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## Ensemble of plasmonic gold-patchy nanoparticles with multiple hot-spots for dual SERS and SEIRA spectroscopy

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Plasmon-enhanced vibrational spectroscopy has shown great potential for biosensing applications based on the signal enhancement in surface-enhanced infrared absorption spectroscopy (SEIRA) or surface-enhanced Raman spectroscopy (SERS)<sup>1,2,3</sup>. Here, we report on the in situ-controlled growth of gold-patchy nanoparticls ensembles for dual SEIRA - SERS applications. Each individual nanoparticle contains multiple nanogaps where the electric field is highly concentrated and amplified under broadband excitation from near to middle infrared (IR). These IR-active plasmonic structures show high sensitivity in sensing the vibrations of biomolecules. In this contribution, we will present our SEIRA study on the detection of trace amount of mercuric ion down to nM level in water by studying the relevant conformational changes of glutathione (GSH) molecules, which is induced by the adsorption of mercuric ions. In addition, this structure also showed large SERS enhancement on methylene blue molecules under NIR laser excitation of 785 nm. Hence, we propose that the ensemble of plasmonic gold-patchy nanoparticles with multiple hot-spots and facile synthesis can be another promising candidate for plasmonic biosensor applications.



**Fig. 1** (a) In-situ controlled growth of plasmonic Au-patchy nanoparticle ensembles (shown in SEM image) by monitoring the evolution of the IR spectrum of water, simulated electric field distribution (at 5  $\mu$ m excitation) around Au-patchy nanoparticles with multiple hot-pots; (b) Hg<sup>2+</sup> sensing mechanism: Hg<sup>2+</sup> binding results in conformational changes of GSH; (c) IR spectra of GSH molecules at low concentrations are measured by using SEIRA of Au-patchy nanoparticle ensembles and (d) detection of Hg<sup>2+</sup> by monitoring the relevant conformational changes of the GSH induced by the adsorption of Hg<sup>2+</sup> in GSH-molecules; SERS application of Au-patchy nanoparticles with multiple hot-spots: (e) Optical image and scanned SERS image of Au-patchy nanoparticle ensembles with adsorbed methylene blue molecules (integrated at 1618 cm<sup>-1</sup> band of methylene blue under 785 nm laser excitation), simulated electric field distribution at different laser excitations of 532 nm (low-enhancement) and 785 nm (high-enhancement), (f) SERS spectra of methylene blue molecules.

References: 1. D. Enders, T. Nagao, A. Pucci, T. Nakayama, and M. Aono, *Phys. Chem. Chem. Phys.*, 2011, 13, 4935.; 2. C. V. Hoang, M. Oyama, O. Saito, M. Aono, and T. Nagao, *Sci. Reports*, 2013, 3; 3. J.-S. Wi, S. Tominaka, K. Uosaki, and T. Nagao, *Phys. Chem. Chem. Phys.*, 2012, 14, 9131.