Thermoplasmonic Hydrogels Revealing Shape-Memory, Self-Healing, Controlled Drug Release and Light-Triggered Mechanical Properties

Itamar Willner, Institute of Chmistry, The Hebrew University of Jerusalem, Jerusalem 91904, ISRAEL

The local heating of the environment by the light-induced excitation of plasmonic nanoparticles or nanorods finds growing scientific interest, and the phenomenon found various applications for imaging, sensing, nanomedical uses (nanosurgery tools, phototherapy), and more. In addition, DNA hydrogels attract growing interest as soft materials, where the signal-triggered reconfiguration of the nucleic acids crosslinking the hydrogels leads to control over the stiffness of the hydrogel matrices. Different stimuli-responsive DNA-based hydrogels revealing control over their stiffness were developed. Different stimuli, such as light, pH or ions were used to trigger the stiffness properties of the hydrogels, and these were applied to develop shape-memory, self-healing and controlled drug-release matrices.[1]

Here we report on the synthesis and characterization of Au nanoparticles (Au NPs) or Au nanorods (Au NRs)-loaded DNA-based hydrogels. The hydrogels are cooperatively crosslinked by covalent or supramolecular bridges and duplex nucleic acids as crosslinkers. The resulting hydrogels exhibit thermoplasmonic properties. Irradiation of the Au NPs-loaded hydrogels (l = 532 nm) or the Au NRs-loaded hydrogels (□□= 808 nm) leads to switchable control of the stiffness of the hydrogels under light/dark conditions. The thermoplasmonic control over the stiffness of the hydrogels is used to develop shape-memory, self-healing and switchable drug-release matrices. In addition, the assembly of thermoplasmonic bilayer hydrogels composed of Au NPs-loaded and Au NRs-loaded layers allows the programmed light-induced, mechanical bending of the hydrogel device by the dictated control over the stiffness (stress) of the hydrogel layers.[2]

In addition, thermoplasmonic hydrogel microcapsules, crosslinked by nucleic acids, loaded with Au NPs or Au NRs and with drugs or drug models will be presented. The light-induced thermoplasmonic control over the stiffness of the microcapsule shells allows the switchable release and programmed release of the loads from the microcapsules. The cytotoxicity of doxorubicin-loaded thermoplasmonic hydrogel microcapsules toward cancer cells will be described.

Besides the introduction of thermoplasmonic hydrogels for nanomedical applications new approaches to organize plasmonic nanoparticles will be introduced. These include:

(a) The use of constitutional dynamic networks for the dynamic reconfiguration of different-sized Au nanoparticle dimers.

(b) The use of switchable DNA origami dimers, functionalized with different sized Au nanoparticles as active units for the triggered, reversible reconfiguration, of different patterns of Au nanoparticles.

1. J.S. Kahn, Y. Hu and I. Willner, Stimuli-Responsive DNA-Based Hydrogels: from Basic Principles to Applications. *Acc. Chem. Res.,* **50**, 680-690 (2017).

2. C.Wang, X.Liu, V. Wulf, M. Vazquez-Gonzalez, M. Fadeev and I. Willner, *ACS Nano* DOI: 10.21/acsnano.8b09470, in press(2019).