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Plasmonic light-harvesting devices for biosensing and optoelectronic modulation

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14. ABSTRACT The goal of this project was to design different plasmonic nanostructures that can gather light from the far-field and concentrate its energy into a volume only a few nanometers across, thereby achieving enormous enhancement in energy densities for various applications. New fabrication technologies were developed. One example is the development of cost-effective electron beam lithography techniques that achieved sub-10-nm diameter with a pitch of ~34 nm resolution. Prototypes using these new fabrication techniques were also demonstrated. There was the successful first demonstration of localized surface plasmon resonance sensing based on fundamental magnetic resonance in the visible spectrum using ultrasmall gold v-shaped split ring resonators. Another example was a n-InAsSb/n-GaSb heterostructure photodiode integrated with plasmonic two-dimensional subwavelength hole array (2DSHA) for room temperature two band photodetection to ~1.4 10 ⁹ Jones and ~1.5 10 ¹¹ Jones for the two bands peaked at 3.4 μm and 1.7 μm, respectively. These are just a couple of innovative ways of controlling light to extend and improve the-state-of-the-art technology in nanoplasmonics and metamaterials, allowing for efficient low-power-consumption harvesting of light on the nanoscale for biosensing and optoelectronic applications.					
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Plasmonic light-harvesting devices for biosensing and optoelectronic modulation

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Introduction

In the past decade, nanophotonics research has experienced great boost due to the ability of surface plasmons (SPs) to collect and concentrate light efficiently into subwavelength volumes. The peculiar nature of SPs thus potentially enables a greater level of integration in photonic devices, and has opened up a wide range of applications. In this project, we design different plasmonic nanostructures that can gather light from the far-field and concentrate its energy into a volume only a few nanometers across, thereby achieving enormous enhancement in energy densities for various applications. Especially, we shall investigate the performance of nanodevices with diminutive geometrical features. Following the theoretical exploitation and experimental demonstration of the concept, we move forward to apply the structures for low-power ultrafast nonlinear devices. This innovative way of controlling light with a plethora of applications will extend and improve the-state-of-the-art technology in nanoplasmonics and metamaterials, allowing for efficient low-power-consumption harvesting of light on the nanoscale for biosensing and optoelectronic applications.

Accomplishments and findings

With our great effort for the past years, we have successfully reached our goal. The achievements obtained are summarized below.

1. Development of new fabrication technologies

1.1 *New processes associated with electron beam lithography for ultra-small resonators*

High density ultrahigh resolution patterning with desired shape and size is a crucial requirement in nanotechnology and its applications. Electron beam lithography (EBL) is the most widely used lithography tool for these applications. However, achieving cost-effective patterning with sub-10-nm critical dimension has been challenging due to the inherent tradeoff between resolution and throughput. In this paper, we developed cost-effective new processes associated with EBL technique, which include optimized resist selection and processing as well as sonicated cold development process. Using this process, we demonstrate sub-10-nm diameter metal dots at a pitch of ~34 nm and sub-15 nm wide metal lines. Based on the same processes, we demonstrate the fabrication of u-shaped split ring resonator array of different metals with smallest fabricated resonator with ~60 nm size and v-shape SRRs with the smallest gap spacing of ~30 nm. By adjusting the SRR gap spacing through its arm length and opening angle, we have successfully demonstrated magnetic and electric resonances across the visible and ultraviolet range.

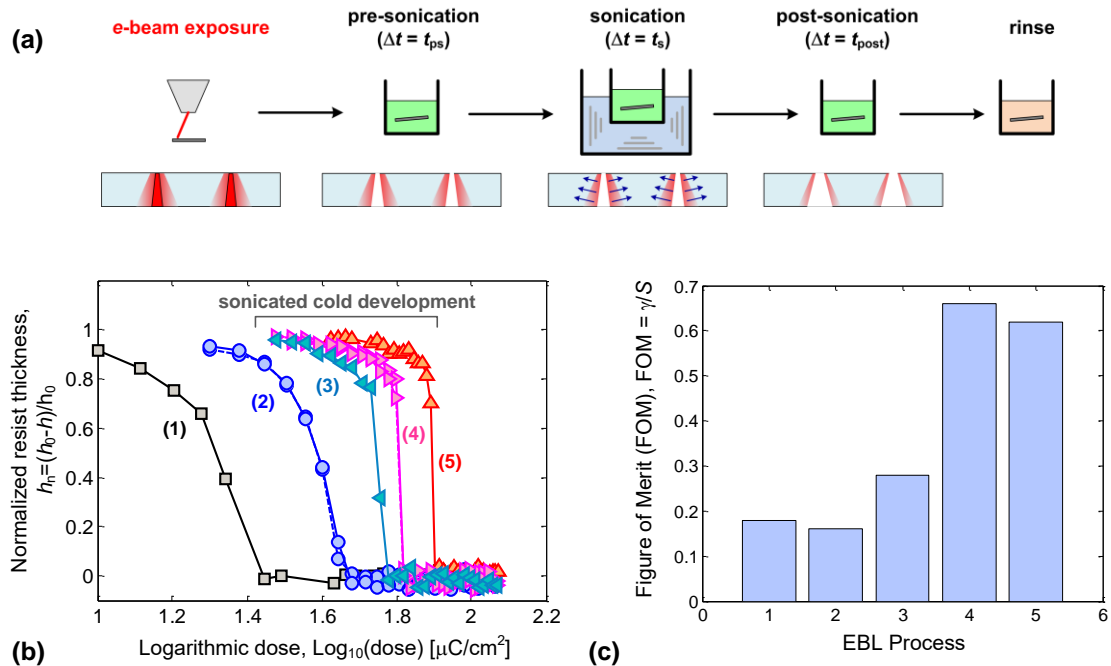


Figure 1. The role of sonicated cold development towards for high resolution high throughput electron beam lithography process. (a) Schematic of the sonicated cold development process. The gel-layer is denoted by the shaded red areas, and the gel-layer removal process is described by the dark blue arrows (b) Contrast curves of (1) standard development, (2) cold standard development, and (3)-(5) sonicated cold development processes. The process details are as follows: (1) *n*-amylacetate (*N*50) for 30s, followed by rinsing in methyl isobutylketone (MIBK) solution for 30s at room temperature; (2) *N*50 at 6°C for 10s, followed by MIBK rinse at 6°C for 10s; (3) in *N*50:IPA=1:1 at $t_{ps}=10\text{s}$, $t_s=10\text{s}$, $t_{post}=20\text{s}$ followed by rinsing in isopropanol alcohol (IPA) rinse at $t_{ps}=10\text{s}$, $t_s=10\text{s}$, $t_{post}=40\text{s}$; (4) in *N*50:IPA=2:1 at $t_{ps}=5\text{s}$, $t_s=10\text{s}$, $t_{post}=20\text{s}$ followed by rinsing in isopropanol alcohol (IPA) rinse at $t_{ps}=10\text{s}$, $t_s=10\text{s}$, $t_{post}=40\text{s}$; and (5) in *N*50:IPA=2.5:1 at $t_{ps}=10\text{s}$, $t_s=10\text{s}$, $t_{post}=20\text{s}$ followed by rinsing in isopropanol alcohol (IPA) rinse at $t_{ps}=10\text{s}$, $t_s=10\text{s}$, $t_{post}=40\text{s}$. The developments in (3)-(5) are all done at 6°C. (c) Figure-of-Merit (FOM) of standard development, cold development, and sonicated cold development processes.

1.2 Reliable fabrication of high aspect ratio plasmonic nanostructures based on seedless pulsed electrodeposition

Strong plasmonic resonance in the visible spectrum requires high aspect ratio metallic resonators with deep subwavelength dimensions, which find applications as part of a cost-effective and practical optics-based sensing platform. Electrodeposition is a highly suitable method for fabricating such structures as it allows deposition of metals with much larger thickness and better morphology than that achieved by physical deposition. Herein, we carry out an in-depth study of pulsed electrodeposition of a gold film directly onto a transparent substrate without a seed layer and development of a reliable and efficient fabrication method for high aspect ratio metallic nanostructures with sub-10-nm features based on this approach. We demonstrate a low-cost fabrication of sub-100-nm metallic nanostructures based on a very high deposition rate (up to 7 nm/pulse) which nonetheless exhibit good surface morphology. Specifically, we realized high aspect ratio rotationally symmetric plasmonic nanostructures suitable for practical sensing platform, which exhibit strong resonances in the visible spectrum with Q factors as high as 10 under unpolarized excitation.

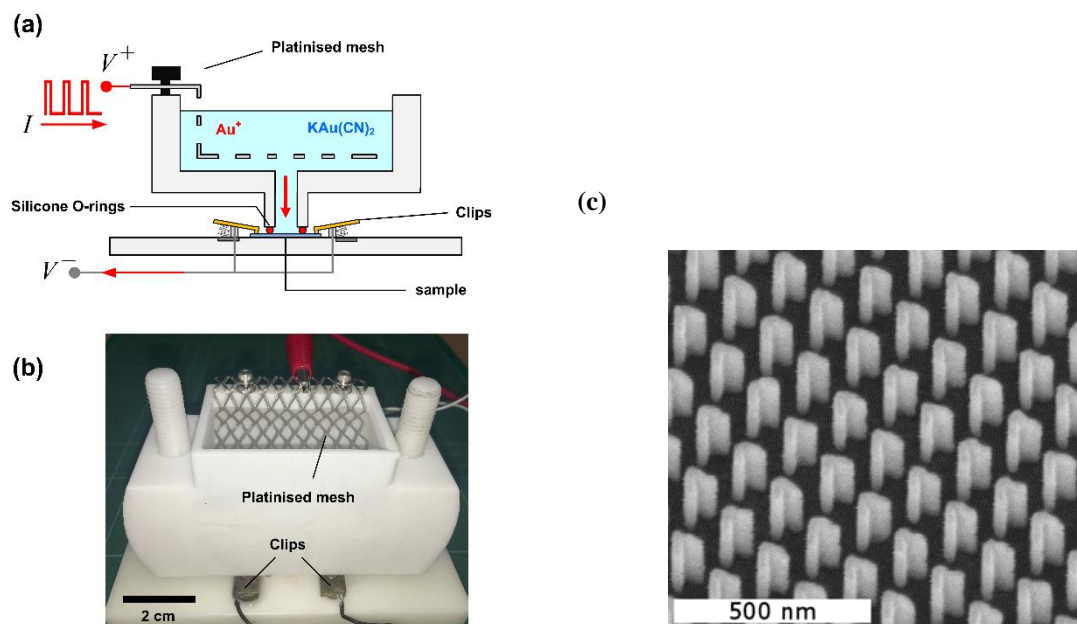


Figure 2. Side view schematic of the dual-substrate electrodeposition holder and (b) a photograph from the front. (c) Image of a 3-D v-shape array.

1.3 Combining sonicated cold development and pulsed electrodeposition for high aspect ratio sub-10 nm gap gold dimers for sensing applications in the visible spectrum

Strong interactions between localized surface plasmons and nanoscale objects have led to the development of highly sensitive biochemical sensing in planar metallic nanostructures with sensing performance mainly dependent on the interaction volume and the local electric field. However, the sensitivity and the interaction volume of these planar structures have been limited by the achievable aspect ratios based on the standard lift-off process. We propose a new technique which involves cold sonicated development and pulsed electrodeposition to overcome this limitation, and demonstrate robust gold square dimers with sub-10 nm gaps and a gap aspect ratio of ~ 8 . We show that smooth gold surfaces can be achieved by growing the gold film directly on a transparent ITO substrate without a gold seed layer, and demonstrate a significant improvement in Q factors and resonance contrast in electrodeposited dimers compared to dimers fabricated by physical vapor deposition. We demonstrate that the electrodeposited dimers exhibit near 50% higher bulk refractive index sensitivity than their planar counterparts. The technique may be used to grow a variety of metals of arbitrary geometries and spatial arrangements.

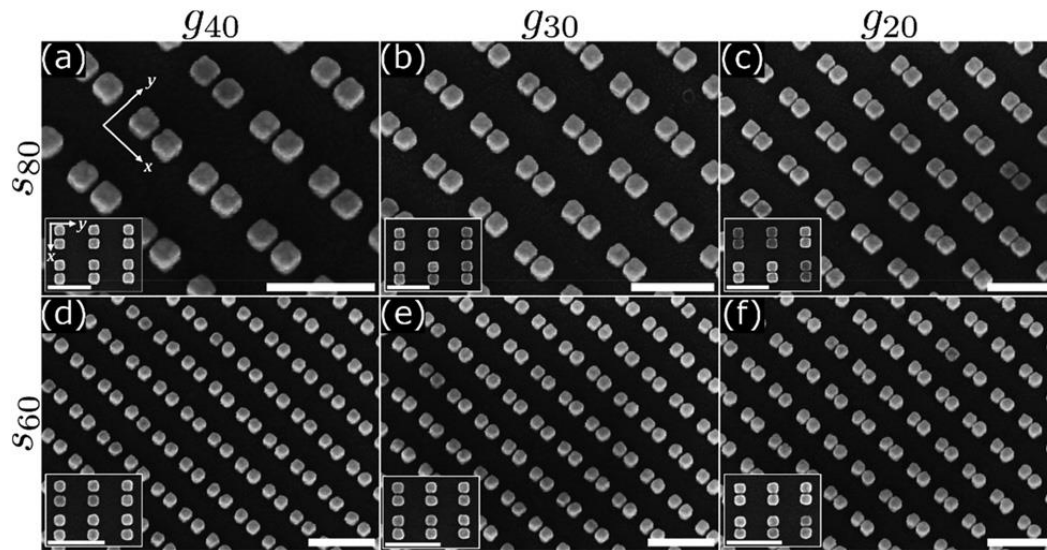


Figure 3 Oblique-incidence SEM images of the fabricated dimer arrays with normal-incidence SEM images (insets). (a)–(c) Design square dimension of 80 nm with gap decreasing from 40 nm to 20 nm and (d)–(f) the same as above but with square dimension of 60 nm. The inclination angle for the oblique images is 25° . All scale bars are 400 nm.

1.4 Nanobridge

We developed a versatile nanofabrication technique based on UV-sensitive AZ 5214E photoresist that is capable of positive, negative, and image-reversal process tones based on unique combinations of e-beam exposure, UV exposure and heat. We demonstrate that the image-reversal e-beam lithography process is capable of overcoming the limitation of a standard e-beam lithography process in realizing patterns with negative wall profiles, which finds applications in lift-off pattern transfer of metal nanostructures with nanoscale gaps. We present reliable lift-off transfers of gold nanohole arrays and nanoring slots with achievable periodicity and features of 500 nm and 60 nm, respectively. By adjusting the interplay of e-beam proximity effects and diffusion of photoactive compounds during the post-exposure bake, we demonstrate the natural formation of nanobridge networks which can be engineered according to pre-defined templates. Employing these naturally-formed nanobridges as a stencil for lift-off process, we realize plasmonic nanostructures with ~ 20 nm gaps which is capable of 4 order of magnitude intensity enhancement in mid infrared range. Designing pre-defined templates for nanobridge formations would enable prospects for diverse plasmonic applications ranging from mid-IR resonator design to SPP-based integrated optics devices.

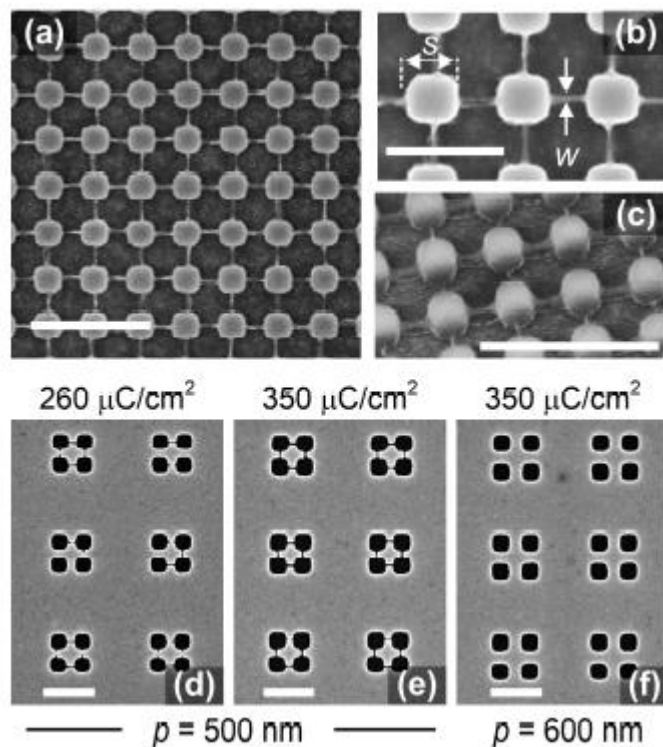


Figure 4. Fabrication of plasmonic nanostructure with ~ 20 -nm gaps through nanobridge formation process. (a)-(c) The natural formation of nanobridges connecting neighbouring AZ pillars with 400 nm periodicity (exposed at $450 \mu\text{C}/\text{cm}^2$). The nanobridges are found to be ~ 20 -nm wide. (d)-(f) The role of exposure dose, pillar size, and inter-pillar spacing in engineering the formation of nanobridges (for $s = 300 \text{ nm}$ and $p = 500 \text{ nm}$). All the scale bars represent $1 \mu\text{m}$.

2. Applications of new technologies

2.1 High figure-of-merit sensing in the visible range using seedless electrodeposited v-shaped split ring resonators

Strong light localization within metal nanostructures occurs by collective oscillations of plasmons in the form of electric and magnetic resonances. This so-called localized surface plasmon resonance (LSPR) has gained much interest in the development of low-cost sensing platforms in the visible spectrum. However, demonstrations of LSPR-based sensing are mostly limited to electric resonances due to the technological limitations for achieving magnetic resonances in the visible spectrum. In this work, we first demonstrated LSPR sensing based on fundamental magnetic resonance in the visible spectrum using ultrasmall gold v-shaped split ring resonators. Specifically, we showed the ability for detecting adsorption of bovine serum albumin and cytochrome c biomolecules at monolayer levels, and the selective binding of protein A/G to immunoglobulin G.

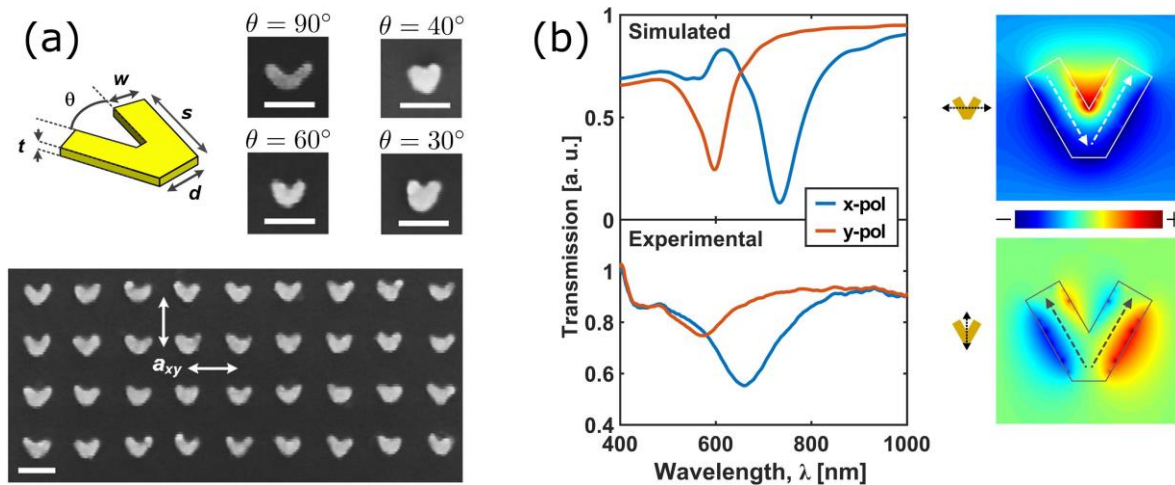


Figure 5. (a) Schematic of vSRRs and SEM images. Scale bars are 100 nm. (b) Simulated and experimental spectra for q60 s60 structures excited with x- and y-polarized normally incident source, with insets showing corresponding Hz fields and dipolar coupling.

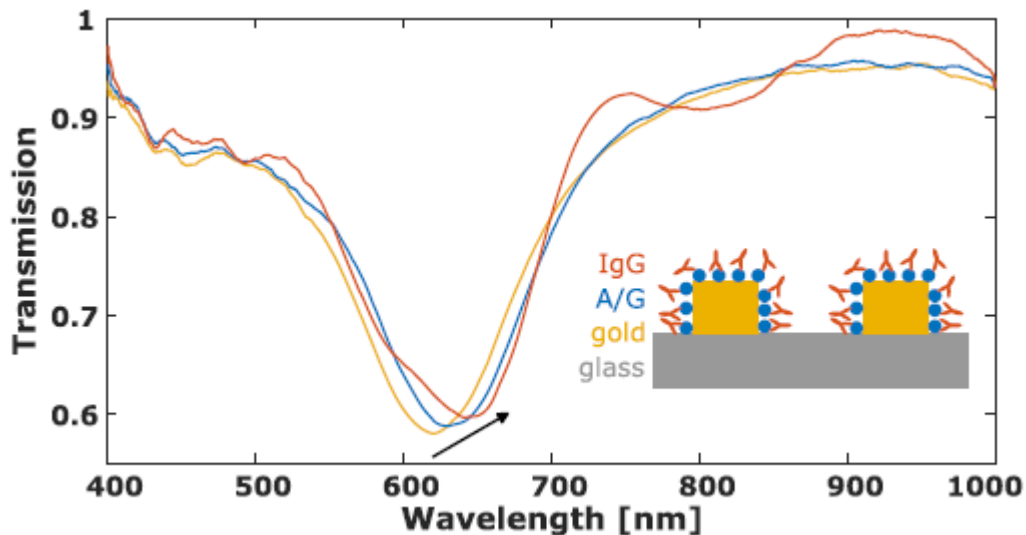


Figure 6. The observed spectrum red-shifting upon binding with biomolecules protein A/G and IgG and (inset) schematic of biomolecule adsorption process.

2.2 Polarization invariant plasmonic nanostructures for sensing applications

Optics-based sensing platform working under unpolarized light illumination is of practical importance in the sensing applications. For this reason, sensing platforms based on localized surface plasmons are preferred to their integrated optics counterparts for their simple mode excitation and inexpensive implementation. However, their optical response under unpolarized light excitation is typically weak due to their strong polarization dependence. Herein, the role of rotational symmetry for realizing robust sensing platform exhibiting strong optical contrast and high sensitivity is explored. Specifically, gammadion and star-shaped gold nanostructures with different internal and external rotational symmetries are fabricated and studied in detail, from which their mode characteristics are demonstrated as superposition of their constituent longitudinal plasmons that are in conductive coupling with each other. We demonstrate that

introducing and increasing internal rotational symmetry would lead to the enhancement in optical contrast up to $\sim 3x$ under unpolarized light illumination. Finally, we compare the sensing performances of rotationally symmetric gold nanostructures with a more rigorous figure-of-merit based on sensitivity, Q-factor, and spectral contrast.

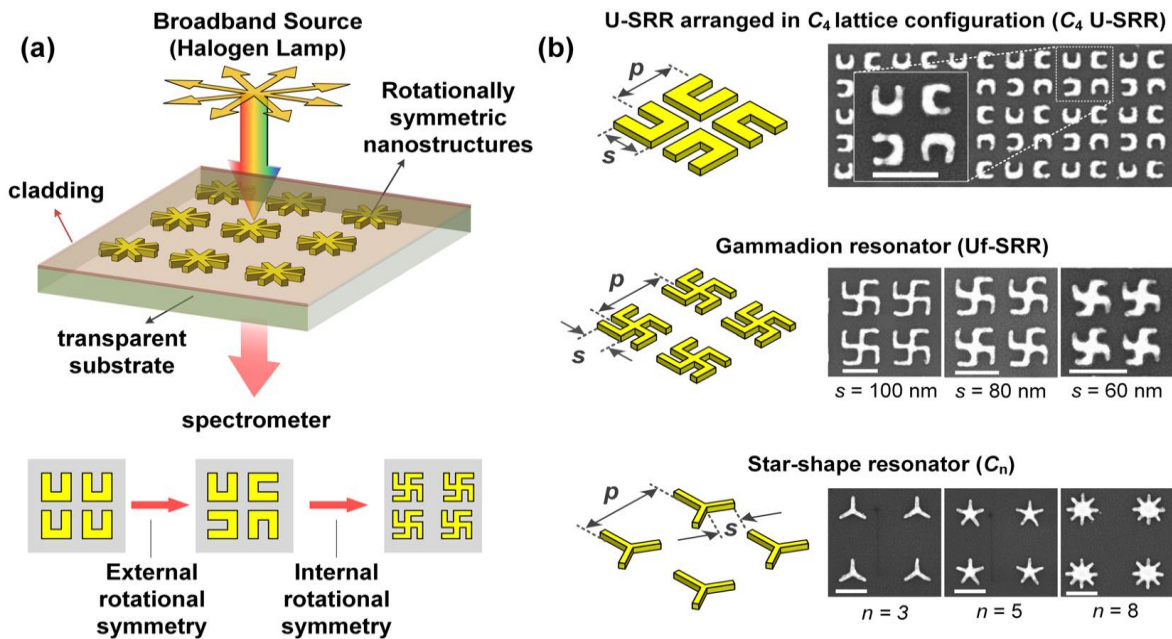


Figure 7. Incorporating rotational symmetry for making robust plasmonic sensing platform. (a) Schematic of polarization-invariant sensing platform based on unpolarised broadband light source and rotationally symmetric metal nanostructures. (b) Plasmonic nanostructures with varying rotational symmetry. (Top) U-SRRs in C_4 lattice configuration with the periodicity normalized to resonator size, i.e., $p = 2 s$. The unit cell is denoted by the dashed line. (Middle) Gammadion structures with periodicity (p) normalized to their arm lengths (s), i.e., $p = 3 s$. (Bottom) Star-shape structures with different rotational symmetry at fixed periodicity of $p = 400$ nm and arm length of $s = 100$ nm. Both the gammadion and star-shaped nanostructure are in square lattice configuration. All scale bars represent 200 nm.

2.3 Polarization-Resolved Plasmon-Modulated Emissions of Quantum Dots Coupled to Aluminum Dimers with Sub-20 nm Gaps

An aluminum dimer nanoantenna with nanogaps is an ideal platform for enhancing light–matter interaction at the nanoscale for the UV–vis spectrum, but its realization has been hindered by the surface oxidation of aluminum nanostructures, aluminum interband loss, and practical limitations in lithographic patterning. Here, we have overcome these problems and demonstrated the successful fabrication of an aluminum dimer antenna with a ~ 10 nm gap, which to the best of our knowledge marks the smallest features of an Al nanoantenna. We present the first in-depth study of strongly polarization-dependent emissions of colloidal quantum dots coupled with Al dimers and elucidate the individual contributions of the excitation intensity, quantum yield, and extraction efficiency enhancements from numerical and experimental perspectives. We estimate the Purcell effect corresponding to a single Al-dimer antenna as ~ 104 by taking into account the ensemble

averaging effect and the distributions in emitter dipole orientations. This finding brings us a step closer toward a cost-effective realization of bright and ultrafast single emitters.

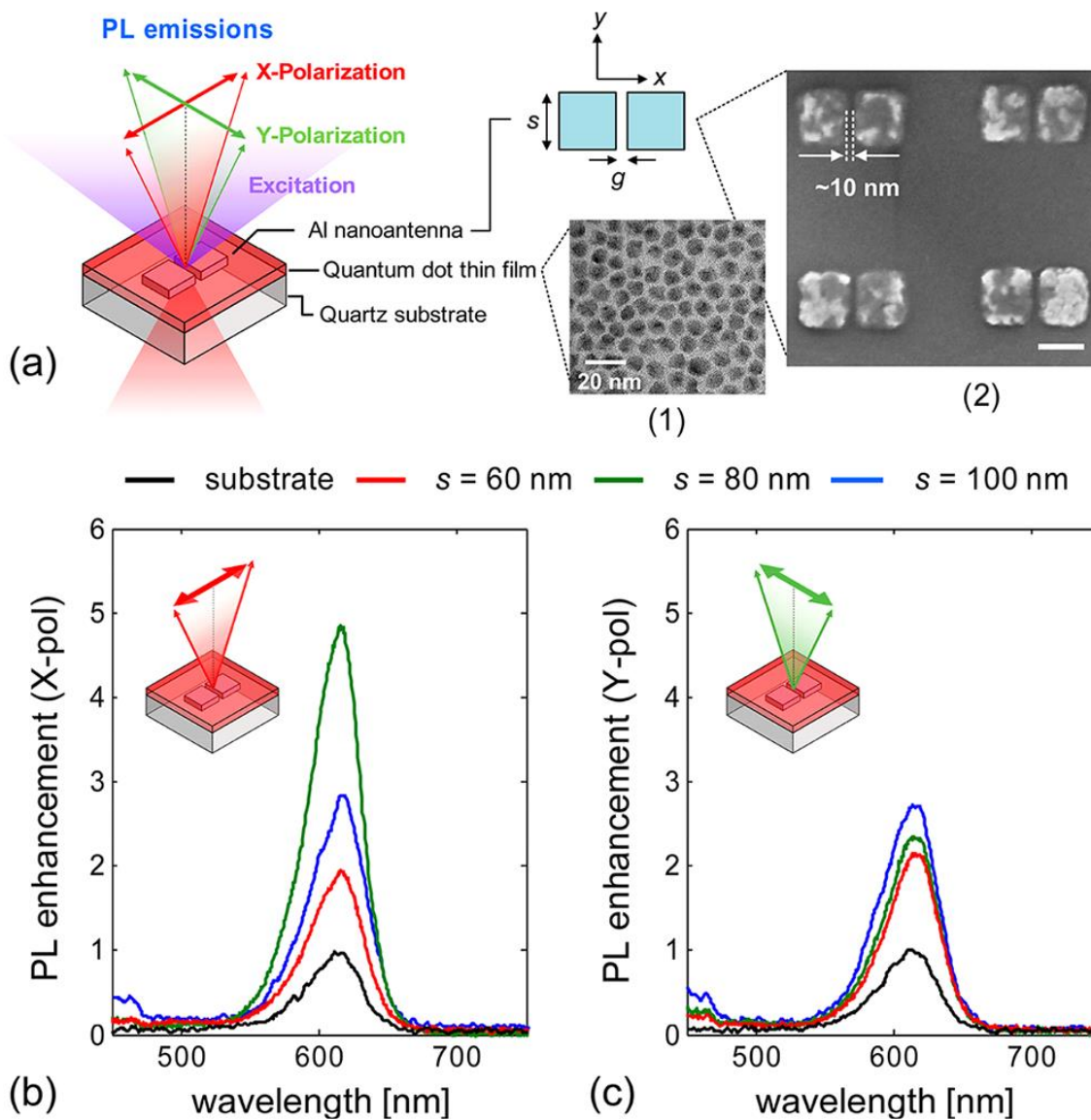


Figure 8. Polarization-resolved PL enhancements of CdSe/CdS colloidal quantum dots by aluminum square dimer structures. (a) Schematic of the Al square dimer. The square disk size is varied from $s = 60$ nm to $s = 100$ nm, while the gap spacing is varied from $g = 10$ nm to $g = 30$ nm. The thickness of the all-Al nanoantenna is $t_{na} = 30$ nm. Insets: (1) TEM image of the CdSe/CdS colloidal quantum dots. (2) SEM micrograph of the fabricated Al square dimers with $s = 100$ nm and $g = 10$ nm. The scale bar represents 100 nm. The black shades are the conductive polymer spin coated prior to SEM. (b, c) PL enhancements by Al square dimers for fixed gap spacing ($g \approx 10$ nm) with different size. The PL signals are normalized to the maximum PL signal from the same QD film outside the dimer regions (i.e., bare QDs on the substrate). The PL signals from the bare QD films are presented for both polarizations as reference.

2.4 Electrically controlled enhancement in plasmonic mid-infrared photodiode

Surface plasmon polaritons (SPPs) have been attracting tremendous attention in application of enhanced optoelectronic devices owing to their capability of localizing electromagnetic waves in deep subwavelength scale. We propose a plasmonic mid-infrared InAsSb-based n-i-p photodiode with electrically-controlled photocurrent enhancement achieved by controlling the overlap between SPP depth and the absorption layer, from which maximum electrically controlled enhancement factors of $\sim 5x$ and $\sim 6x$ have been achieved for room temperature (293 K) and 77 K operation, respectively, corresponding to electrical tuning factors of 11.9 and 26. The maximum detectivities obtained at the two temperatures are 0.8×10^{10} Jones and 5×10^{11} Jones, respectively. This electrically controlled enhancement expands the application capability of plasmonic photodiodes.

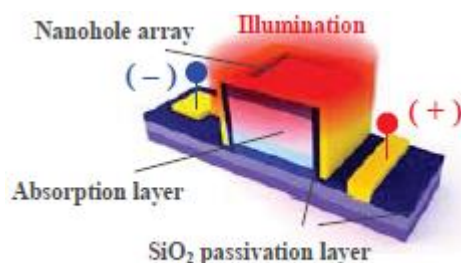


Figure 9. Schematic of the plasmonic InAsSb-based n-i-p photodiode

2.5 Single Plasmonic Structure Enhanced Dual-band Room Temperature Infrared Photodetection

Dual-band photodetection in mid- and near-wave infrared spectral bands is of scientific interest and technological importance. Most of the state-of-the-art mid-infrared photodetectors normally operate at low temperature and/or suffer from toxicity and high cost due to limitations of material properties and device structures. The capability of surface plasmons in confining electromagnetic waves into extremely small volume provides an opportunity for improving the performance for room temperature operation. Here, we report an n-InAsSb/n-GaSb heterostructure photodiode integrated with plasmonic two-dimensional subwavelength hole array (2DSHA) for room temperature two band photodetection. We demonstrate that with a properly designed 2DSHA, room temperature detectivities of the heterostructure device can be enhanced to $\sim 1.4 \times 10^9$ Jones and $\sim 1.5 \times 10^{11}$ Jones for the two bands peaked at $3.4 \mu\text{m}$ and $1.7 \mu\text{m}$, respectively. In addition, we study the photocurrent enhancement in both photoconductor and heterojunction modes in the same integrated structure. The demonstration of single 2DSHA enhanced heterojunction photodiode brings a step closer to high sensitivity room temperature devices and systems which require multiband absorption.

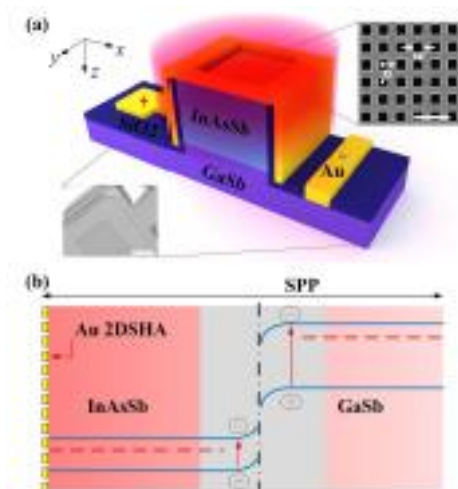


Figure 10. (a) Schematic of the 2DSHA n-InAsSb/n-GaSb heterostructure photodiode (not to real scale). (b) Schematic of the energy band diagram of the 2DSHA n-InAsSb/n-GaSb heterostructure under forward bias for dual-band photodetection. The grey area represents the main absorption region by InAsSb and GaSb, the area with gradually varied red color represents the intensity of SPPs.

Publications in international journals

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- Aaron D. Mueller, Landobasa Y. M. Tobing, Dao Hua Zhang*, “Reliable fabrication of high aspect ratio plasmonic nanostructures based on seedless pulsed electrodeposition”, Advanced materials Technology, 17 Oct. 2018, Adv. Mater. Technol. 2018, 1800364
- Mueller, Aaron; Tobing, L.Y.M.; Zhang, Dao Hua, “Combining sonicated cold development and pulsed electrodeposition for high aspect ratio sub-10-nm gap gold dimers for sensing applications in the visible spectrum”, *Nanoscale*, 10, 5221-5228 2018, DOI: 10.1039/C7NR09410H
- Landobasa Y. M. Tobing, Aaron D. Mueller, Jinchao Tong, Dao Hua Zhang*, “Nanobridges formed through electron beam image reversal lithography for plasmonic mid-infrared resonators with deep nanogaps”, Nanotechnology, accepted.
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- Landobasa Y. M. Tobing¹, Dao Hua Zhang*, Kah Ee Fong, Muhammad Danang Birowosuto, Yuan Gao, Cuong Dang, Helmi V. Demir, “Polarization-resolved plasmon-modulated emissions of quantum dots coupled to aluminum dimers with sub-20-nm gaps”, *ACS Photonics*, 5 (4), pp 1566–1574, 2018, DOI: 10.1021/acsp Photonics.8b00009. Publication Date (Web): March 8, 2018.
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Recommendation

We have gain significant achievements in development of new technologies and novel plasmonic structures. We have also used the plasmonic structures for biochemical sensing, enhancement of light emission and photodetection. We would like to extend the plasmonics to terahertz and millimeter range as there are tremendous applications in the long wavelength range. We have done some work recently and obtained exciting results and we will further explore the new technologies and applications in the terahertz and millimeter range.

Summary

In summary, we developed new technologies for fabricating 2 and 3 dimensional plasmonic structures. With them, we have fabricated and characterized several novel plasmonic structures. We have also explored applications of them, which include biochemical sensing, enhancement of light emission and photodetection from visible to mid-infrared range. A number of papers have been published in high impact international journals. We have also done some work recently in the integration of plasmonics with semiconductors and will further explore the new technologies and applications in the terahertz and millimeter range.