Electrochemical plasmonics:
A path to electrotunable self-assembling optical metamaterials

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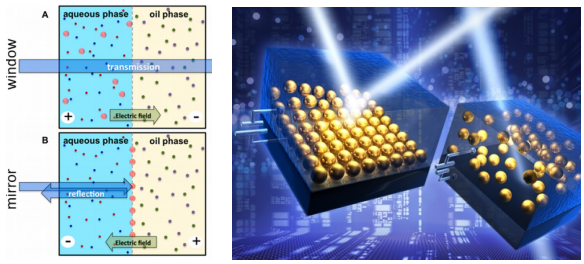
This talk will overview a new direction of research based on voltage-controlled self-assembly of plasmonic nanoparticles at electrochemical interfaces, the optical properties of which can dramatically vary with assembly structure and density.

Progress in photonic metamaterials was made possible by advances in nanotechnology. Many such materials, however, can only perform a single function. Not surprisingly, a premier conference in the field opened with a provocative statement: "The time of meta-materials is over… It is the time of tuneable metamaterials" (N. Zheludev). Realization of such platforms would allow properties of such functional metamaterials to be tuned in real-time, with major implications for absorbers in solar cells, antennae, super-lenses, cloaking, sensors – amongst others.



A sketch of a self-assembled voltage-controlled of negatively charged Au NPs at electrified **i**nterface of **t**wo **i**mmiscible **e**lectrolytic **s**olutions (**ITIES**), in reflecting mode (left) and transmitting mode (right). Switching on/off reflection or modification of the reflection spectra can be achieved by controlling the density of charged nanoparticle arrays adsorbed at the interface through the variation of applied voltage.

Tunability can be reached by utilization of fine physical effects, but also changing the structure of materials in real time. Our team at Imperial (led by J.B. Edel – nanofluidics, optics, analytical science; A.R. Kucernak – experimental electrochemistry; and myself – theory development, theory-based navigation of experiments and analysis of the data) in collaboration with M. Urbakh at Tel Aviv University (theory) have responded to this challenge first with developing the 'nanotechnology-free' concept of chemically tuneable self-assembly of plasmonic **n**ano**p**articles, such as quasi-2D arrays NPs at a liquid|liquid (LLI) and solid|liquid (SLI) interfaces [1,2]. We have demonstrated that such arrays could be used for ultrasensitive SERS detection of trace analytes –e.g. proxies for pollutants, illegal substances, terror agents – that get into 'hot spots' between NP's [3]. The array structure was controlled by tuning the composition of the solutions (electrolyte concentration or pH). We further performed a complex study of the structure and optical properties of such arrays within the same setup, via a combination of grazing incidence, small angle X-ray scattering and in situ optical reflectivity. From the X-ray and optical data, we could determine (from a combination of experimental [4] and original theoretical [5] results) the average distance between NPs, the long-range order, and reflectivity –all as a function of electrolyte concentration. Incorporating the obtained values of array's 'lattice constants' into the theory of optical reflectance from such arrays [5], we could calculate the reflectance spectra for each electrolyte concentration and compare them with those measured in the same system [4]. Excellent match between the theory and experiments has demonstrated that the underlying physics works exactly as expected! These studies gave us confidence that we could chemically control these nanoplasmonic platforms, i.e. generate tuneable self-assembled metamaterials. However, this did not incorporate *real-time reversible control*.

It was clear, that *electrochemistry* will be the game changer here. At electrochemical interfaces, with tiny voltage variation, one can create localised electric fields that may dramatically change the structures of adsorbed charged NP arrays and their optical properties. We demonstrated this by creating the first electrically switchable mirror based on voltage controlled self-assembly of gold NPs at the interface of two immiscible electrolytic solutions [6]. We have shown that it is possible to transition between a mirror and window and back using just 0.5 V - voltage variation through its effect on the density of the NP arrays and their resulting optical response. Furthermore, a different kind of switch based on voltage-controlled adsorption-desorption of NPs on a metal substrate, the principle of which has been described theoretically in [7], was reported in [8]. A set of other scenarios were also considered (see e.g.[9]).

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