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研究課題名（和文）Novel photon control by moire superlattices and plasmonic metasurfaces

研究課題名（英文）Novel photon control by moire superlattices and plasmonic metasurfaces

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研究成果の概要（和文）：本研究ではコロイダルリソグラフィーをベースとしたナノ構造やメタマテリアルの開発を進めた。アルミナノトライアングルを用いたチューナブルな共鳴波長を持つ表面増強赤外吸収センサーを開発した。また、ＩＴＯ膜とコロイダルリソグラフィーとを併せることで、ＩＴＯナノコーンを製作する方法を開発し、それをエネルギー変換材料に用いる方法論を確立した。さらに、ＩＴＯナノロッドを赤外アンテナとして表面増強赤外吸収へと応用可能であることを示し、この構造が特定のたんぱく質・酵素を選択的に対して増強シグナルを示すような表面機能化法を開発した。

研究成果の概要（英文）：We employed colloidal lithography to fabricate a variety of nanostructures and metasurfaces to engineer the light-matter interactions on the nanoscale. Al nanotriangles had been fabricated with great tunability for plasmon-enhanced infrared spectroscopy. ITO nanocone arrays had also been fabricated by combining colloidal lithography and dry etching to enhance solar energy harvesting. In addition, I also explored the application of ITO nanorods as a new platform for infrared biosensing.

研究分野：総合理工

キーワード：colloidal lithography　plasmon　infrared spectroscopy　ITO

１．研究開始当初の背景

Plasmonic metasurfaces and nanostructures provide approaches for effective manipulation of light-matter interaction on the nanoscale. Plasmonic metasurfaces consist of subwavelength two-dimensional resonant nanostructures. The constituent plasmonic nanostructures interact strongly with the incident light due to the excitation of localized surface plasmon resonance (LSPR), which is the collective oscillation of the free electrons in the metallic nanostructures. LSPR can effectively concentrate the incoming photons into nanoscale volumes resulting in enormous near-field intensity and hence significantly enhancing the light-matter interactions, which leads to a variety of promising applications such as surface-enhanced infrared spectroscopy. Most of the plasmonic metasurfaces and nanostructures are fabricated by conventional lithography tools such as e-beam lithography and focused-ion beam milling. Although these instruments provide good control on the morphology of the nanosctures, they are expensive and the fabrication is time-consuming. Colloidal lithography (CL) represents an alternative method to fabricate metallic nanostructures in a scalable and cost-effective fashion. CL, also known as nanosphere lithography (NSL), employs colloidal monolayers as masks to fabricate various metal nanostructures. I have utilized this technique before for nonlinear optical study [Chen, Nano Lett., 2007,7, 254;Chen, J. Colloid Interface Sci., 2010, 344, 315]. The potential of this technique is not fully realized and more exploration is needed.

In conventional NSL, the sphere configurations are limited. To overcome this problem, I looked into the formation of colloidal nanosphere bilayers. Traditionally, these bilayers are fabricated by spontaneous self-assembly and thus the resulted configurations are limited by thermodynamics. By contrast, I fabricated the bilayers in a layer-by-layer fashion such that relative rotation is possible between the crystal domains in the top and bottom layers, which gives rise to a variety of moiré superlattices that have never been reported before [Chen, ACS Nano, 2015, 9, 6031]. Using these moiré superlattices as masks, I can fabricate the corresponding moiré plasmonic metasurfaces [Chen, Nanoscale, 2015, 7, 20391].

Surface-enhanced infrared absorption spectroscopy (SEIRA) employs plasmonic nanostructures to enhance the characteristic absorption band of different molecules. Therefore, this technique can be used for a variety of biosensing applications. Nanostructures based on metal have been widely used [Chen, ACS Nano, 2012, 6, 7998; Chen, Advanced Functional Materials, 2015, 25, 6637]. Other alternative plasmonic materials can also be used for this applications and this kind of exploration is needed.

２．研究の目的

Plasmonic nanostructures are able to provide significantly enhanced near-field that can boost the sensitivity of biosensing applications. We thus intend to fabricate tunable and large-area SEIRA substrates for potential ultrasensitive biosening. In addition, we intend to explore the use of ITO as alternative plasmonic materials in the infrared wavelength and investigate ITO nanostructures for SEIRA applications.

３．研究の方法

(1) We used colloidal lithography to fabricate Al nanotriangles that show plasmon resonances in the Mid-infrared wavelength. We used polystyrene microspheres with different sizes to tune the resonances. Furthermore, we used the fabricated Al nanotriangles as masks to etch the Si substrates to achieve controllable fine-tuning of the resonance.

(2) We collaborated with Dr. Change from Northwestern University and obtained ITO nanorod samples from his group. We modified the surface of ITO nanorods with phosphonic-acid-based biotin molecules and attached streptavidin proteins to the ITO nanorod arrays. We tune the plasmon resonances from the ITO nanorod arrays by simply changing the incident angle of the incoming light.

(3) We used FDTD methods to characterize the near-field enhancement of the Al nanotriangles and ITO nanorod arrays. The mode properties of the ITO nanorods were also well characterized by this method.

４．研究成果

(1) Tunable Al nanotriangles for cost-effective infrared spectroscopy

Most plasmonic nanostructures sit on top of some substrates that is not useful for sensing applications because some of the enhanced near-fields reside inside the substrates, where the target molecules cannot access. Here we did post-fabrication etching on the Al nanotriangles. With the Al nanotriangles as the masks, we were able to etch away the Si substrates. The partial removal of the Si reduces the effective refractive index of the environment and leads to a blue shift of the resonances, which thus provides an effective means to fine-tune the plasmon resonance as the resonance-shift can be precisely controlled by the etching time as shown in Figure 1.

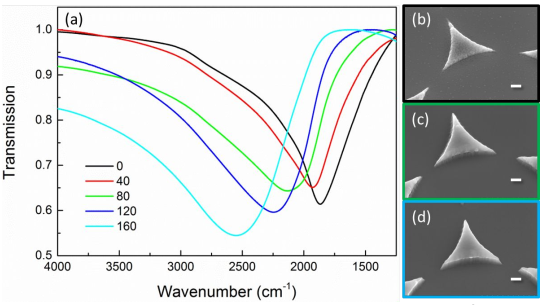

Figure 1. Controllable tuning of the plasmon resonance of Al nanotriangles by dry etching of the Sil substrates.

Thus we can tune the resonances of the Al nanotriangles to achieve good spectral overlap with the absorption bands of the molecules. In addition, such etching frees up the enhanced near-fields from the substrates and increases the effective sensing volumes. This is clearly shown in Figure2. As the etching time increases, the absorption signal from the molecules

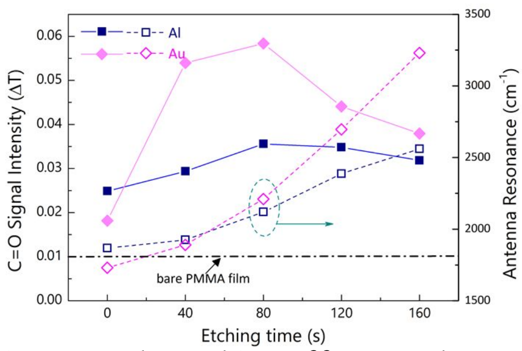

Figure 2. The etching effect on the C=O absorption band intensity and the plasmon resonances from Au and Al nanotriangles.

also increases. There exists and optimal etching time where the signal achieves the largest enhancement, which can be attributed to the shift of the plasmon resonances. Furthermore, we compared the sensing performances of the metal gold and aluminum in the infrared. As expected gold provides better sensing capability as the signal is ~2 times higher than that from the Al, which can be attributed to the 2-3 nm thick Al_2O_3 layer surrounding the Al nanotriangles. However, we should bear in mind that the price of Al is much cheaper than that of Au and therefore Al can also find some applications as alternative plasmonic materials.

(2) ITO nanorod arrays for infrared biosensing applications

We collaborated with Dr. Robert Chang from Northwestern University on this research topic. Dr. Chang ' s group can grow single crystal ITO nanorod arrays. By controlling parameters during the growth, they are able to tune the resonances of the ITO nanorods. We found that the plasmon resonances can be further tuned by simply changing the incident angle of the light as shown in Figure 3. Due to the coupling between the nanorods, the plasmon resonances can be effectively tuned in this facile fashion, which can be used to tune the resonance achieving better overlap with the molecular absorption bands.

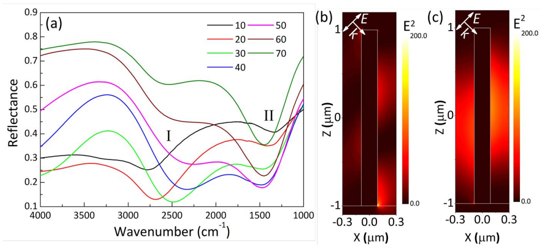

Figure 3. Controllable tuning of the plasmon resonances of the ITO nanorod arrays by changing the incident angle.

We also demonstrated surface functionalization of ITO nanorods using phosphonic-acid-based biotin molecules and achieved selective sensing of streptavidin proteins using the specificity between biotin and streptavidin. Using the tuning method as described above, we achieved selective enhancement of certain absorption bands by changing the incident angle.

５．主な発表論文等

（研究代表者、研究分担者及び連携研究者には下線）

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