanoparticles of a rod-like geometry (AuNRs) were employed. The second important component of the proposed hybrid materials is cellulose in a form of nanofibres (CNFs). Due to rich surface chemistry CNFs enable immobilization of gold nanorods and stabilization of their optical properties.

First section of the dissertation (Introduction) consists of two chapters. Chapter 1 presents motivation for undertaking this research project and sets four rational criteria for the hybrid materials. Moreover, objectives and hypotheses of the dissertation are presented. Chapter 2 constitutes a review of general literature knowledge in four crucial areas, namely plasmonic nanoparticles (their properties and synthesis are discussed), plasmon-related effects as important catalytic tools (here different phenomena, such as local field enhancement, hot charge carriers generation, and thermoplasmonic effect are presented), cellulose as component of advanced materials (special emphasis is put on nanocellulose composites with gold nanoparticles and organic dyes), and hybrid materials based on azobenzenes (Azo) and gold nanostructures.

Second section of the dissertation (Results, discussion, and methodology) consists of four chapters focused on the presentation of the experimental results and their discussion.

Chapter 3 establishes general protocol for the preparation of AuNRs-CNFs materials. Immobilization of nanostructures on cellulose nanofibers grants great stability of nanocrystals' plasmonic properties under intense illumination, elevated temperatures, and in a wide range of pH. This chapter presents also functionality of the proposed formulation as a photocatalyst and introduces a conceptually new plasmon-assisted photochemical process of simultaneously coupled dehydrogenation of sodium formate and regeneration of cofactor molecules in the presence of plasmonic hybrid material under visible light irradiation.

Chapter 4 addresses current challenges in the field of plasmonic-photochromic hybrid systems by establishing general protocol for the preparation of multifunctional, water-based, CNFs-stabilized plasmonic-photochromic hybrid material. In this chapter mutual interactions between CNFs and AuNRs, as well as CNFs and the chosen Azo photochrome are analysed. The proposed formulation enables efficient transfer of Azo to water, a solvent in which it is not normally soluble. Moreover, the exceptional stability of AuNRs-CNFs in ethanol is investigated and the comparative analysis of the IR spectra confirms role of CTAB on the surface of AuNRs in maintaining material's structural integrity. Notably, both functional components maintain their functionality and optical properties. Results presented in this

chapter constitute an important step forward in the field of Azo-AuNPs hybrids, since the incorporation of big, anisotropic nanostructures enables beneficial spectral separation of Azo and AuNRs.

Chapter 5 focuses on the influence of AuNRs on the isomerization of the photochromic component in the hybrid Azo-AuNRs-CNFs formulation. Presence of AuNRs grants catalytic enhancement of both, photoinduced and thermal Azo isomerization. Based on the observed coherent and reversible changes in the position of l-LSPR band of AuNPs (about 2-4 nm) the electron transfer mechanism of the catalytic influence is proposed. The results obtained for samples containing AuNRs of different sizes indicate that catalytic enhancement increases with the decreasing aspect ratio of AuNRs, however, the postulated size effect is presumably a convolution of more than one descriptor of samples' composition. Moreover, this chapter presents a complete sets of thermodynamic parameters describing thermal back-isomerization of Azo component in the hybrid materials. For all Au-containing samples, thermal relaxations in the dark were characterized by activation energy lower by 20 kJ/mol compared to hybrid sample without Au.

Chapter 6 presents plasmon-assisted *Z-E* isomerization of the photochrome in two forms, as free Azo molecules in solution and as a component of the hybrid formulation. Upon red-NIR irradiation (650-1100 nm), photochrome exhibits dramatic increase of the *Z-E* isomerization rate in the presence of AuNRs. Based on the exponential correlation between isomerization rate constants in hybrid materials and irradiation intensity, the predominant influence of thermoplasmonic effect is proposed. The observed kinetic changes of Azo can be recalculated to estimate the extent of the thermoplasmonic effect, and hence value of 21°C is obtained. Hence, the dissertation introduces application of Azo type photochromes as molecular thermometers. Chapter 6 proposes also specific experimental design in which hybrid Azo-AuNRs-CNFs material is subjected to the interval dark and light irradiation conditions. Novel, at least from chemical point of view, statistical modelling tools are also proposed to analyse the obtained data. The statistical modelling based on the Autoregressive Integrated Moving Average approach enables conclusion on the statistical significance of the observed kinetic changes in the Azo isomerization in the presence of AuNRs. Hence, indirect photocontrol over the *Z-E* isomerization of Azo in the ON-OFF manner is possible. Statistical modelling also enabled final conclusion on the predominant contribution of the thermoplasmonic effect triggered upon irradiation.

Third section of the dissertation (Summary) consists of three parts. Chapter 7 presents general conclusions of the research and summarizes its key aspects and findings. Moreover, further research directions for each experimental chapter are proposed. Second part showcases scientific activities and achievements of the author. Bibliography is the final, third part of the last section.

In summary, this dissertation provides important insight into the preparation and operation of hybrid plasmonic and plasmonic-photochromic CNFs-based materials. AuNRs incorporated in the proposed systems enable control over the course of the chemical process via light-induced plasmon-related effects. Presented work is at the intersection of chemical sciences and material science and contributes to both fields.