ACADEMIA | Letters

ENHANCED PLASMONIC PROPERTIES OF METAL NANOPARTICLES/WS2 HYBRIDS

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INTRODUCTION

Two-dimensional transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), have attracted a growing interest due to their atomically thin layered structures with unique electrical, optical, plasmonic, electrochemical, and electrocatalytic properties. In a WS_2 monolayer with hexagonal configuration, each W atom is anchored by three pairs of S atoms forming alternating corners (S–W–S) in a honeycomb network, which might be considered as a graphene-like material [1]. Furthermore, WS_2 is a semiconductor with an indirect bandgap in its bulk form (1 eV) and a direct bandgap in its monolayer phase (2 eV) [2] opening new opportunities in optoelectronics and nanoelectronics.

Integrating WS_2 nanosheets with plasmonic nanoparticles to form hybrid nanostructures has been revealed as a promising strategy to optimize its optical properties thus originating a material with outstanding optical properties. In these hybrid nanosystems, the plasmonic metal part induces a strong plasmonic effect (the interaction between free electrons in metal nanoparticles and incident light) that improves some features such as enhanced light absorption, enhanced photogeneration rate, plasmon-induced "hot carriers" and improved conductivity, so that they can be successfully exploited in various applications, such as photoluminescence spectroscopy (PL), SERS, and SPR sensors, in optoelectronic devices (as for example photodetector or solar cells) or plasmon-enhanced catalysis [3, 4]. In this work the

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applications of WS_2 nanomaterials decorated with metal nanoparticles with plasmon enhance properties are reviewed.

PLASMON ENHANCED OPTICAL SIGNALS

Spr sensing

Thanks to their unique advantages such as label-free and real-time detection, during the last decades biosensors based on surface plasmon resonance (SPR), have attracted great interest [5]. The surface plasmons (SPs) are waves of electron density that propagating at the interface between dielectric and metal that can be excited by the light wave. To excite SP waves (SPWs), the incident photons or electrons should oscillate with the free electrons on the metal surface to form the resonances. When the wavevector of incident light along the interface matches the wavevector of SPWs that stays confined at the interface and downfalls exponentially in a transverse way, a resonated excitement of the electron occurs and is accompanied by a sharp dip of reflectance. The angle at which the reflectance spectrum shows a dip in the resonance shrinking curve is known as the SPR angle (SPR) [6, 7, 8].

An SPR sensor configuration based on the Kretschmann attenuated total reflection (ATR) [9] exploiting a silicon nanosheet and two-dimensional transition metal dichalcogenides has been designed in the work of Ouyang [10]. A gold thin film is deposited onto the bottom of a SF10 prism, and coated with a silicon nanosheet and 2DMX_2 film (MoS_2/$MoSe_2$/WS_2/WSe_2), obtaining four different configurations. The 2DMX2 final layers consists of the sensing medium and biomolecular analytes.

The results demonstrated that 2DMX_2 layer affects the SPR sensor performances in two ways. Firstly, due to the high charge transfer efficiency: under resonance conditions, the electrons can be transferred from the surface of the MX_2 layers to the gold surface. Secondly, it acts as sensing platform to capture the biomolecules through the Van der Waals interactions. The thickness of gold film, silicon nanosheet and MX_2 layers has been optimized in order to obtain the best SPR enhanced performances achieving a sensitivity of 155,68°/RIU using a 35 nm gold layer, a 7 nm thick silicon nanosheet and a WS_2 monolayer by employing 600 nm excitation light wavelength.

In the work of Luo [11], the metal film of the SPR sensor has been modified with an overlayer of WS_2 nanosheets. A thin layer of chromium and a gold film were successively deposited onto the surface of a cleaned glass slide, where chromium enhanced the adhesion force between the gold film and the glass slide. After ultrasonication, a suspension of WS_2 nanosheets in ethanol was dropped directly onto the slides, thus modifying the Au film. WS_2

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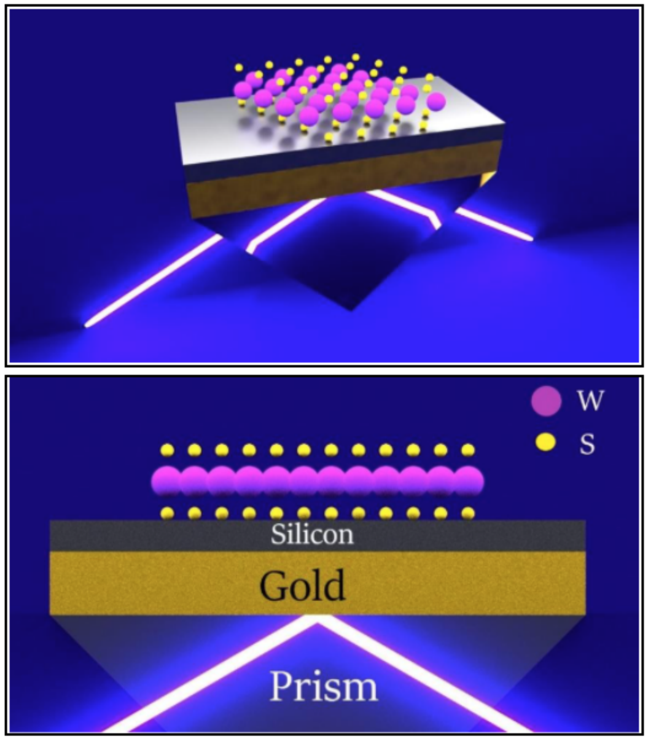

Fig. 1: Schematics of the SPR sensor configuration developed by Ouyang [10].

nanosheets greatly enhanced the sensing sensitivity. Tailoring the WS_2 nanosheets thickness overlayer by using WS_2 ethanol suspensions at different concentrations or by the number of repeated processes of post coating, a sensitivity of 2459.3 nm⁄RIU) has been achieved. The WS_2 modified SPR sensor showed a considerable potential in biochemical detection, exploiting additional advantages such as protection from oxidation and tunability of the resonance wavelength region.

The performances of a new SPR sensor based on different 2D materials such as MoS_2, graphene and WS_2 have been theoretically investigated and compared among them [12] and with the results obtained in other works [10, 13]. The SPR sensor has been developed by depositing a layer of ZnO onto the surface of a BK-7 prism, followed by the coating with a silver layer. A layer of BaTiO3 is taken above the Ag layer. On the top of BaTiO3, a layer of graphene, MoS_2 and WS_2 has been deposited separately thus creating three different sensing configurations. The results showed that the SPR sensor with a monolayer of WS_2 has higher sensitivity (180°/RIU) compared to MoS_2 (174°/RIU) and graphene (157°/RIU) monolayer.

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Sers

Surface-enhanced Raman scattering (SERS) has emerged as a powerful technique for non-invasive, rapid and reliable sensing of chemicals and biomolecules. Graphene and its derivative such as graphene oxide (GO) or reduced graphene oxide (r-GO) have emerged as material for SERS substrates. Firstly, its unique structure its favourable for interactions with analytes via π–π stacking and hydrophobic interactions, and secondly, it has been showed that contributed to SERS signal enhancement with a magnitude depending on the degree of GO chemical reduction [14]. Much efforts have been made to create hybrids of plasmonic nanoparticles and graphene derivatives to improve the SERS analysis [15, 16]. After graphene and its derivatives, SERS substrates based on TMD, such as WS_2, started to be developed obtaining successful results. Sow explored the feasibility of WS_2 monoflakes decorated with gold nanoparticles (AuNPs) as substrate for SERS [17]. The so created AuNPs/WS_2 nanohybrid has been tested to detect R6G molecules obtaining a SERS signal enhancement.

An approach to exploit the unique properties of a nanohybrid formed by AuNPs deposited onto exfoliated nanosheets WS_2 was presented in the work of Sabherwal [18] for the label-free detection of Myoglobin, a cardiac biomarker. The Au NPs/WS_2 nanohybrid has been prepared by the in-situ reduction of gold salt precursor, and then the surface was functionalized with specific aptamers to impart high selectivity towards Myoglobin. The prepared nanohybrid was tested for SERS detection. The Au NPs/WS_2 nanohybrid system allowed the Myoglobin detection with a LOD of 10-2 pg mL-1.

Jiang [19] designed a remarkable SERS platform based on AuNPs/WS_2@AuNPs nanohybrids. Firstly, annealing an Au film deposited onto a SiO_2 substrate, a layer of Au NPs has been created. Successively, by means of a thermal decomposition process, a bilayer WS_2 film has been grown onto the AuNPs surface, and finally, the second layer of AuNPs was deposited onto the WS_2 film by means of a further annealing process, thus obtaining the AuNPs/WS_2@AuNPs nanohybrids. Introducing the bilayer WS_2 film as a nanospacer between the two layers of plasmonic structures, a highly enhanced local electromagnetic field has been generated. Using Rhodamine 6G (R6G) as a probe molecule to test the performance in SERS analysis, the AuNPs/WS_2@AuNPs nanohybrids showed an excellent sensitivity with the minimum detectable concentration of 10-11 M.

Photoluminescence (PL)

The effect of the Au nanoparticles hybridization with WS_2 nanosheets on the optical properties of WS_2 nanosheets was investigated by Sow [17]. After the decoration of triangular-shaped and star-shaped WS_2 flakes with Au nanoparticles, the effects on the fluorescence properties

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have been investigated under imaging of fluorescence microscopy (FM) and photoluminescence (PL) spectroscopy. As a result of decoration, a slight enhancement in fluorescent intensity is observed for the WS_2 edge of the monoflakes, already emitting bright fluorescence light. In addition, in the inner region of the monoflakes, there are dark areas that produce fluorescence emission as a result of decoration with AuNPs, and this newly activated fluorescence area followed the general shape of the WS_2 monoflake, namely a star or triangular pattern. Comparing the PL spectra obtained before and after AuNPs decoration, the PL peak is sharpened as a result of the plasmonic effect combined with the electrostatic screening reduction.

PLASMON-ENHANCED OPTOELECTRONIC DEVICES

subsection*Photodetectors

During last years, TMDs have made significant steps forwards in photodetection due to their favourable band gaps and light matter interaction compared to of graphene. In the work of Liu [20] a photodetector has been developed hybridizing a WS_2 monolayer with AuNPs. The WS_2 film has been grown directly onto sapphire substrate by chemical vapor deposition (CVD) process and then transferred onto a Si/SiO_2 substrate. By means of lithography, sputtering and lift-off process the molybdenum (Mo) source/drain electrodes have been defined. Finally, the WS_2 layer has been decorated with AuNPs, reaching a responsivity of 1050 A/W at the wavelength of 590 nm. The enhanced responsivity has been related to the plasmonic effect of the metal nanoparticles. In addition, the photodetector exhibited an excellent temperature stability after annealing at 300 °C on air environment.

SUMMARY

In this work, the state-of-the-art of devices based on plasmonic metal nanoparticles hybridized with WS_2 nanosheets has been reviewed. The physical phenomena behind the light-matter interactions such as carrier generation in photodetector devices or changes in exciton dynamics in photoluminescence (PL) have been discussed, nevertheless the application of devices based on WS_2 nanosheets hybridized with plasmonic metal nanoparticles is still in an early stage thus revealing a great potential in a broad range of applications. For example, it is provided a new way to develop a high-performance photodetector stable in harsh environment or improved SPR sensor for clinical diagnosis.

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SPR SENSING		
SENSOR CONFIGURATION	SENSITIVITY	REFERENCE
SF10 prism / Gold / Silicon / WS_2	155,68°/RIU	[5]
Prism / Glass slide / Chromium / Gold / WS_2	2459.3 nm/RIU	[6]
BK-7 prism / ZnO / Ag / BaTiO3 / WS_2	180°/RIU	[7]
BK-7 prism / ZnO / Ag / BaTiO3 / MoS_2	174°/RIU	
BK-7 prism / ZnO / Ag / BaTiO3 / Graphene	157°/RIU	
SERS SENSING		
SENSOR CONFIGURATION	Limit Of Detection (LOD)	REFERENCE
Si Substrate / Au / WS2 nanohybrids decorated with Anti-Mb DNA aptamer	10^{-2} pg mL^{-1}	[13]
SiO2 substrate / Au nanoparticles / WS_2 monolayer / Au nanoparticles	10^{-11} M	[14]
PHOTODETECTOR		
MATERIAL	RESPONSIVITY	REFERENCE
Si / SiO2 substrate / WS_2 monolayer / Au NPs	1050 A / W	[17]
PHOTOLUMINESCENCE (PL)		
EFFECTS OF WS2 DECORATION		REFERENCE
Sharpened PL peak, Dark areas in pristine flakes became fluorescence active, Fluorescence intensity higher.		[12]

Tab. 1: Summary and comparison of the systems based on 2D WS2 and plasmonic material reviewed.

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