Organic and Medicinal Chemistry
International Journal
ISSN 2474-7610

Juniper Publishers
key to the Researchers

Mini Review
Volume 10 Issue 5 - June 2021
DOI: 10.19080/OMCIJ.2020.10.555796

Organic & Medicinal Chem IJ

Prospects of Nanomaterials in Medicinal Photo-Physical-Chemistry

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Submission: April 12, 2021; **Published:** June 08, 2021

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Abstract

During the last few decades, nanotechnology and lasers have made their way into many applications, including the medical field. For instance, noble metal nanoparticles (MNPs) and semiconductor quantum dots (QDs) have been used in medical diagnostics, photothermal therapy (PTT), drug delivery, and biolabeling. In a PTT process, the tumor area is exposed to an infrared laser with a frequency selected accordingly with respect to the localized surface plasmon resonance (LSPR) of the MNPs injected around the tumor; the local increase in the temperature of MNPs may lead to the burning of the surrounding tumor cells. Although several research efforts have targeted these concepts, most of the investigations were limited to the examination of the efficiency of the overall process and its dependence on the physical and chemical properties of MNPs and their biofunctionalization. Here, we present an opinion to shed light on the fundamental photophysical and photochemical aspects of the nanomaterials-based PTT process, which may open new horizons for the incorporation of nanomaterials in the medical field.

Keywords: Nanomaterials; Energy transfer; Photothermal therapy

Abbreviations: MNPs: Metal Nanoparticles; QDs: Quantum Dots; PTT: Photothermal Therapy; LSPR: Localized Surface Plasmon Resonance; GCO: Global Cancer Observatory

Introduction

According to the Global Cancer Observatory (GCO), nearly ten million deaths worldwide were caused by cancer in 2020 [1]. Despite the continuous efforts to battle this disease using various therapies, such as chemotherapy, radiotherapy, immunotherapy, and surgery, a comprehensive approach that has no side effects is not achieved. In the last few decades, a therapy based on nanomaterials and lasers, called photo-thermal therapy (PTT), emerged as a promising way of treating cancer due to its capability of reducing undesired side effects and enhancing efficacy [2-7]. In this therapy, noble metal nanoparticles (MNPs) are tailored and synthesized with shapes and sizes to specifically absorb in the infrared (IR) spectrum. MNPs are injected around the tumor area; then, following exposure to an IR laser (which can penetrate through tissue, their temperature increases drastically due to absorption of the IR light through the localized surface plasmon resonance (LSPR). This leads to the burning and destruction of the neighboring cancer cells [8]. Unlike other heat-based cancer therapies-where the region of the body containing the tumor is heated up to ~ 6°C above the physiological temperature (37 °C) [9] in PTT, the heating only occurs in the surroundings of MNPs, and the increase in local temperatures can reach tens to hundreds of degrees above the physiological temperature [5]. Although sizable research efforts have aimed to understand and develop efficient nanomaterials-based PTTs [10,11], the dynamic photophysical-chemistry aspects of the heat transfer from MNPs to cancer cells have not been well explored.

Photophysical-Chemistry Perspectives

The photophysical aspect of the MNP-based PTT process at the molecular level is depicted in Figure 1A. The femtosecond pump-probe spectroscopy technique can be an excellent strategy for exploring the dynamics of plasmonic energy transfer from MNPs to cancer cells. In this technique, a first laser pulse (pump) resonantly excites the MNP LSPRs at time t0, as shown in Figure 1B; then, a second laser pulse (probe) that is in resonance with the vibrational stretch frequencies of the various chemical bonds of the biomolecular adsorbate (e.g., DNA base-pairs) is sent at later times as depicted in Figure 1C. Since cancer cells are networks of various chemical bonding such as O-H, N-H, C-N, and C-H, which are typically characterized by infrared frequencies of their vibrational stretches (~ 3200-3500 cm^{-1} for O-H and 3100-3300 cm^{-1} for N-H) [12,13] the probe laser pulse should be in the mid-infrared (mid-IR) spectral domain, and it should be spectrally broad in order to probe the state of different chemical bonds simultaneously. The transfer of the plasmonic energy to the biomolecular adsorbate leads to excitation of the various vibrational stretches in the adsorbate. Monitoring the dynamics of this vibrational excitation (now propagating within the chemical bonding network of the biomolecule) using the mid-IR probe provides snapshots of the process of the breaking of chemical bonds of the adsorbate, which consequently leads to the destruction of the cancer cell in a real PTT application.

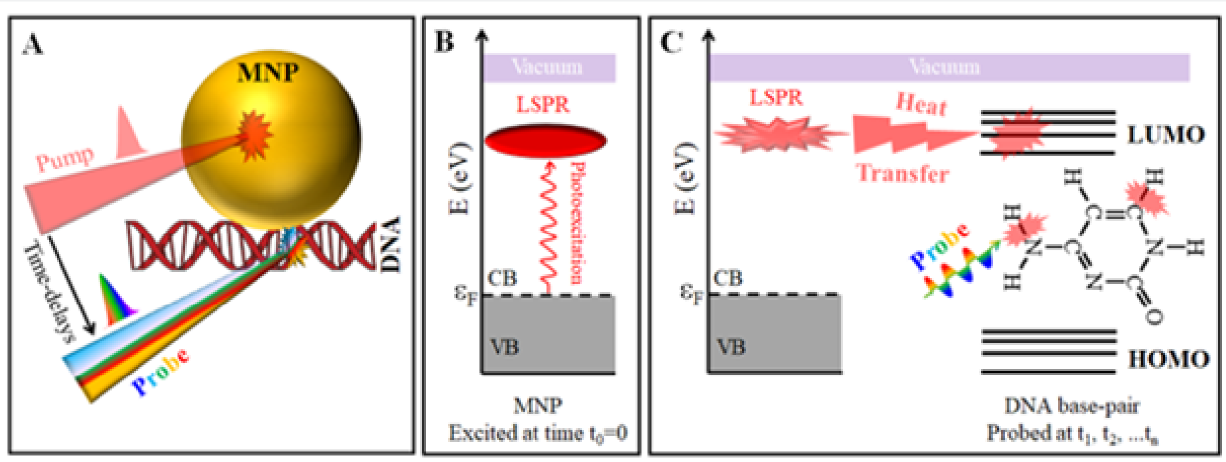

Figure 1: A) Depiction of using femtosecond pump-probe spectroscopy to study fundamental concepts of photothermal therapy at the molecular level. A first laser pulse (pump) resonantly excites MNPs at time t0; then after different time delays with respect to t0, a second mid-infrared laser pulse (probe), is sent to examine the state of different chemical bonds of biomolecules (e.g. DNA base pair) adsorbed on MNPs. B) Depiction of the energy band structure of an MNP, outlining its localized surface plasmon resonance (LSPR) energy level. The CB and VB indicate the conduction and valence bands, respectively, and εF is the Fermi level of the MNP. The vertical wavy arrow indicates the laser pump pulse that resonantly excites LSPRs of the MNP at time t0=0. C. The transfer dynamics of the heat produced at the MNPs can be probed by the mid-infrared probe pulse that is delayed by t1, t2, …, tn with respect to t0. The HOMO and LUMO energy levels are the highest occupied and lowest unoccupied molecular orbitals, respectively.

Conclusion

Understanding the ultrafast dynamics of vibrational energy transfer from the MNPs to DNA base-pair molecules, and thereafter, the redistribution of this energy within their chemical bonding network is necessary for advancing the field of nanomaterials-based PTT not only at the exploration stage but at the clinical level as well. This type of investigation will provide information about which chemical bond (O-H, N-H, C-H, ...etc.) is first in line for breaking, which allows an intelligent design of capping ligands of MNP that may serve as facilitators and guides of the transfer of energy from MNPs to cancer cells.

Acknowledgment

This work is supported by NIH with grant numbers NIGMS RL5GM118975 and TL4GM118977.

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How to cite this article: Pouya B, Dillon C, Abdelaziz B. Prospects of Nanomaterials in Medicinal Photo-Physical-Chemistry. Organic & Medicinal Chem IJ. 2021; 10(5): 555797. DOI: 10.19080/OMCIJ.2021.10.555797

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