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Plasmonic and 2D-TMD nanoarrays for large-scale photon harvesting and enhanced molecular photo-bleaching

Giulio Ferrando[1], *Matteo* Gardella[1],*Matteo* Barelli[1], *Debasree* Chowdhury[1], *Pham Duy* Long[2], *Nguyen Si* Hieu[2], *Maria Caterina* Giordano[1] *and Francesco* Buatier de Mongeot[1,*]

[1]Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, I-16146 Genova, Italy

[2]Institute of Materials Science, Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

Header The urgent environmental and energy challenges require novel solutions for efficient light harvesting and conversion in new-generation ultra-thin devices. Plasmonic nanoantennas and flat optics nanogratings can promote light matter interaction at the nanoscale being very attractive for ultra-thin photonics and sensing applications. In this work we developed two light trapping solutions based on large-scale nanomaterials. The first system is a large-scale (cm^2) plasmonic metasurface based on self-organized gold nanostripes. The second is based on the periodic re-shaping of ultra-thin semiconducting MoS_2 layers forming large-area flat-optics nanogratings. Under this condition Rayleigh Anomalies can be resonantly excited thus promoting in-plane light confinement and photon absorption into the few-layers material. To demonstrate the impact of these nanopatterned systems in photon harvesting we probed their efficiency into a prototypal photochemical reaction: the photo-bleaching of Methylene Blue (MB). We demonstrate the resonant enhancement of the photo-bleaching of these polluting dye molecules promoted either by the localized plasmon resonance in Au nanostripes or by the Rayleigh Anomaly in flat-optics MoS2 nanogratings. We investigate this effect through a quantitative analysis of the solution photodissociation induced by a monochromatic light. These results show the strong potential of flat-optics templates for light-harvesting and energy conversion in ultra-thin photonic devices.

ABSTRACT

Light harvesting platforms are crucial in the development of novel solution for energy and environmental applications. An emerging class of materials that is particularly interesting are the Transition Metal Dichalcogenides (TMDs). In fact, when confined in a 2D regime, they present a semiconducting behavior [1] characterized by tunable optoelectronic properties. Nevertheless, a big issue deals with the poor photon absorption of these ultra-thin layers, limited to about 10% in the few-layer regime. In parallel conventional light trapping solutions adopted in thick semiconducting devices are not viable. To address these issues nanophotonic systems such as plasmonic nanoantennas and/or flat-optics gratings are very attractive [2,3]. The latter can be interesting itself, because it enables to strongly confine the incident light in a subwavelength volume enhancing light scattering and absorption cross sections. These properties are gaining an increasing interest for their application in photochemical processes [4] with a promising implementation in waste water treatment and energy storage (exploiting a water splitting process).
However, for this kind of applications is crucial to develop fabrication techniques that are usable over large-areas. To overcome these constraints we developed a self-organized method [5] capable to fabricate (cm^2, scalable to m^2) glass nanorippled templates that can substain the growth of laterally separated gold nanowires. Thus by means of this type of substrates it was possible to obtain a system that shows a Localized Surface Plasmon Resonance (LSPR).
In order to demonstrate the effectiveness of the sample functionalization induced by his surface nanostructuration we employed that kind of sample in a photochemical reaction: the photobleaching of the Methylene Blue (MB). In particular we investigate [6] this effect through a quantitative analysis of the photodissociation of the solution performed using the illumination set-up reported in figure 1.

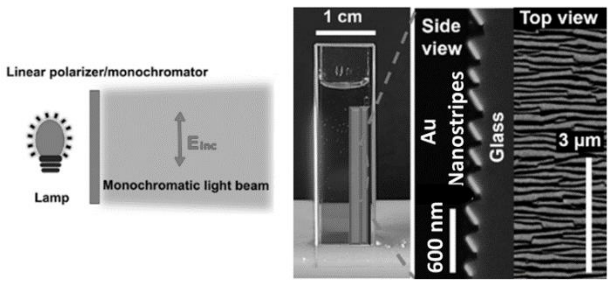

Figure 1 We show a cross-section sketch of the experimental setup. In the right part of the figure, we report a photograph of the sample inside a cuvette containing the MB solution and two SEM images. The two SEM images are the side view and the top view of the sample, with the proper dimensions.

Specifically, using a monochromatized and polarized illumination, we observed a higher MB's photodissociation rate at the wavelength at which the LSPR is tuned in resonance with the MB's maximum optical absorption. That kind of observation is crucial to

* Corresponding author: buatier@fisica.unige.it t

demonstrate the active role of the plasmonic resonance in the photodissociation process and to optimize the fabrication of the plasmonic substrate for the photodissociation of colored dye molecules. Therefore, these findings underline the potential of nanophotonics solutions in environmental applications such as waste water treatment.

Into a second experiment we develop a photon harvesting strategy that can be applied directly into 2D Transition Metal Dichalcogenides (TMDs) materials, such as MoS_2. For this type of materials, we explored a different approach based on a "flat optics" solution that is particularly interesting as it allows to make the material the active element for light trapping [7-9]. Specifically, we used a custom Laser Interference Lithography (LIL) method to nanostructure periodically a large-area surface. On his top we conformally deposited an ultra-thin film of MoS_2 enabling a film re-shaping.

Under this condition Rayleigh Anomalies can be observed and they promote in-plane light confinement and photon absorption into ultra-thin MoS_2 film. In order to demonstrate the potential of this solution we used that kind of samples in the photo-bleaching of the MB using the set-up reported in figure 1. We observed a strong enhancement of the MB photodegradation for the wavelength at which the Rayleigh Anomaly condition is satisfied, thus demonstrating the effectiveness of the light trapping solution.

Thus, both the light trapping solution shows a great potential in environmental application such as the waste water treatment. In addition, using the described illumination system it was possible to have wavelength resolved information of the photobleaching process paving the way for an improvement of the samples. Furthermore, the properties of the analysed samples are not limited to photochemical applications but can find a wide use in other fields such as solar harvesting and sensor application.

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