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2017

Zhang, N. M. Y., Li, K., Zhang, T., Shum, P., Wang, Z., Wang, Z., . . . Wei, L. (2017). Electron-rich two-dimensional molybdenum trioxides for highly integrated plasmonic biosensing. *ACS Photonics*, 5(2), 347-352. doi:10.1021/acsphotonics.7b01207

<https://hdl.handle.net/10356/90115>

<https://doi.org/10.1021/acsphotonics.7b01207>

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Electron-Rich Two-Dimensional Molybdenum Trioxides for Highly Integrated Plasmonic Biosensing

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ABSTRACT: Two-dimensional (2D) plasmonic materials facilitate exceptional light-matter interaction and enable in-situ plasmon resonance tunability. However, surface plasmons of these materials mainly locate intrinsically at long wavelength range that are not accessible for practical applications. To address this fundamental challenge, transition metal oxides with atomically layered structure as well as free carriers doping capability have been considered as an alternative class of 2D plasmonic material for achieving tunable plasmonic properties in visible and near-infrared range. Here, we synthesize few-layer α - MoO_3 nanoflakes that are heavily doped with free electrons via H^+ intercalation. The resultant sub-stoichiometric MoO_{3-x} nanoflakes provide strong plasmon resonance located at ~ 735 nm. Moreover, the MoO_{3-x} nanoflakes carrying positive charges show stable attachment to polyanions functionalized microfiber and good affinity to negatively charged biomolecules. Our experimental demonstration of fiber-optic biosensing platform provides a detection limit of bovine serum albumin as low as 1 pg/mL, and proves the feasibility and prospects of employing 2D MoO_{3-x} plasmonic nanoflakes in highly integrated devices compliant with frequently used and cost-effective optical system.

KEYWORDS: 2D Materials, Transition Metal Oxides, MoO_{3-x} , Surface Plasmons, Biosensing

Tailoring light-matter interaction at the nanoscale is of great importance in diverse disciplines. Amongst various forms of light-matter interaction, surface plasmons conventionally induced by the collective electron oscillations of noble metals have delivered exceptional performance in photovoltaics¹, energy storage and conversion², bioimaging³ and biosensing⁴. With the recent breakthroughs in 2D materials, plasmon-matter interaction can be enhanced by confining surface plasmons to the subwavelength surface vicinity and more importantly, can be tuned optically, electrically and chemically⁵⁻⁸. The *in-situ* tunability of plasmonic properties of 2D materials is realized by altering the free carrier density, which cannot be commonly achieved in metals⁹. Besides the plasmonic tunability, 2D materials also possess considerable surface-to-volume ratio that facilitates efficient immobilization of target molecules thereby providing an enhanced plasmon-matter interaction on sensing platforms¹⁰. However at the current stage, surface plasmons of most 2D materials either locate intrinsically at terahertz or mid-infrared range¹¹ that are not accessible for practical applications where the difficul-

ties of integration, miniaturization, and cost effectiveness of a device have to be taken into account¹², or rely on precisely defined metallic nanostructures to form metal/2D-material hybrid plasmonic architectures that may result in enhanced plasmonic behaviors¹³⁻¹⁷. Therefore, a plasmonic 2D material that is compliant with frequently used visible or near-infrared (NIR) optical systems and compatible with simple fabrication of hybrid architectures is highly demanded. Driven by such purpose, heavily-doped ultrathin transition metal oxides (TMOs) are proposed as an alternative class of 2D plasmonic material^{12,18-20}. As semiconductors, TMOs are benefited from the outer-d valence electrons so as to achieve tunable plasmon resonance by tailoring the ionic intercalation to obtain appreciable free carrier concentrations^{20,21}. A representative TMO, molybdenum trioxide (MoO_3), has recently been proven feasible of forming atomically thin layers with high ionic intercalation capability^{18-20,22}. Advantageously, the highly doped MoO_3 nanoflakes offer a large dielectric constant enabling a plasmon resonance in visible and NIR regions meanwhile delivering quasi-metallic properties^{12,23}. Moreover,

MoO₃ is comprised of earth-abundant elements thereby it can serve as a substitution of high-priced noble metals. Although the surface plasmons of heavily-doped MoO₃ nanoflakes have captured considerable research efforts recently, the feasibility of integrating plasmonic MoO₃ nanoflakes in a sensing carrier as well as its potential for biological detection still remain unexplored. Here, to utilize plasmonic 2D TMOs in sensing applications, we demonstrate a biosensor where heavily-doped MoO₃ nanoflakes with the plasmonic resonance locating in NIR range are integrated with an optical microfiber. Optical fibers are preferable sensing platforms in biological detection owing to their high integration, miniaturization, flexibility and *in-situ* sensing capability^{24,25}. Adopting bovine serum albumin (BSA) as a model analyte, MoO₃ nanoflakes show good affinity to analyte molecules and the demonstrated fiber-based biosensor provides a detection limit as low as 1 pg/mL.

FIG. 1a schematically illustrates our proposed biosensing platform that the surface of microfiber is covered with a

Figure 1. (a) Schematic diagram of fiber-optic biosensor integrated with heavily-doped MoO_{3-x} nanoflakes. Inset 1: Crystal structure of stable orthorhombic α-MoO₃. Inset 2: Molecular structure of BSA protein. (b) Low-magnification TEM of the exfoliated MoO₃ nanoflakes. (c) SAED pattern of MoO₃ nanoflakes. (d) HRTEM of MoO₃ nanoflakes. (e) AFM measurement of MoO₃ nanoflakes. The average thickness of nanoflakes is ~2.8 nm and the lateral dimensions range from tens of nm to ~1 μm.

thin layer of heavily-doped α-MoO₃. The strong evanescent field of microfiber effectively excites the surface plasmons of MoO₃ nano-layer. BSA molecules are then immobilized onto the surface of MoO₃ nanoflakes and interact with surface plasmons leading to the change of transmission spectrum. 2D morphology of α-MoO₃ nanoflakes can be easily synthesized by liquid phase exfoliation (see more details of MoO₃ nanoflakes synthesis in the Methods). Three polymorphs of MoO₃ have been discovered, namely the stable orthorhombic α-MoO₃, the metastable monoclinic β-MoO₃, and the hexagonal h-MoO₃²². α-MoO₃ is particularly suitable for the preparation of 2D morphologies due to its layered crystalized structure. Each two adjacent atomically thin planar units form a double-layer in which distorted MoO₆ octahedra are joined by sharing zigzag edges. The 1.4 nm thin double-layers are held together by the weak van der Waals force²⁶. The morphology of the exfoliated MoO₃ nanoflakes is characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The low-magnification TEM clearly indicates that as-prepared α-MoO₃ samples are flake-like in shape (FIG. 1b). The square array of diffraction dots in the corresponding selected area electron diffraction (SAED) pattern (FIG. 1c) reveals the single crystal nature of orthorhombic α-MoO₃ nanoflake. The lattice fringes of α-MoO₃ nanoflakes can be clearly observed under HRTEM, and the interval between two adjacent fringes is ~2.3 Å, corresponding to the d-spacing of the (2 0 0) plane²⁷ (FIG. 1d). The thicknesses and the lateral dimensions of the MoO₃ nanoflakes are assessed by atomic force microscopy (AFM). It shows that the average nanoflake thickness is ~2.8 nm (FIG. 1e), exactly the thickness of two double-layer planar units.

The doping of free carriers is realized by the H⁺ intercalation process, which induces oxygen vacancies in MoO₃ nanoflakes. Before doping, pristine MoO₃ nanoflakes only absorb ultraviolet wavelengths while barely induce loss to visible and NIR bands (FIG. S1). As we gradually add NaBH₄ to the suspension of pristine MoO₃ nanoflakes, sub-stoichiometric molybdenum trioxide (MoO_{3-x})^{12,28} forms and the color of supernatant evolves from colorless to dark blue (FIG. 2a). The absorption spectra start to show an increment beyond 700 nm which gradually evolves into a distinct absorption peak associated with plasmon resonance (FIG. 2b). Along with the increasing doping extent, the absorption increases steadily and meanwhile, the resonant wavelength undergoes a blue-shift from 767 nm to 738 nm. The blue-shift of wavelength along with the enhancing doping concentration is predictable since the plasma frequency is directly related to the electron density ($\omega_p \propto n^{1/2}$) described by the Drude model²⁹, meaning that the increase of free electron density in sub-stoichiometric MoO_{3-x} leads to the increase of surface plasmon frequency that corresponds to a shorter resonant wavelength. The formation of sub-stoichiometric MoO_{3-x} is further verified by X-ray photoelectron spectroscopy (XPS) measurements shown in FIG. 2c and 2d. Before the H⁺ intercalation, only two binding energy peaks locate at 233.1 eV and 236.2 eV correlated with Mo⁶⁺ 3d_{5/2} and Mo⁶⁺ 3d_{3/2}, respectively (FIG. 2c). After the doping of free

carriers, the lower oxidation state Mo^{5+} with binding energy peaks at 231.9 eV and 235.1 eV, coexists with Mo^{6+} in MoO_{3-x} samples³⁰. Evaluated from the peak areas corresponding to the two oxidation states, Mo^{6+} and Mo^{5+} ions account for 71.7% and 28.3%, respectively (FIG. 2d). The increased free electron density of sub-stoichiometric MoO_{3-x} originates from the two leftover electrons per oxygen vacancy once an oxygen atom is removed from the oxide^{31,32}. These leftover electrons facilitate the collective oscillations at the surface of MoO_{3-x} nanoflakes at the resonant frequency.

Figure 2. (a) Color variations of MoO_3 nanoflakes suspensions along with increasing doping extent. (b) Evolution of absorption spectrum along with increasing doping extent. 2 mL pristine MoO_3 nanoflakes suspensions are added with 50 μL , 60 μL , 70 μL and 80 μL 0.01 M NaBH_4 respectively. (c) XPS analysis of pristine MoO_3 . (d) XPS analysis of highly doped MoO_3 nanoflakes. Mo^{6+} and Mo^{5+} coexist after doping.

The microfiber is fabricated using the heating and pulling method³³. The thinnest part of microfiber has a diameter of 2 μm and a length of 10 mm. To stably immobilize the MoO_{3-x} nanoflakes, we adopt polyelectrolytes to functionalize the fiber surface. Since MoO_{3-x} is positively charged³⁴, it undergoes strong electrostatic attraction to polyanions. Therefore, we functionalize the microfiber with self-assembled poly(allylamine) (PAA)/poly(styrene sulfonate) (PSS) bilayer to introduce evenly distributed negative charges on the outer surface (see more details in the Methods). Then the functionalized microfiber is immersed in 50 μL MoO_{3-x} solution. When monitoring the real-time transmission intensity of microfiber within 745 nm – 755 nm, we observe a sharp drop followed by a gradual eased decline which corresponds to a typical self-assembly process of plasmonic nanomaterials to optical fibers (FIG. S2). The SEM image of the morphology of the immobilized MoO_{3-x} nanoflakes is shown in FIG. S3a. To validate the proposed plasmonic fiber-optic sensor, we apply it to the detection of BSA. BSA is a well-known negatively charged protein so that it can be efficiently adsorbed to MoO_{3-x} nanoflakes surfaces via electrostatic in-

teractions as well as collective van der Waals forces³⁴. To verify the affinity between the negatively charged BSA molecules and the positively charged MoO_{3-x} nanoflakes, we functionalize the MoO_{3-x} coated fibers with different concentrations of cyanine 3 (Cy3) dye labeled BSA molecules and observe them under a fluorescence microscope. FIG. 3a presents the fluorescent microscopic images of four microfibers functionalized with 0, 10 $\mu\text{g/mL}$, 20 $\mu\text{g/mL}$, and 40 $\mu\text{g/mL}$ Cy3-BSA, respectively (see more functionalization details in the Methods). The even brightness along the fiber at each concentration indicates the even distribution of the stably adsorbed Cy3-BSA molecules, which also implies the uniformity of the immobilized MoO_{3-x} nano-layer. As expected, the brightness enhances as the Cy3-BSA concentration increases, indicating the incrementing quantity of adsorbed Cy3-BSA molecules. To investigate the impact of the bonded BSA molecules on the plasmonic behaviors of heavily-doped MoO_{3-x} , we measure the absorption spectra of MoO_{3-x} suspensions mixed with different concentrations of BSA. 1 mL of MoO_{3-x} suspensions is blended with 2 mL of BSA solutions with concentrations of 100 ng/mL, 1 $\mu\text{g/mL}$, and 10 $\mu\text{g/mL}$, respectively. As shown in FIG. 3b, the peak absorption of MoO_{3-x} slightly reduces when adding with relatively small BSA concentration of 100 ng/mL. The plasmonic peak intensity further attenuates as the BSA concentration increases. This is owing to the repulsion between the negatively charged BSA molecules and the free electrons at MoO_{3-x} nanoflakes surface, which reduces the free electron density participated in the plasmonic resonance^{12,20}.

Figure 3. (a) Fluorescent microscopic images of MoO_{3-x} nanoflakes coated fibers that are functionalized with different concentrations of BSA molecules labelled with Cy3 dyes. (b) Absorption spectrum when MoO_{3-x} nanoflakes are mixed with different BSA concentrations. (c) Transmission spectra of the proposed biosensor when detecting incrementing BSA concentrations. (d) Linear response of transmission minimum as a function of BSA concentration in log-scale.

As MoO_{3-x} nanoflakes are bonded to the microfiber surface, a plasmon resonance centered at 735 nm forms on the transmission spectrum (the black curve in FIG. 3c). 100 μL of BSA analyte with concentrations range from 1 $\mu\text{g/mL}$

to 100 ng/mL are sequentially tested using the MoO_{3-x} coated microfiber. The resonance on the transmission spectrum gradually attenuates as the BSA concentration increases. The shallowing of plasmon resonance can be explained by the reduction of free carrier density. An obvious weakening of the plasmon resonance appears when the BSA concentration is as low as 1 pg/mL. Compared with the detection limit of 100 ng/mL obtained from the absorption measurement shown in FIG. 3b, such a low detection limit of the proposed fiber-optic biosensor is benefited from the full utilization of the high aspect ratio of 2D MoO_{3-x} nanoflakes. As the MoO_{3-x} is immobilized by electrostatic attraction, only a nano-scaled layer of nanoflakes can stably attach to the microfiber, and additional layers of MoO_{3-x} with positive charges repel each other which will be washed away. This leads to the fact that the surface of immobilized MoO_{3-x} nanoflakes fully interacts with the BSA molecules and 100 μ L of analyte is a considerably large amount compared with the nano-scale MoO_{3-x}. Therefore, this fiber-based biosensing platform effectively reduces the required amounts of 2D plasmonic material and biological analyte. Furthermore, the transmission minimum corresponding to the peak plasmon resonance increases linearly with the log-scale increment of BSA concentration (FIG. 3d). In addition, the entire microfiber length enables a long interaction path between the bio-liquid sample and the light, which helps to extend the active sensing area intensely. The biosensing performance can be further improved by employing nanofibers and optical fiber nanowires of which the subwavelength diameters effectively strengthen the evanescent field^{35,36}. Also, longer interaction length along the fiber longitude can further promote the light-matter interaction³⁷. Microstructured optical fibers (MOFs) such as suspended core fiber³⁸ and side-channel photonic crystal fiber³⁹ provide evanescent fields as strong as microfibers and the interaction between the evanescent field and the analyte filled in cladding holes can extend along the entire fiber length. By the precise design of MOF cladding holes arrangement, a narrower resonance spectral width and a better SNR can be achieved⁴⁰.

The plasmonic property of a semiconductor abundant with free electrons can be described by the Drude model¹⁹, where the complex dielectric function is defined as:

$$\varepsilon(\omega) = \varepsilon' + i\varepsilon'' = \varepsilon_b - \frac{\omega_p^2}{(\omega^2 + \gamma^2)} + i \frac{\omega_p^2 \gamma}{(\omega^2 + \gamma^2)\omega} \quad (1)$$

here ε_b denotes the background permittivity which is the polarization response from the core electrons. ω_p is the bulk plasma oscillation frequency associated with free carriers, and γ is the collision frequency that numerically equals to the linewidth of the plasmon resonance band⁴¹. The plasmon resonance frequency is determined by:

$$\omega_{sp} = \sqrt{\frac{\omega_p^2}{1 + 2\varepsilon_m} - \gamma^2} \quad (2)$$

where ε_m represents the dielectric constant of the ambient medium. Based on the plasmon resonance band shown in FIG. 3c (the black curve in FIG. 3c), we are able to deduce the values of parameters of Equation (1) and (2) summarized in Table 1 (See detailed deduction of the in S₃ of

supporting information). The deduced parameters in Table 1 are their average values since there is size distribution of MoO_{3-x} nanoflakes.

Table 1. Drude Model Parameters of MoO_{3-x}

ω_{sp} (eV)	γ (eV)	ε_m	ω_p (eV)	ε_b
1.687	0.416	1.333	3.327	3.520

Based on the Drude model parameters in Table 1, we carry out eigenmode analysis to simulate the electromagnetic field distribution of MoO_{3-x} nanoflakes coated microfiber. In the simulation, the fiber diameter is constructed to be 2 μ m which exactly equals to that of the microfiber in our experiment. The thickness of MoO_{3-x} nano-layer surrounding the microfiber is set to be 5.6 nm, which is the thickness of two stacked layers of MoO_{3-x} nanoflakes. We calculate the plasmon resonance band as plotted in FIG. 4a and it matches well with the experimental spectrum. The inset of FIG. 4a presents the core mode profile of the MoO_{3-x} coated microfiber. The evanescent field distributed in the vicinity of MoO_{3-x} nano-layer surface can be clearly observed. The electric field distribution of the entire core mode profile is shown in the inset of FIG. 4a, while FIG. 4b plots the magnified electric field distribution in the vicinity of MoO_{3-x} nano-layer. MoO_{3-x} nano-layer strongly absorbs and confines the electric field of the guided mode in fiber, which gives rise to the attenuation band in transmission spectrum.

Figure 4. (a) Simulated plasmon resonance band with the deduced Drude model of MoO_{3-x}. Inset: Core mode profile of MoO_{3-x} nano-layer coated microfiber. (b) Simulated electric field distribution near the MoO_{3-x} nanolayer. Inset: Electric field distribution over the whole fiber diameter.

In conclusion, electron-rich MoO_{3-x} nanoflakes enrich the plasmonic window of 2D materials in NIR range, which enables vast practical applications of 2D plasmonic materials associated with well-developed optical systems (e.g. telecommunication optical fibers). We experimentally demonstrated that when integrated with microfiber, small amount of MoO_{3-x} nanoflakes would induce strong plasmon resonance and provide a promising detection of protein molecules. The quasi-metallic properties of MoO_{3-x} can be depicted by the Drude model. The repulsive interaction between negatively charged biomolecules and free electrons at MoO_{3-x} nanoflakes surface also inspires us that the thickness of adsorbed molecular monolayer is detectable for the molecules of which the net charge is related to molecular length such as nucleic acids. It could be a complement to the nanometer-thick molecular monolayer

sensing previously realized by noble metal nanoclusters⁴². Therefore, employing TMOs as an alternative class of 2D plasmonic materials shows unprecedented potentials in highly sensitive and integrated plasmonic devices and paves the way for molecule identification.

METHODS

Synthesis of MoO_{3-x} Nanoflakes: 0.4 g α -MoO₃ (Alfa Aesar) powder is ground for 1 hour and then dissolved in 50 mL solution of ethanol/DI water (1:1, v/v). After 2 hours of sonication, the solution undergoes 20 min centrifugation with 10000 rpm. 15 mL of lucid supernatant with MoO₃ nanoflakes evenly dispersed is then collected. After adding with 600 μ L 0.01 M NaBH₄ (Alfa Aesar), the color of supernatant turns into dark blue.

Microfiber Surface Functionalization: A microfiber with a diameter of 2 μ m is tapered from a standard single-mode silica fiber. We immobilize the microfiber in a flow chamber and fill up the chamber with DI water. Then we flow 100 μ L 1 M NaOH (Alfa Aesar) solution into the chamber and monitor the real-time transmission intensity of the microfiber. The transmission intensity stabilizes in about 10 min. Then the microfiber as well as the chamber are rinsed with DI water for 5 times. 100 μ L 0.05 wt% positively charged PAA (Sigma-Aldrich) is then flowed into the chamber and stagnated for 20 min, meanwhile the real-time transmission of microfiber tends to steady intensity. After 5 times rinsing with DI water, 100 μ L 0.05 wt% PSS (Sigma-Aldrich) carried with negative charges is flowed into the chamber and stagnated for 20 min. Again, the microfiber is rinsed with DI water for 5 times to wash away redundant PSS. Now the microfiber is functionalized with evenly distributed negative charges.

Cy3-BSA Immobilization on Microfiber: Four microfibers with diameters of $\sim$ 10 μ m are prepared and immobilized with a nano-layer of MoO_{3-x} using the abovementioned functionalization process. Then the four microfibers are respectively immersed in 100 μ L Cy3-BSA (Nanocs Inc.) solutions with concentrations of 0, 10 μ g/mL, 20 μ g/mL, and 40 μ g/mL for 20 min. The four microfibers are then rinsed with DI water to wash away non-adsorbed Cy3-BSA molecules.

ASSOCIATED CONTENT

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Absorbance Characterization; MoO_{3-x} Nanoflakes Immobilization; Numerical Analysis

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported in part by the Singapore Ministry of Education Academic Research Fund Tier 2 (MOE2015-T2-1-o66 and MOE2015-T2-2-o10), Singapore Ministry of Education

Academic Research Fund Tier 1 (RG85/16), and Nanyang Technological University (Start-up grant M4081515; Lei Wei).

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