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Hybrid Plasmonic-Semiconducting Fractal Metamaterials for Superior Sensing of Volatile Compounds

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ABSTRACT

Localized surface plasmon resonance (LSPR) is a subwavelength optical phenomenon that has found widespread use in bio- and chemical- sensing applications thanks to the possibility to efficiently transduce refractive index changes into wavelength shifts. However, is it very hard to transpose the successes demonstrated in liquid and physiological environment toward the detection of gasous molecules. In fact, the latter typically adsorb in an unspecific manner and induce very minute refractive index changes tipicaly below the sensor sensitivity.

Here, we show first insights on the aerosol large-scale self-assembly of metasurfaces made of monocrystalline Au nano-islands with uniform disorder over large scale. Notably, these architectures show tuneable disorder levels and demonstrate high-quality LSPR, enabling the fabrication of highly performing optical gas sensors detecting down to 10^{-5} variations in refractive index.

Next, we use our aerosol synthesis method to integrate tailored fractals of dielectric TiO_2 nanoparticles onto resonant plasmonic metasurfaces. We show how this integration strongly enhances the interaction between the plasmonic field and volatile organic molecules and provides a means for their selective detection. Interesting, the improved performance is the result of a synergetic behavior between the dielectric fractals and the plasmonic metasurface: in fact, upon this integration, the enhancement of plasmonic field is drastically extended, all the way up to a maximum thickness of 1.8 μm.

Optimal dielectric-plasmonic structures allow measurements of changes in the refractive index of the gas mixture down to $<8x10^{-6}$ at room temperature and selective identification of three exemplary volatile organic compounds (VOCs).

These findings provide a basis for the development of a novel family of hybrid dielectric-plasmonic materials with application extending from light harvesting and photo-catalysts to contactless sensors for non-invasive medical diagnostics.

Keywords: plasmonic, gas sensing, fractal, hybrid, volatile organic compounds

1. INTRODUCTION

Current technological advances demand more and more precise measurement of existence or absence of certain substances, with extremely low concentrations, in various environments. High sensitivity, fast response, and good selectivity are the target requirements for a high-throughput sensor in today's technology. Among all the nanotechnology-enabled gas sensors, the optical ones are most promising and attracting options thanks to their high selectivity, long lifetime, high resistivity to electromagnetic noise and the possibility to work at room temperature [1]. In this panorama, metal nanoparticles (NPs) have been extensively studied because of their characteristic localized surface plasmon resonance (LSPR) and it has been shown that they can be employed for sensing applications thanks to their high reactivity to changes in the local environment[2]. Gold NPs are the ideal candidates for plasmonic applications because of their stable and strong LSPR efficiency in the visible region. So far lots of gold morphologies have been proposed and synthesized in order to optimize the plasmonic properties and improve the sensibility. Despite the many attempts, the optimal plasmonic substrate that couples good robustness with high reproducibility, cost-effectiveness and large-scale production is still object of research.

Here, we demonstrate the efficiency of a rapid high-temperature aerosol synthesis technique (flame spray pyrolysis, FSP [3]) for the facile and scalable fabrication of an inexpensive resonant metasurface made of aperiodic monocrystalline Au nanoislands (Figure 1a-c) in timeframes of seconds[4]. Importantly, the morphology and disorder level can be promptly tuned and hence a good control on the plasmonic properties is achievable. Molecular dynamics simulations have been performed to investigate the driving mechanism that led to the formation of disconnected nanoislands instead of a uniform thin film, and it has been found that a coalescence process drives the synthesis. Additionally, we have exploited

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these random metasurfaces toward the room temperature detection of VOCs, achieving the detection of refractive index changes as low as 10^{-5} [5].

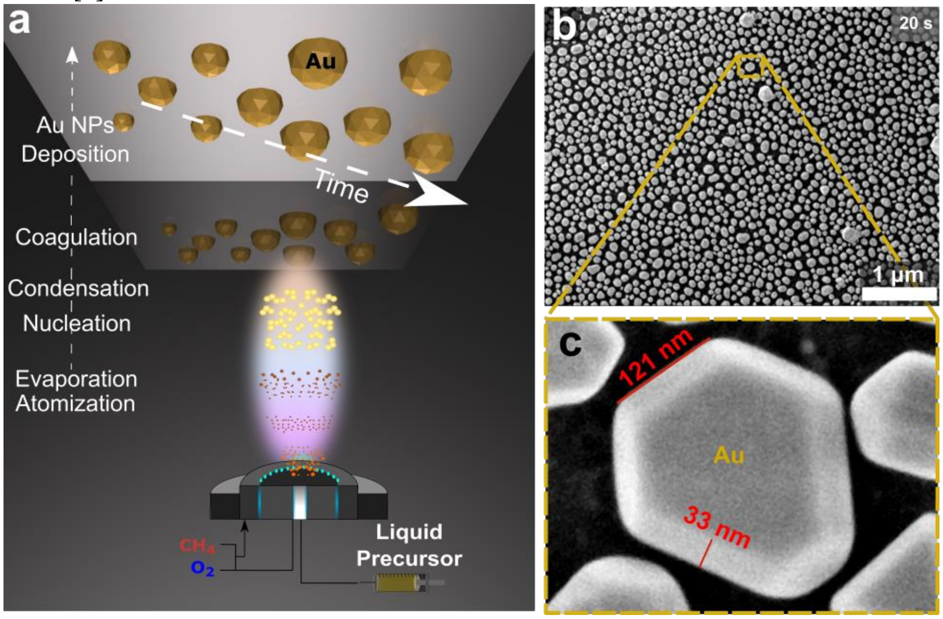

Figure 1: a, Schematic representation of the high-temperature aerosol setup and phenomenon during the Au deposition processes. b, Exemplary top-view scanning electron microscope (SEM) image of the Au NIs film, showing high uniformity on large scale. c, zoom into a single crystal, faceted Au nanoisland. Published in Ref 5.

In order to improve the performances, we then integrated an ultra-porous fractal layer on TiO_2 nanoparticles, deposited by using the same aerosol FSP technique, onto more regular plasmonic metasurfaces made by hole mask colloidal lithography, as shown in Figure 2a,c [6]. The intrinsic deposition properties of the FSP in the diffusion regime, lead to the self-assembly of the TiO_2 nanoparticles in a fractal morphology, showing an ultra-porous network with hierarchical pore size distribution and feature repeating at different magnifications.

Gas sensing performances have been investigated as a function of the fractal layer thickness and we demonstrated the excellent sensitivity toward the room temperature detection of different volatile organic compounds, measuring refractive index changes as low as $<8x10^{-6}$ at room temperature (Figure 2d-f). The synergistic interplay between the tailored TiO_2 fractals and the plasmonic metasurfaces has been studied with electrodynamic simulations and shows a drastic Enhancement of the interaction between the plasmonic field and the volatile organic molecules. Additionally, we exploited the VOCs condensation onto the high-surface area fractals to selectively discriminate the different gases. In fact, for any given VOCs the vapor pressure, which is directly correlated to the condensation rate, is a function of the temperature and the higher the concentration the higher is its vapor pressure. Indeed, by little increases of the temperature, is possible to reduce the amount of condensed VOCs, which in turn leads to a smaller plasmonic shift and providing a platform for the selective detection of gaseous molecules.

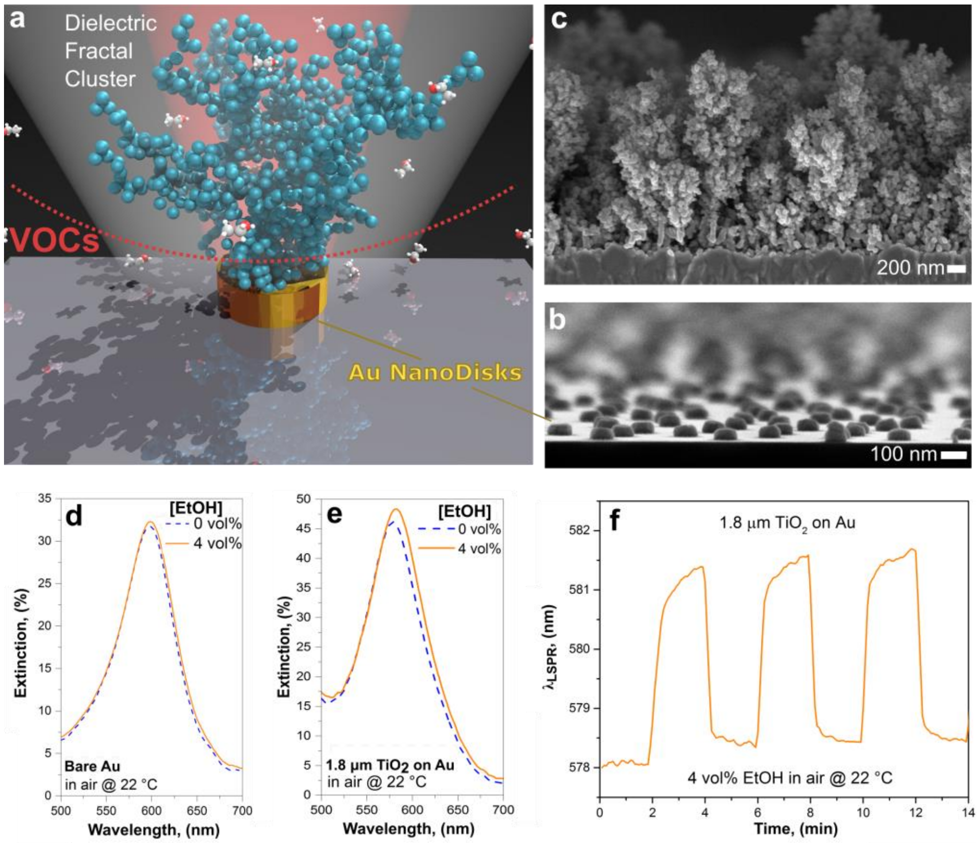

Figure 2: a, Three-dimensional rendering of the fractal TiO_2-Au nanodisks layout (not in scale). b-c, Cross-section SEM images of the Au nanodisks metasurface and the ultraporous TiO_2 dielectric fractals, respectively. d,e, Extinction measurement in a 0% and 4% air-ethanol mixture for the bare Au substrate and the one with the integrated TiO_2, respectively. f, Dynamic responses of the same sample to different cycles of air/ethanol. Published in Ref 6.

2. CONCLUSIONS

We have synthesized tunable and plasmonic hybrid novel nanostructured material, comprising of resonant metasurfaces and tailored dielectric fractals, for enhancing the interaction of the plasmonic field with a gaseous environment. These findings could pave the way toward a new class of contactless optical sensors with applications ranging from non-invasive diagnostic to pollution monitoring and safety.

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