

## Electrochemical plasmonics for dynamic control of optical properties of self-assembling metamaterials

J.B.Edel<sup>1</sup>, A.A.Kornyshev<sup>1\*</sup>, A.R.Kucernak<sup>1</sup>, Y.Ma<sup>1</sup>, Y.Montelongo<sup>1</sup>, D.Sikdar<sup>1,2</sup>, M.Urbakh<sup>3</sup>,  
L.Velleman<sup>1</sup>, C.Zagar<sup>1,4</sup>

<sup>1</sup> Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City, W12 0BZ London, UK

<sup>2</sup> Department of Electronics and Electrical Engineering, Indian Institute of Technology Guwahati, Guwahati-781039, India

<sup>3</sup> School of Chemistry, University of Tel Aviv, Tel Aviv 69978, Israel

<sup>4</sup> Department of Physics, Imperial College London, South Kensington, SW7 2AZ London, United Kingdom

\*corresponding author, E-mail: [a.kornyshev@imperial.ac.uk](mailto:a.kornyshev@imperial.ac.uk)

### Abstract

This talk will overview a new direction of research based on self-assembly of plasmonic nanoparticles at electrochemical liquid-liquid or solid-liquid interfaces. Optical properties of such systems can be varied in real time via voltage-control over the structure and density of the nanoparticle assemblies. Potential applications involve switchable mirror-windows, tunable color mirrors, optical cavities, and pixels.

### 1. Introduction

Progress in photonic metamaterials was made possible by advances in nanotechnology. Many of such materials, however, can only perform a single target function. Not surprisingly, already Meta-2014 was opened with a provocative statement: “The time of metamaterials 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. Tunability can be reached by utilization of fine electrodynamic effects, controlling light by light, etc, but also via changing the structure of metamaterials in real time. To make the latter kind of tuning and switching fast, is a challenge, but not an unsolvable one. Our team pursued this direction of research, and its current status is summarised below.

### 2. Chemical tuning of nanoplasmonic meta-arrays

We responded to this challenge first with developing the ‘nanotechnology-free’ concept of chemically tunable self-assembly of plasmonic nanoparticles (NPs), 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].

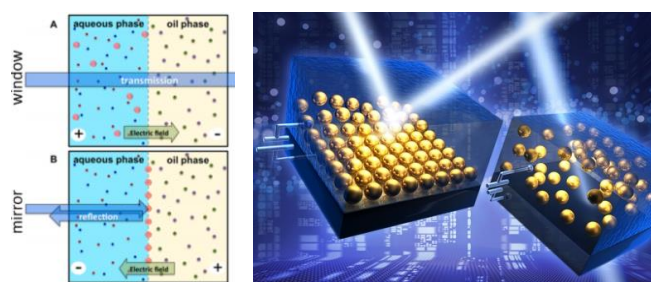
The array structure was controlled by tuning the composition of the solutions (electrolyte concentration or pH). Indeed, NPs are functionalized by ligands that dissociate, in the aqueous phase, leaving negative charges at

their terminal groups. This is necessary to prevent NPs to agglomerate in the bulk of the solution, otherwise driven by Vand-der-Walls attraction. pH and electrolyte concentration control the repulsion between NPs. More basic pH will increase dissociation of ligands and thereby increase the charge. Increase of electrolyte concentration will decrease the Debye length and will weaken the repulsion.

Starting with arbitrary conditions that do not allow NPs’ agglomeration in the bulk, we cannot expect them to come too close to each other at the surface. Still, they come much closer to each other there, than in the bulk: because of the strong driving force for them to be at the interface, they have to tolerate the proximity of each other. For instance, at an oil|water interface each individual NP strongly adsorbs, to block the energetically unfavorable contact between water and oil; the effect called ‘capillary attraction’. One can obtain denser quasi-2D monolayers of NPs by minimizing their charges down to and maximizing the electrolyte concentration up to the values that yet do not allow their agglomeration in the bulk. We have been able to establish the conditions of this fine balance.

We performed a complex study of the structure and optical properties of such NP arrays at DCE/water interface. Within the same setup, we performed 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 concentration electrolytes, either of inorganic electrolyte in water, or organic electrolyte in oil. 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]. The excellent match between the theory and experiments demonstrated that the *physics worked exactly as expected!* These studies gave us confidence that we could control these novel nanoplasmonic platforms by smart ‘physical chemistry, i.e. generate tunable self-assembled metamaterials. But it was not a *real-time reversible control*.

### 3. Voltage-controlled tuning of meta-arrays and switching dynamics in electrochemical cells



A sketch of a self-assembled voltage-controlled of negatively charged Au NPs at electrified interface of two immiscible electrolytic solutions (ITIES), in reflecting mode (left) and transmitting mode (right). Switching on- and 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.

It was clear to us, 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 NP arrays and their optical properties. We demonstrated this by creating the first electrically switchable mirror based on voltage controlled self-assembly of functionalized gold NPs at the interface of two immiscible electrolytic solutions [see video at https://youtu.be/68J0yLrvvJE](https://youtu.be/68J0yLrvvJE) [6]. We have shown that it is possible to transition between a mirror and window and back again using a mere 0.5 V - voltage variation through its effect on the density of the NP arrays and their resulting optical response.

The reflectivity spectrum, the maximum of which is centered near the frequency of coupled localized plasmon resonances in NPs, gradually shifts to the blue and its intensity gradually vanishes with reduction of the density of the NPs array, making the interface transparent. This process is controlled by the voltage drop across the interface: polarizing water positively, we invite negatively charged NPs to leave the potential wells at the interface and move to the aqueous bulk; polarizing water negatively we stimulate adsorption of NPs.

A switch of a different kind, based on voltage-controlled adsorption-desorption of NPs on a metal substrate, described earlier in detail theoretically [7], was reported in Ref. [8]. The difference of this system from the LLI case is as follows. Metallic electrode (in our study – silver, covered by thin protective film of titanium nitride) reflects light itself, but when covered by a dense array of plasmonic NPs (Au, in our case), an effect of resonance quenching of reflection by increased absorption of light in the NP-array/metallic substrate system turns on. This causes a dip in reflectivity spectrum, centered near the frequency of localized plasmons in NP. The latter shifts to the red, with denser population of the surface by NPs. All-in-all, some range of frequencies are get reflected less, and the mirror becomes colored. The density of NP arrays is again controlled by voltage:

positively polarized electrode will cause stronger adsorption (‘electrosorption’) of negatively charged NPs, decreasing the average inter-NP distance. Through affecting this distance, voltage controls the color of the mirror.

Both for LLI and SLI, studying the evolution of the spectra with time, we learn about the kinetics of voltage-controlled adsorption/desorption of NP, by fitting the spectra to the theory that relates the latter with the density of NP arrays at the interface. Generally, reproduction by the theory [5,7] of the experimental data both for the LLI and SLI systems [6,8] is amazing; the theory itself, systematically tested against COMSOL simulations, shows excellent correspondence with the latter.

A set of other interesting scenarios have been also considered (see e.g. [9,10]). Several other papers are submitted for publication, whereas the disclosure of some other results awaits patenting.

### Acknowledgements

The project was supported by an Engineering and Physical Sciences Research Council Grant, “Electrotunable Molecular Alarm”, EP/L02098X/1. J.B.E. also acknowledges receipt of European Research Council Consolidator Grant (NanoPD). Y.M. has been supported in part by a China Scholarship Council, Imperial Scholarship (201506320194).

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