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Two-dimensional molybdenum disulfide (MoS_2) with gold nanoparticles for biosensing of explosives by optical spectroscopy

Jiajia Wu[a], Yanli Lu[a], Zhiqian Wu[b], Shuang Li[a], Qian Zhang[a], Zetao Chen[a], Jing Jiang[c], Shisheng Lin[b], Long Zhu[d], Candong Li[d], Qingjun Liu[a,*]

[a] Biosensor National Special Laboratory, Key Laboratory for Biomedical Engineering of Education Ministry, Department of Biomedical Engineering, Zhejiang University, Hangzhou, 310027, PR China
[b] State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, Hangzhou 310027, PR China
[c] Micro and Nanotechnology Lab, University of Illinois at Urbana-Champaign, IL, 61801 USA
[d] Collaborative Innovation Center of TCM Health Management, Fujian University of Traditional Chinese Medicine, Fuzhou, 350122, PR China

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ABSTRACT

As one of the most important transition-metal dichalcogenides (TMDs) materials, molybdenum disulfide (MoS_2) has gained extensive attention for its marvelous optoelectronic properties. In this study, nanocomposites of two-dimensional (2D) molybdenum disulfide (MoS_2) with plasmonic noble metal nanoparticles were synthesized by a one-step green process. Under irradiation, 2D MoS_2 in the nanocomposites absorbed photons and generated carriers in a wide spectrum. Then MoS_2 coupled to gold nanoparticles and produced the enhanced electromagnetic field in the nanosturctures, leading to outstanding optical properties. In virtue of bio-compatibilities of the particles, the nanocomposites were chemically modified with specific peptides to construct an optical biosensor for explosive detection. When exposed to 2,4,6-trinitrotoluene (TNT), the biosensor showed significant absorption peak changes in visible spectra with a concentration-dependent behavior. The biosensor could detect TNT at the concentration as low as 2×10^{-7} M. For selectivity, the biosensor could differentiate TNT from other nitroaromatic explosives that have extremely similar structures to TNT, such as 4-nitrotoluene (4-NT) and 2,6-dinitrotoluene (DNT). All the results suggested that the biosensor based on the nanocomposites of 2D MoS_2 coupling to plasmonic nanoparticles exhibited remarkable optical performance, which provided a promising approach to design versatile biosensors to detect biochemical molecules.

1. Introduction

Two-dimensional (2D) materials are an emerging and important class of materials, and have unique physical and chemical properties that drastically differ from their bulk counterparts [1–5]. Many kinds of 2D materials, such as graphene, hexagonal boron nitride, and layered transition metal dichalcogenides (TMDs), have been extensively studied [1,6–9]. In particular, 2D molybdenum disulfide (MoS_2), as one of prototypical layered TMDs, has drew significant attention, due to its extraordinary catalytic, optical, mechanical, and electronic properties [10,11]. The bandgap of MoS_2 ranges from 1.3 to 1.8 eV and exhibits an indirect to direct transition from bulk to monolayer, making them extremely suitable for light absorbents in a wide spectrum [12,13]. However, the light absorption of 2D MoS_2 is considerably weak compared to bulk materials, resulting in limited light-harvest ability [14]. Moreover, without any active group, the pristine 2D MoS_2 sheets are generally difficult to be chemically modified with bio-components to design biosensors [15]. Therefore, efficient utilizations of MoS_2 are still far from the practical optical devices for biosensing. To solve this problem, various strategies have been developed to integrate 2D materials with plasmonic nanomaterials [16–18]. Among those approaches, integration of noble metal nanoparticles with MoS_2 to form hybrid nanostructures of plasmonic metal and 2D MoS_2 has drew extensive attention [19–21].

Owing to unusual chemical and physical properties, especially bio-compatibilities and optical features, noble metal nanoparticles have been widely applied in biosensing systems [22,23]. When combining the nanoparticles with 2D MoS_2 sheets, the plasmonic-electrical effect, including the plasmon-induced "hot electrons", could play a significant role in enhancing optical properties of optic devices [24]. Moreover, the combination of the individual

* Corresponding author.
E-mail address: qjliu@zju.edu.cn (Q. Liu).

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properties, that derived from the noble metal particles and MoS_2 also could provide a multifunctional nanoplatform for various applications [25–27]. Therefore, the nanocomposits of noble metal particles and 2D MoS_2 could take advantages of each nanomaterial to present outstanding optical properties for biosensing.

Several approaches have been proposed to combine MoS_2 with metal nanoparticles. Typically, it was done by either simply mixing the individual constituents, or adding MoS_2 sheets among the metal precursors and reducing agents, to generate nanoparticles on the sheets [28,29]. However, these means often could not achieve chemical bonding or would induce extra reagents in the experiments. Actually, chemically exfoliated MoS_2 sheets have great redox behavior, which could directly reduce metal precursors to allow a very straightforward synthesis of metal-decorated 2D materials sheets, as a green process [30,31].

After integrating MoS_2 with noble metal nanoparticles, the nanocomposites could assemble with a wide variety of biorecognition components, such as nucleic acids, proteins, cells and tissues, through bio-friendly nanoparticles [32–36]. As specific amino acid sequences extracted from proteins, peptides exhibited excellent abilities in biosensing [37,38]. They were easy to be prepared according to standard synthetic protocols. Meanwhile, peptides had great chemical and conformational stability, so they could be preserved for a long time and applied in harsh conditions [39]. In addition, the peptide sequences could be specially designed to bond with different nanomaterials, which made them obtain growing concerns as bio-sensitive elements. For example, explosive-specific peptides have been found and reveal great performance in binding to explosives which are a thorny problem for public security and the environment [40,41]. Meanwhile, explosives are not only an enormous threat for public security, but also major environmental contaminants during the production of shells, bombs and grenades. Obviously, it is of great significance to detect explosives effectively. Therefore, specific peptides can be chosen to assemble with nanocomposites to fabricate biosensors for explosive detection.

In this study, nanocomposites of gold nanoparticles and 2D MoS_2 sheets (AuNPs@MoS_2) were synthesized by a one-step green approach. Theoretical analyses were carried out to confirm the enhanced plasmonic resonance of the nanocomposites. Then the explosive-specific peptides self-assembled on the nanocomposites through Au-S covalent bonds. Thus, a label-free optical biosensor for detection of explosives, such as 2,4,6-trinitrotoluene (TNT), was constructed as a proof-of-concept application. By optical absorption spectra, the biosensor verified the plasmonic resonance of the nanocomposites.

2. Materials and methods

2.1. Synthesis of the AuNPs@MoS_2

To chemically combine MoS_2 and gold nanoparticles, the synthesis was carried out by one-step conjugation in aqueous solvents without any reducing reagent [42]. Then the specific peptides self-assembled on the nanocomposites to form the biosensor for explosive detection. Fig. 1 depicted the overview of the processes to synthesize the nanocomposites and construct the biosensor for TNT detection in this study.

Pristine MoS_2 was composed of covalently bonded S-Mo-S sheets that were bound by weak wan der Waals forces (Fig. 1a). In the synthesis process, 60 mL MoS_2 aqueous dispersion (0.1 mg/mL) from the intercalation-exfoliation was sonicated for 2 h, then was added into a 100 mL Erlenmeyer flask. While the MoS_2 aqueous dispersion under vigorous stirring, Gold (III) tetrachloride trihydrate ($HAuCl_4{\cdot}3H_2O$) was added to it until the concentration of $HAuCl_4$ became 0.01%. After stirring for 10 min under room temperature (~22 °C), the reaction mixture was heated to 60 °C for 5 min. Finally, the nanocomposites of MoS_2 with gold nanoparticles (AuNPs@MoS_2) was purified by centrifugation and stored at 4 °C in an opaque glass container for the sensing studies (Fig. 1b).

For observing the morphology of the nanocomposites, transmission electron microscopy (TEM) images were recorded by JEM-1230 (JEOL, 120 kV). In addition, Raman spectra were performed to further confirm the nanocomposites by Raman spectroscopy (Renishawin ViaReflex) with the excitation wavelength of 532 nm.

At the same time, for comparing the optical performance between AuNPs@MoS_2 and pure gold nanoparticles (AuNPs), AuNPs were prepared based on reduction of $HAuCl_4$ by trisodium citrate ($Na_3C_6H_5O_7$) [43]. Firstly, 10 mL $HAuCl_4$ solution (0.01%) in a 25 mL Erlenmeyer flask was heated to 80 °C, then 185 μL $Na_3C_6H_5O_7$ solution (1%) was added for reduction of the $HAuCl_4$. The heating was kept at 80 °C for 60 min, while the stir was lasted for 75 min. Finally, AuNPs solution was obtained after centrifugation at 3000 r.p.m for 10 min and stored in an opaque glass container at 4 °C for further experiments.

2.2. Theoretical calculations

To clarify the mechanism of interaction between MoS_2 with noble metal nanoparticles, the electric field distribution of the nanocomposites was calculated using the three-dimensional finite-difference time-domain (3D-FDTD) method [44–46].

In this calculation model, two AuNPs with a gap of 2 nm on a MoS_2 sheet in aqueous solution illuminated by a linearly polarized plane wave with an electric field amplitude of 1 V/m. The diameter of the AuNPs, thicknesses of the MoS_2 sheet, and the Yee cell size were 30, 2.5, and $1 \times 1 \times 1$ nm, respectively. Moreover, the refractive indexes of solution and MoS_2 used here were 1.3 and $5.2 + 1.2i$ [47,48]. For comparison, the electric field distribution of pure AuNPs with same parameters was simulated. All the calculations were performed using commercially available Lumerical FDTD Solutions software (Lumerical Solutions, Inc. Vancouver, Canada). The theoretical calculations of the nanocomposites' optical performance were then analyzed with the spectra to guide the design of the biosensor.

2.3. Optical measurements

Visible absorption spectra were performed to characterize the nanocomposites and detected explosives by a spectrophotometer (USB2000+, Ocean Optics Inc, Dunedin, USA) with 0.38 nm optical path.

The spectrophotometer was calibrated with light intensity and other parameters to prevent light saturation, and the reference spectra were recorded before every trial. Then the absorption spectra from 400 nm to 700 nm of those solutions in cuvettes were measured. Finally, the plasmonic peaks of samples were read in the spectra as the statistical data to analyze the results.

2.4. Bio-functionalization of the nanocomposites

To equip the nanocomposites with the ability to detect explosives, peptides were chosen as the bio-recognition components to modify AuNPs@MoS_2. As a typical explosive, TNT was chosen as the targets for explosive detection in this system.

The TNT-specific peptide chain (WHWQRPLMPVSIC) was designed based on reports about TNT-specific amino acids [40,49]. Peptides were synthesized with solid phase peptide synthesis (SPSS) by stepwise addition of protected amino acids to growing peptide chains. The quality of the synthesized peptides was tested by high-performance liquid chromatography (HPLC) and