Review article

Michele Cotrufo, Liuyang Sun, Junho Choi, Andrea Alù* and Xiaoqin Li*

# Enhancing functionalities of atomically thin semiconductors with plasmonic nanostructures

https://doi.org/10.1515/nanoph-2018-0185
Received October 31, 2018; revised February 19, 2019; accepted February 22, 2019

**Abstract:** Atomically thin, two-dimensional, transition-metal dichalcogenide (TMD) monolayers have recently emerged as a versatile platform for optoelectronics. Their appeal stems from a tunable direct bandgap in the visible and near-infrared regions, the ability to enable strong coupling to light, and the unique opportunity to address the valley degree of freedom over atomically thin layers. Additionally, monolayer TMDs can host defect-bound localized excitons that behave as single-photon emitters, opening exciting avenues for highly integrated 2D quantum photonic circuitry. By introducing plasmonic nanostructures and metasurfaces, one may effectively enhance light harvesting, direct valley-polarized emission, and route valley index. This review article focuses on these critical aspects to develop integrated photonic and valleytronic applications by exploiting exciton–plasmon coupling over a new hybrid material platform.

**Keywords:** exciton–plasmon coupling; metasurface; single-photon emission; TMD; valley polarization.

***Corresponding authors: Andrea Alù**, Photonics Initiative, Advanced Science Research Center, City University of New York, NY 10031, USA; Physics Program, Graduate Center, City University of New York, NY 10016, USA; and Department of Electrical Engineering, City College of The City University of New York, NY 10031, USA, e-mail: aalu@gc.cuny.edu; and **Xiaoqin Li**, Department of Physics, Complex Quantum Systems, and Texas Materials Institutes, The University of Texas at Austin, Austin, TX 78712, USA, e-mail: elaineli@physics.utexas.edu. https://orcid.org/0000-0002-2279-3078
**Michele Cotrufo:** Department of Electrical and Computer Engineering, The University of Texas at Austin, Austin, TX 78712, USA; and Photonics Initiative, Advanced Science Research Center, City University of New York, NY 10031, USA
**Liuyang Sun and Junho Choi:** Department of Physics, Complex Quantum Systems, and Texas Materials Institutes, The University of Texas at Austin, Austin, TX 78712, USA

## 1 Introduction

Two-dimensional semiconductors have attracted much interest in the last decade as a new material platform for valleytronics and optoelectronics [1–4]. Particular attention has been devoted to monolayer (ML) transition-metal dichalcogenides (TMDs), which are formed by a layer of transition-metal atoms [such as molybdenum (Mo) and tungsten (W)] sandwiched between two layers of chalcogenide atoms [such as sulfur (S) and selenium (Se)], with the metal and chalcogen atoms occupying the A and B sites of a hexagonal lattice (Figure 1). Exciton resonances in Mo- and W-family materials exhibit distinct optical properties because of their different spin orientations in the lowest conduction bands. In Mo-based TMD monolayers, the lowest exciton resonance is a dipole-allowed transition, while this transition corresponds to dark excitons in W-based TMD monolayers [5, 6]. These materials feature a combination of unique optical properties. Their electronic bandgap lies in the visible and infrared, and as the layer thickness is reduced, the electronic band structure changes significantly [7, 8]. In some TMD materials (e.g. $MoS_2$), an indirect-to-direct gap transition occurs when a bilayer is thinned down to a monolayer [9–11], thus strongly enhancing light emission and absorption in the MLs.

Mobile excitons in TMD monolayers exhibit large binding energy and oscillator strength, leading to strong resonant coupling to light [12–17]. In addition to mobile excitons, ML TMDs can also host localized excitons that are bound to the defects and behave as spectrally narrow single-photon emitters [18–20]. These localized emission centers often appear at the ML edges, but they can also be created or enhanced at specific positions by locally engineering the strain. Moreover, excitons form at the K and K′ points located at the Brillouin zone boundary. Because of the broken inversion symmetry of the ML and the strong spin–orbit coupling, the electronic states of the two K and K′ valleys have opposite spins, leading to spin-valley locking [21–23]. Because of the valley-contrasting optical selection rule, the valley index can be addressed and manipulated by light. Optoelectronic applications

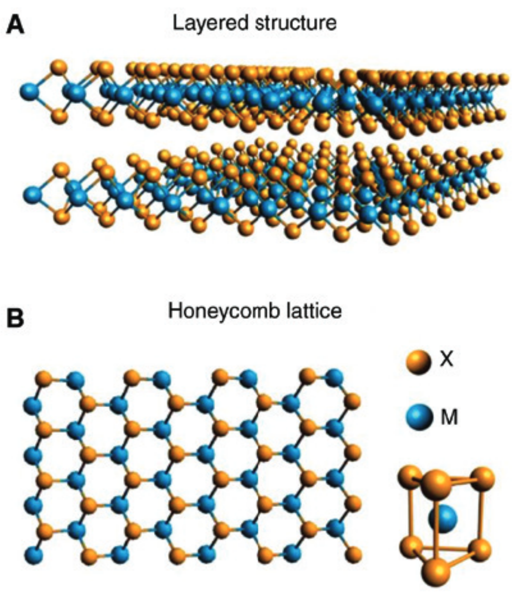


**Figure 1:** Atomic structure of TMDs.
(A) Three-dimensional schematic of a layered $MX_2$ (M = Mo, W; X = S, Se, Te) structure. In a TMD monolayer, a layer of transition metal atoms (M, blue spheres) is sandwiched between two layers of chalcogen atoms (X, yellow spheres). (B) Top and side views of a honeycomb lattice of a TMD with two sublattice sites occupied by metal and chalcogen atoms, respectively.

of TMDs are often limited by their low quantum yield. Improving the quantum yield of TMD monolayers remains therefore an active and important area of research [24, 25]. Additionally, light emitted from mobile or localized excitons needs to be efficiently collected and properly routed on chip for any integrated application.

In this review, we discuss how plasmonic nanostructures are particularly well suited for enhancing the optical properties of TMD MLs. Because of their two-dimensional nature, TMD MLs can be positioned very close, and optimally aligned, to a metallic structure. We have chosen to focus on emerging new directions in controlling a single emitter and valley index using plasmonic structures, and we anticipate rapid developments in these areas in the next few years. Because of the vast body of literature on TMD monolayers and many excellent reviews, we have omitted several interesting topics, including light–matter interaction in the strong coupling regime leading to the formation of polaritons [17, 26]. In Section 2, we briefly summarize the optical properties of TMD monolayers and the use of plasmonic nanostructures to control spontaneous emissions. In Section 3, we discuss different approaches to increase emission from mobile or localized excitons into either free space (mediated by plasmonic antennas) or plasmonic waveguides for on-chip propagation. In Section 4, we focus on recent experiments where the chirality of plasmonic fields is combined with the valley-selective response of TMD materials to increase valley polarization, direct valley-selective emissions, and a spatially separate valley index by exploiting exciton–plasmon coupling.

## 2 Basic concepts

### 2.1 Excitons in TMD monolayers

Excitons in TMD monolayers have several unique properties, including a small Bohr radius as well as large binding energy and oscillator strength [12–16]. Assuming a simple hydrogenic model, the $n$th exciton resonance binding energy in 2D materials is determined by

$$E_b^{(n)} = \frac{\mu e^4}{2\hbar^2 \varepsilon^2 (n-1/2)^2},$$

where $\mu$ is the reduced mass [$\mu = 1/(m_e^{-1} + m_h^{-1})$] and $\varepsilon$ is the dielectric constant. While the static value of the dielectric constant $\varepsilon$ is often used in traditional semiconductors, the proper value of this quantity for 2D materials is often debated because of the large exciton binding energy. It has been suggested that the contribution of optical phonons to dielectric screening should be taken into account [27], and further investigations are necessary [28].

Deviation from this simple model has been explicitly observed in $WS_2$ monolayers [29]. Nevertheless, it provides a simple estimate of the exceptionally large exciton binding energy in TMD monolayers, which has been determined to be a few hundred milli-electron volts [29–32], or nearly two orders of magnitude larger than in conventional semiconductor quantum wells [33, 34]. This large binding energy originates from an increased effective mass [11] and the insufficient screening in the direction perpendicular to the 2D plane (Figure 2) and, consequently, an enhanced Coulomb attraction between electrons and holes and a small Bohr radius [14, 29, 32, 35–38]. The large binding energy of excitons, trions (an exciton bound with an extra electron or hole [12]), and higher order bound states such as biexcitons [39, 40] make these many-body states relevant for various optoelectronic devices, even at room temperature [41–44].

A small exciton Bohr radius leads to a large spatial overlap between the electron and hole wavefunctions and, therefore, a large oscillator strength as manifested in the strong exciton absorption (i.e. 5–10% for TMD monolayers). A large oscillator strength should, in

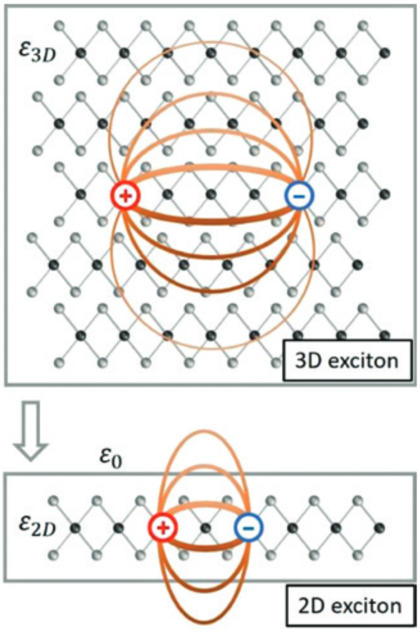


**Figure 2:** Illustration of Coulomb interaction leading to the formation of excitons, i.e. bound electron–hole pairs in a bulk and a 2D material.

principle, lead to a rapid radiative decay. Calculations suggest that the exciton radiative decay is on the order of a few hundred femtoseconds in perfect TMD monolayers [45, 46]. Deviations from ideal crystals lead to exciton localization and likely a longer exciton radiative lifetime. Directly measuring this radiative lifetime is difficult because commonly available techniques, such as pump/probe and time-resolved photoluminescence (PL), can only measure the total lifetime, determined by both radiative and nonradiative processes (we will discuss further this problem in Section 2.4). In addition, these experiments cannot distinguish intrinsic exciton recombination processes from those that repopulate the exciton resonances. Measurements often report a temperature- and excitation intensity-dependent exciton decay time, related to exciton–phonon and exciton–exciton interactions [46–50]. Ultrafast spectroscopy measurements have suggested that the total exciton recombination lifetime at low temperature is ~1 ps or shorter [51, 52]. This total lifetime is limited by the nonradiative decay because of the low quantum yield of commonly available TMD monolayers. Earlier measurements reporting longer lifetimes [46, 50, 53] were often limited by the temporal resolution of the technique. Exciton thermalization process following an impulse excitation further complicates the interpretation of the measured exciton decay times [54]. Placing TMD monolayers near plasmonic nanostructures likely shortens the lifetime further, making it even more difficult to accurately measure it. Explicit measurements of these dynamics in hybrid TMD–plasmonic materials are largely missing in the existing literature, despite being critical for enhanced light emission and modified valleytronic phenomena. The large oscillator strength also facilitates strong coupling to light, as reported in various coupled TMD–plasmonic systems [55, 56].

## 2.2 Single-photon emitters in TMD monolayers

Localized excitons, with completely different properties than 2D excitons, are also found in TMD monolayers. Indeed, several groups have reported that defects hosted in TMD monolayers (especially $WSe_2$) can trap excitons, and their subsequent radiative recombination features good single-photon emission properties at low temperature [18–20, 57, 58]. These excitons are typically localized at the flake edges and give rise to sharp emission lines (line widths ~100 μeV) that are red-shifted by 40–100 meV from the delocalized valley excitons [19] (Figure 3A). The quantum statistical properties of these single-photon emitters have been characterized by second-order photon correlation measurements [18–20, 57], and the measured lifetimes range from hundreds of picoseconds to few nanoseconds, similar to the values typically found in InAs self-assembled semiconductor quantum dots [60]. This long lifetime is in strong contrast with the short lifetime (~1 ps) of unbound excitons in ML TMDs, which is typically dominated by nonradiative decays.

High-resolution magneto-optical measurements have shown that the emission from these localized excitons is composed of a doublet (Figure 3B), which features orthogonal linear polarizations [18–20, 57]. When a magnetic field is applied perpendicular to the monolayer plane, the doublet splitting increases (Figure 3C) and the emission polarization evolves from linear to circular [19]; the handedness of circular polarization can be controlled by the magnetic field sign [19]. No clear dependence of the splitting and polarization on the magnetic field is observed when the field is parallel to the plane, similar to the case of unbound excitons.

The nature of these defects is not fully understood yet. It has been suggested that they can be due to vacancies, impurity atoms, or local strain [58]. Indeed, the defects initially investigated appeared mainly close to the edge of the monolayer, which limits their potential in practical applications. Many groups have therefore investigated the possibility of deliberately creating these defects with controlled positions. It has been shown that by placing ML