Review article

Vincenzo Ardizzone*, Luisa De Marco, Milena De Giorgi, Lorenzo Dominici,
Dario Ballarini and Daniele Sanvitto

Emerging 2D materials for room-temperature polaritonics

<https://doi.org/10.1515/nanoph-2019-0114>

Received April 12, 2019; revised June 18, 2019; accepted June 21, 2019

Abstract: Two-dimensional semiconductors are considered intriguing materials for photonic applications, thanks to their stunning optical properties and the possibility to manipulate them at the nanoscale. In this review, we focus on transition metal dichalcogenides and low-dimensional hybrid organic-inorganic perovskites, which possess the same characteristics related to planar confinement of their excitons: large binding energies, wide exciton extension, and high oscillator strength. We describe their optoelectronic properties and their capability to achieve strong coupling with light, with particular attention to polariton-polariton interactions. These aspects make them very attractive for polaritonic devices working at room temperature, in view of the realization of all-optical logic circuits in low-cost and easy-to-synthesize innovative materials.

Keywords: transition metal dichalcogenides; hybrid organic-inorganic perovskite; polaritons; strong light-matter coupling.

1 Introduction

Over the past decade, two-dimensional (2D) materials have triggered an impressive research effort covering several fields of study, ranging from chemistry to physics and biology.

This review focuses on a class of 2D materials possessing relevant optical properties and, more specifically, on 2D materials that have been used in systems showing strong light-matter coupling at room temperature. Examples of such materials are transition metal dichalcogenide (TMD) monolayers (MLs) or hybrid organic-inorganic halide perovskites (PVKs).

In spite of their differences, these materials share some important properties, such as a direct bandgap and excitons with binding energies largely exceeding $k_B T$ at room temperature. Thanks to the 2D confinement of electrons and holes, they show well-defined excitonic transition with high oscillator strengths up to room temperature. Strong coupling between excitons and photons can be achieved when a 2D material is embedded inside or on the surface of a high-quality optical resonator [1–4].

One of the most common way to achieve strong coupling is shown in Figure 1A, in which an active medium (i.e. a material possessing an exciton transition) is embedded in a Fabry-Perot cavity formed by two planar highly reflecting mirrors. Strong exciton-photon coupling occurs when the energy exchange rate γ between the exciton and the electromagnetic field is higher than other energy dissipation rates of the system, namely the optical losses γ_c and the exciton non-radiative losses γ_x . Energy exchange rate γ is related to the exciton oscillator strength, making TMD MLs and PVKs good candidates to observe strong coupling at room temperature. When these conditions are fulfilled, the system can be described in terms of two new eigenstates called upper and lower exciton-polaritons, respectively UP and LP, whose energy dispersions are depicted in Figure 1B.

The energy dispersion of these new eigenstates are given by $E_{UP,LP} = \frac{1}{2}(\Delta \pm \sqrt{\delta^2 + \Omega_R^2})$, in which $\Delta = E_c + E_x$, $\delta = E_c - E_x$ and Ω_R is the Rabi splitting, related to the exciton-photon coupling strength [5].

Exciton-polaritons have attracted great interest because they behave as half-light half-matter quasiparticles possessing strong intrinsic non-linearities inherited from their excitonic component, extremely small effective mass, and

*Corresponding author: Vincenzo Ardizzone, CNR Nanotec, Institute of Nanotechnology, via Monteroni, 73100 Lecce, Italy; and Dipartimento di Matematica e Fisica, Università del Salento, via Arnesano, 73100 Lecce, Italy, e-mail: v.ardizzone85@gmail.com
Luisa De Marco, Milena De Giorgi, Lorenzo Dominici, Dario Ballarini and Daniele Sanvitto: CNR Nanotec, Institute of Nanotechnology, via Monteroni, 73100 Lecce, Italy. <https://orcid.org/0000-0002-6855-5438> (L. De Marco)

Figure 1: Strong exciton-photon coupling in a semiconductor microcavity.

(A) A microcavity sample: an active material (exciton) is embedded between two high-reflective mirrors. (B) A typical polariton dispersion [upper (UP) and lower (LP) branches] arising from the strong coupling between excitons and a cavity mode (Cav).

long coherence length inherited from their photonic component [2, 6]. These properties enable the study of a large set of phenomena comprising Bose-Einstein condensation [7], superfluidity [8], quantum vortices [9, 10], pseudospin Rabi oscillations [11], and optical spin Hall effect [12, 13].

From a more applied point of view, exciton-polaritons could be used as interacting photons for communication and computing applications [6, 14]. For example, polaritonic devices could be used to implement logic functions such as logic gates, switches, or routers. The advantage given by polaritonic logic would be to use the polaritons to both carry and – thanks to polaritonic non-linearities – manipulate information, instead of completely converting traveling photons in interacting electrons and vice versa. It has also been proposed that polariton lattices can act as analogue quantum or classical simulators for solving specific exponentially complex problems [15–17]. Nevertheless, in order to develop realistic polaritonic devices, it is necessary to obtain room-temperature highly interacting polaritons, which remains an intriguing challenge.

For instance, the majority of exciton-photon coupling experiments have been demonstrated at cryogenic temperatures in III-V and II-VI semiconductors, such as GaAs and CdTe quantum wells (QWs) in microcavities. These materials possess narrow exciton linewidths; however, their excitons do not reach temperatures >100 K because of their small binding energy.

Even if room-temperature polaritons have been observed in III-nitrides and ZnO-based microcavities [18–21] as well as in organic semiconductor-based microcavities [22], excitons in these materials possess a small Bohr radius resulting in a reduction of exciton-exciton spatial overlap. As a consequence, polariton-polariton interactions are usually very small compared to standard III-V or II-V heterostructures.

For example, in GaAs QW-based polaritons at cryogenic temperatures, the polariton-polariton interaction constant g_p is of the order of $1\text{--}10 \mu\text{eV} \mu\text{m}^2$ [23]. Meanwhile,

non-linearities from very localized excitons (also called Frenkel excitons in contrast to the large Wannier-Mott excitons in GaAs QWs) observed until now for organic polaritons lead to a much smaller interaction constant g_p of $10^{-3} \mu\text{eV} \mu\text{m}^2$ [24, 25].

For all these reasons, materials with a 2D confinement of excitons such as PVK and TMD MLs are becoming an interesting platform to harness high polariton non-linearities at room temperature. Thanks to the strong excitonic oscillator strength and large binding energy, these materials could be good candidates to realize real polariton devices.

In the first part of this review, we report on the observations of polaritonic effects in TMD MLs. In the second part, we summarize the work that has been done on polaritons in 2D hybrid organic-inorganic PVKs.

2 Polaritons in TMDs

2.1 Excitons in TMDs

TMDs are a group of layered materials in which two adjacent layers are kept together by van der Waals interactions. They can be described by the chemical formula MX_2 , in which M is a transition metal and X is a dichalcogenide.

These materials have recently attracted enormous interest [26] due to the fact that they have a direct bandgap when thinned down to a single ML. As a consequence, their properties can be addressed by optical measurements. From a fundamental point of view, they offer an almost ideal system to study truly 2D excitons in semiconductor materials with new spin-valley degrees of freedom and the possibility to be deployed almost on any substrate and shapes via van der Waals forces. Recently, there has also been a growing interest on the formation of indirect excitons using stacks of different TMDs, allowing for new

Figure 2: Polaritons in TMD MLs.

(A) Sketch of a MoS_2 ML inserted in a Fabry-Perot cavity and scheme of K and K' valleys at the corners of the hexagonal first Brillouin zone, adapted from Ref. [35]. (B) Band diagram at the K and K' points for a MoS_2 ML; the black arrows represent allowed optical transition, showing the spin-valley locking effect. (C) Sketch of a tunable microcavity embedding a MoSe_2 flake [36]. (D) Anticrossing of the upper polariton branch (UP) and the lower polariton branch (LP) in the tunable microcavity of C; by modifying the voltage applied to the piezoelectric mirror, the energy of the cavity mode is modified [36]. (E) PL intensity of the $\sigma+$ and $\sigma-$ polarized LP under non-resonant excitation with a $\sigma-$ polarized pump; the pump polarization is partially retained by polaritons, which is a demonstration of the spin-valley locking for polaritons in TMD MLs. (F) Polarization degree as a function of temperature for MoS_2 bare A-excitons, LP and UP; remarkably, at high temperatures, valley polaritons are more effective than bare excitons in retaining valley polarization [37].

optical properties to be exploited with virtually no limit imposed by lattice matching constraints, typical of more standard semiconductor heterostructures [27]. On a more technological side, TMD MLs seem to be an excellent new platform for developing optoelectronic functionalities comprising logic gates, photodetectors, light-emitting diodes, or photoinduced valley currents [28, 29].

TMDs with $M = \text{W}$ or Mo and $X = \text{S}, \text{Se}, \text{or Te}$ are particularly relevant in optics. In fact, as it has been recently shown [30, 31], they behave as semiconductors with a direct bandgap of several hundreds of meV when they are in an ML form. Typically, small flakes of TMD MLs are obtained by micromechanical cleavage or exfoliation. However, the development of other techniques such as chemical vapour deposition or van der Waals epitaxy are actively explored and could be beneficial in increasing the size and the availability of ML samples [32–34].

Figure 2A represents a single ML of a MoS_2 TMD with atoms disposed according to a hexagonal pattern, the Mo plane being sandwiched by two S planes. The resulting

hexagonal first Brillouin zone is also sketched in Figure 2A. Direct bandgap occurs at the corners of the hexagon, with K and K' points being associated to different optical transitions. In fact, optical absorption in K and K' is allowed for photons having respectively clockwise ($\sigma+$) and anti-clockwise ($\sigma-$) circular polarization. This property, also referred as valley polarization, is a consequence of both the lack of inversion symmetry of the crystal structure and the strong spin-orbit coupling [26].

Spin-orbit coupling is one of the most peculiar features of TMD MLs and lifts the spin degeneracy of valence and conduction band at K/K' points. This is sketched in Figure 2B for MoX_2 materials. The spin-orbit-induced splitting can be as high as hundreds of meV for the valence band and tens of meV for the conduction band. Vertical arrows represent the fundamental allowed valley optical transitions. Crucially, spin and valley degrees of freedom are locked for photogenerated carriers in TMD MLs, which opens an entire new field of studies often referred as “valleytronics.”

Due to the (i) almost perfect 2D confinement of electrons and holes, (ii) the reduced dielectric screening of the Coulomb interaction, and (iii) the relatively large masses of electrons and holes in the K , K' valleys, the excitonic binding energy ranges from 200 meV for MoS_2 to 700 meV for WS_2 [29].

Optical properties are then dominated by excitonic resonances up to room temperature. These strong excitons in TMD MLs are characterized by a Bohr radius of a few nanometers. Being delocalized over several lattice units, they are fully consistent with the Wannier-Mott picture [38]. As we will see later on, this is a key point in the realization of strongly interacting polaritons at room temperature.

2.2 Strong exciton-photon coupling in TMD MLs: valley polaritons

The strong interaction of TMD ML excitonic transitions with light has triggered a huge interest with the observation of exciton-polaritons in these materials demonstrated by the pioneering works of Liu et al. [35] and Dufferwiel et al. [36]. These studies, initially motivated by the large excitonic binding energy and the possibility to observe strong coupling at high temperatures [39], have started to explore peculiar properties of exciton-polaritons in TMD MLs. For example, exciton-polaritons in TMD MLs inherit spin-valley polarization from their excitonic component, which gives access to unprecedented degrees of freedom in polaritonics [37, 40, 41].

Moreover, in TMD ML-based systems, it is possible to mix optical and electrical control of carriers, which is not easily achieved in more standard polaritonic systems such as in III-V semiconductors. As an example, real-time control of exciton-photon interaction has shown the possibility of electrically switching strong coupling on or off [42].

The first observation of strong coupling between a photonic mode and an excitonic mode in ML MoS_2 has been reported by Liu et al. by using the sample sketched in Figure 2A [35]. In this case, the active medium has been embedded in a dielectric microcavity formed by two distributed Bragg reflectors (DBRs) spaced by two SiO_2 layers. The authors measured angle-resolved reflectivity and photoluminescence (PL) and reported a Rabi splitting $\hbar\Omega = 46$ meV at room temperature.

Following this first demonstration, several different experimental configurations have been explored to achieve strong coupling between a photonic mode and a TMD ML exciton.

Figure 2A shows the configuration used by Dufferwiel et al. [40] in which a flake of ML MoSe_2 is encapsulated by two MLs of hexagonal boron nitride and deposited on a planar DBR. A second concave DBR is micropositioned to form a tunable 0D hemispheric optical cavity. Alternatively, the open-cavity geometry with two planar DBRs has also been demonstrated by Król et al. [43]. Thanks to the large excitonic oscillator strength, values of Rabi splitting of several tens of meV are routinely observed at room temperature in TMD-based systems.

At the time of writing this review, several groups have reported strong exciton-photon coupling in TMD ML-based systems in a Fabry-Perot configuration [37, 40, 41]. Most of these works focus on how spin-valley degrees of freedom of excitons are mirrored on polaritonic properties.

Remarkably, it has been observed that polaritons retain the valley-spin degree of freedom when excited with a circularly polarized pump. For example, Figure 2E shows the polarization resolved PL emission from a microcavity-embedded ML WS_2 flake obtained by Sun et al. [41]. Polaritons are created by resonantly pumping the bare excitonic mode with a σ - polarized pump laser. The authors observed that most of the PL emissions share the same polarization as the pumping laser, demonstrating spin-valley locking for polaritons. Similar results are obtained when pumping is resonant with the polariton modes. For these reasons, polaritons formed from excitons in TMD MLs are also called valley-polarized polaritons or simply valley polaritons.

Chen et al. [37] have shown that in MoS_2 , polaritons are even more effective than bare excitons in retaining valley polarization, as it is shown in Figure 2F in which the degree of polarization is reported as a function of temperature for A-excitons and both upper (UP) and lower polaritons (LP). As can be seen for temperatures >100 K, A-excitons start losing their polarization while polaritons remain $>10\%$ polarized even at room temperature. This remarkable behavior is explained by a polariton decay rate in the optical modes that is larger than the intervalley mixing rate. Moreover, when coupled to the photonic modes, excitons are more delocalized and then less sensitive to local disorder effects, which are also responsible for intervalley mixing and loss of valley coherence.

Other studies have proven that excitons in TMD MLs can be coupled to photonic modes in systems different from Fabry-Perot microcavities. For example, Zhang et al. [44] have shown that it is possible to couple an ML of TMD (WS_2 or WSe_2) to a photonic crystal mode supported by a periodic grating. Barachati et al. [45] have coupled a WS_2 single flake to a Bloch surface mode in a planar SiO_2 /

Ta₂O₅ DBR. The authors, as sketched in Figure 3A, showed that this system can sustain Bloch surface wave polaritons (BSWPs) with a room-temperature Rabi splitting of 43 meV and propagation length as long as 33 μm . These systems allow coupling excitonic transition to small-volume photonic modes, also reducing the complexity of the standard microcavity structure.

TMD-based polaritons also offer unprecedented possibilities to mix optical and electrical control of exciton-polaritons. For example, Chakraborty et al. [42] have shown that it is possible to switch from strong to weak coupling by applying a gate voltage to a WS₂ field effect transistor shown in Figure 3C and D. In this case, bottom and top mirrors are metallic and can be used as electrodes. The transistor functionality is achieved by adding a lateral contact to apply a gate voltage V_g , as it is shown in Figure 3C. The authors observed that, upon increasing V_g , the PL emission is strongly reduced and blueshifted in energy. They explained this behavior as a reduction in the oscillator strength due to screening effects from the injected charges, eventually resulting in the loss of strong coupling. Transition from strong coupling to weak coupling by varying the gating voltage is shown in Figure 3D.

The on/off switching of the strong coupling could be exploited for the realization of polariton-based modulators or switches.

2.3 Non-linearities

Harnessing polariton-polariton interactions is key for developing effective polaritonic devices [6]. Several manifestations of polariton interaction, such as four-wave mixing, parametric generation, and bi-stability, have been extensively studied in standard semiconductors at cryogenic temperatures. Thanks to the strong excitonic binding energy and high oscillator strength, TMD MLs are one of the promising candidates to exploit polariton non-linearities at room temperature.

To date, only a few studies have focused on the non-linear properties of polaritons in TMD MLs. Thanks to the sample sketched in Figure 3A, Barachati et al. [45] have observed, for the first time, polariton non-linearities at room temperature in TMD MLs. By resonantly pumping the propagating polariton mode of a BSWP, they measured an excitation density-dependent blueshift and deduced

Figure 3: Polaritons in TMD MLs: nonlinearities and electrical control.

(A) Coupling between a Bloch surface wave (BSW) at the DBR interface and a WS₂ ML; interacting BSW polaritons propagating at high speed have been observed on this sample [45]. (B) Thanks to polariton-polariton interactions, a non-linear polariton source is obtained by resonantly pumping the device of Figure 1A. (C) A WS₂-based field effect transistor in which the gate voltage V_g is used to reversibly switch the system from strong to weak coupling [42]. (D) Energy-resolved PL from the sample of Figure 2C as a function of the applied voltage V_g [42].

an exciton interaction, $g_{xx} = 6 \times 10^{-2} \mu\text{eV } \mu\text{m}^{-2}$. Although this value is somewhat lower than available theoretical predictions [39], the authors were able to demonstrate a non-linear polariton source relying on these polariton interactions: as it is shown in Figure 3B, when a slightly blue-detuned excitation beam is used to pump the low BSWP branch, the polariton flow varies non-linearly with increasing excitation power. For small incident power, only a small fraction of the incident laser is coupled to the BSWP mode. When the BSWP population increases, the mode is blueshifted and an increasing fraction of the incident power is coupled to BSWP, resulting in a non-linear polariton flow.

BSWPs are interesting for polaritonic devices because they could be used for both information processing, thanks to their non-linear nature, and optical interconnects between different devices, thanks to their fast and low-loss propagation.

TMD ML excitons could also be a promising system to engineer long-range dipolar interactions in polaritons. Dipolar polaritons in GaAs QWs [46, 47] are triggering a huge interest because they seem to provide interaction constants as high as $2.4 \text{ meV } \mu\text{m}^2$, offering an enhancement of more than two orders of magnitude in the non-linear response compared to the standard exchange interaction. In standard QWs, a permanent excitonic electric dipole can be obtained by applying a static electric field perpendicular to the QW plane. Alternatively, when multiple QWs are present, indirect excitons can be used [48]. In this case, when indirect excitons are formed, the electron and the hole are created in different QWs. The spatial separation between opposite charges is responsible for the permanent electric dipole.

TMD MLs seem to be promising for both the application of an electrical perturbation and the creation of indirect excitons [27, 49]. In particular, it has already

been shown that in TMD hetero-bilayers, it is possible to observe indirect excitons [50].

3 Polaritons in hybrid organic-inorganic PVKs

3.1 2D PVK structural and optical properties

Another interesting 2D system is the one represented by the 2D hybrid organic-inorganic PVKs in which the organic chain is long enough to electronically separate each inorganic layer. This class of materials combine the advantages of organics, such as the easy and low-cost manufacturing, and those possessed by inorganic compounds, like robustness and excellent charge transport character [51, 52].

Compared with conventional semiconductors, one of their most attractive features is the easy bandgap engineering, which can be achieved by controlling the stoichiometry and/or the nature of the precursors: for example, changing the halide (from Cl to Br to I), the emission can be tuned from deep blue to near infrared (from 400 to 700 nm) [53, 54].

The common structure of 2D PVK is A_2BX_4 , where A is a long chain alkylammonium, B is the metal cation (typically Pb or Sn), and X is halide anion (Cl, Br, or I). The structure is a superlattice of QWs consisting of the inorganic layers of $[\text{PbI}_6]^{2-}$ octahedra sandwiched between interdigitating bilayers of intercalated alkylammonium cations (Figure 4A).

The inorganic component offers high carrier mobility and the possibility of a wide range of bandgap, while the organic component provides structural diversity and plastic mechanical properties. In comparison to their 3D

Figure 4: Structure of 2D PVK.

(A) Sketch of a 2D PVK superlattice consisting of lead iodide inorganic layers sandwiched between interdigitating alkylammonium cations [55]. (B) Schematic energy band structure of a 2D PVK.

counterparts, layered 2D PVKs offer more tunability of their optoelectronic properties due to their larger degrees of freedom in chemistry changing the anions, as well as in the number of inorganic layers, n , simply altering their stoichiometry during the synthesis [56]. This degree of freedom allows to further tune the optical bandgap: for example, increasing n from 1 to 4 in $(\text{BA})_2(\text{MA})_{n-1}\text{PbI}_{3n+1}$, the corresponding bandgap progressively decreases from 2.43 to 1.91 eV [57].

The schematic energy-band structure of a 2D PVK is displayed in Figure 4B. Excitons with the lowest energy are associated with the inorganic layers, while the higher-band-gap organic layers behave as a potential barrier. Therefore, each inorganic layer is *de facto* a 2D QW. The resulting quantum confinement in 2D PVKs increases the exciton binding energy more than an order of magnitude compared to the 3D PVKs: [58, 59] from approximately 10 to 50 meV in bulk PVKs [55, 60, 61] to >150 meV in 2D PVKs with $n=1$. Consequently, these crystals are characterized by high PL and huge oscillator strengths even at room temperature [58, 59, 62]. Moreover, quantum confinement in one dimension blueshifts the conduction and valence bands and increases the effective band gap [63].

PVKs are synthesized by low-temperature solution processing methods that allow preparing both

polycrystalline films deposited by spin coating and high-quality single crystals. As van der Waals materials, it is possible to mechanically exfoliate single crystals in order to obtain nanosheets that can be transferred to any substrates, including DBRs for microcavity fabrication, without the need to fulfill the lattice matching conditions.

Some studies have demonstrated differences in the exciton properties between thick (>20 layers) and ML 2D PVKs. Niu et al. [64] prepared ultrathin flakes of phenethylammonium lead iodide PVK by mechanical exfoliation (Figure 5A–C) and reported exciton blueshift and decreased linewidth for few-layer-thick PVKs (Figure 5D); this modulation of the electronic properties was ascribed to changes in the strain, disorder, and layer structure. Yaffe et al. [65] showed how the exciton binding energy of exfoliated butylammonium lead iodide PVK was larger than that of the corresponding layered bulk material, reaching the value of 490 meV for a bilayer PVK. Thickness-dependent PL emission has also been confirmed by a recent investigation [44] in which an approximately 40 meV blueshift of the exciton peak was observed by reducing the thickness from bulk to ML. Figure 5E,F respectively shows optical and atomic force microscopy (AFM) images of thin phenethylammonium lead iodide

Figure 5: Optical properties of PVKs: the role of the crystal thickness.

Optical microscope images in (A) bright and (B) dark field on an exfoliated phenethylammonium lead iodide PVK. (C) AFM image of the same area; fitted exciton. (D) Amplitude, wavelength, and linewidth from reflectivity spectra taken from Ref. [64]. (E) Optical and AFM (F) images of thin phenethylammonium lead iodide PVK nanosheets; thickness-dependent PL spectra (G) and exciton peak energy (H) taken from Ref. [44].

PVK nanosheets used in Ref. [44]. Figure 5G shows that the PL wavelength blueshifts when the thickness of the flake is reduced. Figure 5H shows how the exciton peak energy depends on the number of layers in the nanosheet.

An interesting aspect of these materials is related to the fact that their optoelectronic properties can be easily manipulated. As an example, strong ultrafast spin-selective optical Stark effect have been recently observed in polycrystalline 4-fluorophenethylammonium lead iodide PVK: exciton spin states are tuned by 6.3 meV using circularly polarized optical pulses [66]. Moreover, a quantum-confined Stark effect has been reported in layered quasi-2D PVK nanoplatelets having $n=3$. Indeed, upon application of an electric field, a blueshift of the excitonic peak was revealed and attributed to a decrease of the exciton binding energy caused by the reduced electron-hole interaction [67].

3.2 Exciton-photon coupling in hybrid organic-inorganic PVK

Given the high oscillator strength, the ease of tunability, and the sharp absorption of PVK excitons, there has been a florid literature on exciton-photon coupling in different structures as well as different types of PVKs.

Polaritons with normal mode splitting of 100 meV were first observed at room temperature in a distributed feedback (DFB) cavity consisting of a polycrystalline film of phenethylammonium lead iodide PVK, $(\text{PEAI})_2\text{PbI}_4$, deposited onto a polystyrene grating (Figure 6A) [68].

The same material was later embedded in a Fabry-Pérot microcavity consisting of dielectric or metallic mirrors, showing a strong coupling regime between the PVK exciton and the confined photon mode with anticrossing values up to 190 meV (Figure 6B) [69, 72–75].

In addition, strong coupling between layered PVK excitons and surface plasmon of a silver grating was reported [70]. In this system, the interaction between excitons and their electromagnetic field reflected by the metallic surface is observed, resulting in “image biexcitons.” These biexciton states mediate the coupling between in-plane PVK excitons and out-of-plane surface plasmon polariton grating modes, enabling the observation of strong coupling with Rabi splittings of 150 and 125 meV for the exciton and image biexciton, respectively (Figure 6C).

These seminal papers demonstrated that low-dimensional PVK materials, despite being in polycrystalline form, could be excellent candidates for room-temperature polariton applications due to their large Rabi splittings and exciton binding energies.

Figure 6: Strong coupling in PVKs.

(A) Structure of a DFB microcavity taken from Ref. [68]. (B) Dispersion of the UPB and LPB for PVK microcavity and its schematic structure taken from Ref. [69]. (C) AFM image of the PVK-coated Ag grating, its schematic cross section, and simulated reflection spectra for in-plane (on the left) and out-of-plane (on the right) exciton dipoles taken from Ref. [70]. (D) Exciton-photon coupling in 2D PVK single crystals not embedded in reflective mirror microcavity taken from Ref. [71].

However, a more interesting form of the 2D PVK is when grown in full single crystals. Polaritons made of 2D single-crystal PVKs have been investigated only in the last few years. Zhang et al. [76] have reported strong coupling of photons and excitons of methylammonium lead bromide (MAPbBr_3) PVKs in confined Fabry-Perot microwire cavities. In particular, they have observed that reducing the dimension of the microwire, the Rabi splitting increases from 268 to 390 meV due to the decrease of the optical modal volume.

Later, Fieramosca et al. [71] have reported strong coupling in different types of 2D PVK single-crystal waveguides in which different organic layers (butylammonium, phenethylammonium, or octylammonium) were used in a lead iodide PVK $[(\text{BAI})_2\text{PbI}_4, (\text{PEAI})_2\text{PbI}_4, \text{ and } (\text{OCT})_2\text{PbI}_4, \text{ respectively}]$. These PVKs were synthesized by an antisolvent vapor-assisted crystallization method that allows for very extended and thin single crystals to be formed with extremely flat surfaces. This allows such single crystals to behave as Fabry-Perot cavities without the need for metallic or dielectric mirrors. Figure 6D shows typical polariton dispersions due to coupling of the PVK exciton with the modes of the Fabry-Perot microcavity formed between the top and bottom of the single crystal. Interestingly, varying the polarization of the incident electromagnetic radiation, a finite contribution of both the in-plane and the out-of-plane exciton-polaritons was observed. This is in contrast to what it is observed in III-V inorganic semiconducting heterostructures. For example, out-of-plane excitons are not observed in GaAs QWs because the vertical transition between $3/2$ (p-type) valence band and $1/2$ (s-type) conduction band is forbidden. Such constrain is lifted in 2D PVK single crystals where the optical transition is between $1/2$ spin hole and $1/2$ spin electron and out-of-plane excitons can be formed [71].

Polaritons in similar 2D PVK single crystals have also been studied in DBR microcavities showing large Rabi splitting (242 meV) [77]. In addition, in these structures, multimode polariton dispersions involved not only 2D PVK excitons and cavity modes but also Bragg modes of the DBR, indicating a reversible energetic transfer among these three states.

3.3 Non-linearities

For the realization of room-temperature all-optical integrated logic circuits, transistors, switches, and routers, up to now only demonstrated at cryogenic temperatures in GaAs-based semiconductors, the use of room-temperature polaritons in materials that are easy to synthesize is highly

desirable. Therefore, the understanding and control of exciton-exciton interactions are of paramount importance to assess the material potentialities for room-temperature polaritonics.

Polariton condensation and polariton lasing have been reported for all-inorganic cesium lead halide (CsPbX_3) PVK nanoplatelets and nanowires [78–81]. With the increase of pump fluence [79], polariton emission shows the typical feature of phase transitions into a condensate state along with a continuous blueshift in emission energy (Figure 7A), suggesting that polariton interactions in these kinds of materials could be much higher than standard organic-based polaritons where Frenkel excitons remain very confined in small molecules or polymers at best.

A direct measurement of the exciton-exciton interaction in PVKs has been made on a 2D single-crystal PVK phenethylammonium lead iodide $[(\text{C}_6\text{H}_5(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4 (\text{PEAI})]$ by directly estimating the interaction energy via resonant excitation of the polariton modes with a pulsed femtosecond laser [82]. The single crystal was embedded in an optical cavity formed by two dielectric DBRs. The 2D PVK was a large flake of high optical quality with negligible non-radiative losses and grain-to-grain heterogeneity usually present in polycrystalline films. The observed blueshift of the polariton modes, arising from exciton-exciton interactions, provided an estimation of the interaction constant, g_{xx} , of the order of $1\text{--}5 \mu\text{eV} \mu\text{m}^2$, one of the highest observed thus far at room temperature and orders of magnitude higher than that observed in organic polaritons [24, 83, 84]. Remarkably, such interactions appear to be polarization dependent, revealing that interactions in these materials depend on the spin state: polaritons with the same spin manifest strong repulsive interactions while those with opposite spin are only weakly interacting. As a result, the energy blueshift obtained with a circularly polarized laser is higher than the one measured with a linearly polarized laser given that in the latter case only half of the excited polaritons share the same spin (Figure 7B, right panel).

These works demonstrate the possibility to work at room temperature while still keeping highly interacting polaritons, which, up to now, is only possible at cryogenic temperatures in inorganic GaAs-based microcavities [85, 86]. In particular, 2D PVK single-crystal flakes have shown the highest exciton-exciton interactions measured thus far at room temperature.

These results suggest that 2D PVKs are promising candidates to obtain optoelectronic devices exploiting polaritonic non-linearities and working at room temperature.

Figure 7: Polariton condensation and nonlinearities in PVKs based microcavities.

(A) Polariton condensation in a CsPbCl₃ crystalline nanoplatelet embedded in a planar microcavity formed by a bottom and a top HfO₂/SiO₂ DBR. Energy blueshift (on the right) with respect to the polariton emission energy at the lowest pump fluence as a function of pump fluence [79]. (B) Schematic representation of a 2D PVK single crystal embedded in an optical cavity formed by two DBRs and transmittivity spectra corresponding to different resonant excitation power for linear and circular polarized excitation laser; blueshift (right) of the polariton modes in the case of a linear (L) and a circular (C) polarized laser [82].

4 Conclusion and perspectives

In this review, we have reported on recent developments in room-temperature strong coupling between excitons in 2D materials and confined optical modes. Thanks to the planar confinement of electrons and holes, excitons in materials such as TMD MLs and hybrid organic-inorganic PVKs possess high oscillator strengths and large binding energies, which make them ideal candidates for room-temperature polaritonics.

It has been demonstrated that room-temperature polaritons from excitons in TMD MLs keep spin-valley locking up to room temperature. This opens an entire new way of optically controlling polaritons which is unparalleled.

Nevertheless, polariton-polariton interactions, which are currently considered the cornerstone of polaritonic devices, despite being higher than standard organic semiconductor-based polaritons, are smaller than expected and could hinder the exploitation of these materials in realistic applications. As a possible way out, several studies have reported the formation of indirect excitons in hetero-bilayers or van der Waals structures [27, 49, 50].

Indirect excitons in TMD heterolayers could trigger further studies of polaritonic non-linearities in TMDs, achieving higher interaction constants from dipolar interactions.

Hybrid organic-inorganic PVKs show the remarkable property of sustaining polariton modes even without need to be embedded in high-quality mirrors [55, 66, 72] and showing polariton lasing at room temperature [69]. For this reason, together with the fact that they do show PL emission even with no need for exfoliation down to the single layer, PVKs should greatly simplify the observation of room-temperature strong coupling. Most important, the polariton non-linearities observed in these materials are the highest reported so far at room temperature. Even if serious fabrication efforts still need to be made in order to increase the environmental stability of these materials, 2D PVKs offer a great flexibility in tuning the energy of their PL emission by acting on both the chemical composition and the thickness of the inorganic layers.

Besides increasing their ambient stability, further studies on these materials should address the engineering of the photonic modes by patterning the PVK crystals in order to realize optical circuits or logic for polaritons behaving as highly interacting photons.

References

- [1] Weisbuch C, Nishioka M, Ishikawa A, Arakawa Y. Observation of the coupled exciton-photon mode splitting in a semiconductor quantum microcavity. *Phys Rev Lett* 1992;69:3314–7.
- [2] Carusotto I, Ciuti C. Quantum fluids of light. *Rev Mod Phys* 2013;85:299–366.
- [3] Ballarini D, De Liberato S. Polaritonics: from microcavities to sub-wavelength confinement. *Nanophotonics* 2019;8:641–54.
- [4] Lerario G, Cannavale A, Ballarini D, et al. Room temperature Bloch surface wave polaritons. *Opt Lett* 2014;39:2068.
- [5] Hopfield JJ. Theory of the contribution of excitons to the complex dielectric constant of crystals. *Phys Rev* 1958;112:1555–67.
- [6] Sanvitto D, Kéna-Cohen S. The road towards polaritonic devices. *Nat Mater* 2016;15:1061–73.
- [7] Kasprzak J, Richard M, Kundermann S, et al. Bose-Einstein condensation of exciton polaritons. *Nature* 2006;443:409–14.
- [8] Amo A, Lefrère J, Pigeon S, et al. Superfluidity of polaritons in semiconductor microcavities. *Nat Phys* 2009;5:805–10.
- [9] Dominici L, Carretero-González R, Gianfrate A, et al. Interactions and scattering of quantum vortices in a polariton fluid. *Nat Commun* 2018;9:1467.
- [10] Lagoudakis KG, Wouters M, Richard M, et al. Quantized vortices in an exciton-polariton condensate. *Nat Phys* 2008;4:706–10.
- [11] Colas D, Dominici L, Donati S, et al. Polarization shaping of Poincaré beams by polariton oscillations. *Light Sci Appl* 2015;4:e350.
- [12] Kavokin A, Malpuech G, Glazov M. Optical spin Hall effect. *Phys Rev Lett* 2005;95:136601.
- [13] Leyder C, Romanelli M, Karr JPH, et al. Observation of the optical spin Hall effect. *Nat Phys* 2007;3:628–31.
- [14] Ballarini D, De Giorgi M, Cancellieri E, et al. All-optical polariton transistor. *Nat Commun* 2013;4:1778.
- [15] Berloff NG, Silva M, Kalinin K, et al. Realizing the classical XY Hamiltonian in polariton simulators. *Nat Mater* 2017;16:1120–6.
- [16] Kalinin KP, Berloff NG. Simulating Ising and n-state planar Potts models and external fields with nonequilibrium condensates. *Phys Rev Lett* 2018;121:235302.
- [17] Ghosh S, Opala A, Matuszewski M, Paterek T, Liew TCH. Quantum reservoir processing. *Npj Quantum Inf* 2019;5:35.
- [18] Christopoulos S, von Högersthal GBH, Grundy AJD, et al. Room-temperature polariton lasing in semiconductor microcavities. *Phys Rev Lett* 2007;98:126405.
- [19] Christmann G, Butté R, Felten E, Carlin J-F, Grandjean N. Room temperature polariton lasing in a GaN/AlGaIn multiple quantum well microcavity. *Appl Phys Lett* 2008;93:051102.
- [20] Das A, Heo J, Jankowski M, et al. Room temperature ultralow threshold GaN nanowire polariton laser. *Phys Rev Lett* 2011;107:066405.
- [21] Guillet T, Mexis M, Levrat J, et al. Polariton lasing in a hybrid bulk ZnO microcavity. *Appl Phys Lett* 2011;99:161104.
- [22] Orosz L, Réveret F, Médard F, et al. LO-phonon-assisted polariton lasing in a ZnO-based microcavity. *Phys Rev B* 2012;85:121201.
- [23] Ferrier L, Wertz E, John R, et al. Interactions in confined polariton condensates. *Phys Rev Lett* 2011;106:126401.
- [24] Daskalakis KS, Maier SA, Kéna-Cohen S. Spatial coherence and stability in a disordered organic polariton condensate. *Phys Rev Lett* 2015;115:035301.
- [25] Lerario G, Ballarini D, Fieramosca A, et al. High-speed flow of interacting organic polaritons. *Light Sci Appl* 2016;6:e16212.
- [26] Wang G, Chernikov A, Glazov MM, et al. Colloquium: excitons in atomically thin transition metal dichalcogenides. *Rev Mod Phys* 2018;90:021001-1–25.
- [27] Calman EV, Fogler MM, Butov LV, Hu S, Mishchenko A, Geim AK. Indirect excitons in van der Waals heterostructures at room temperature. *Nat Commun* 2018;9. Article number: 1895.
- [28] Grosso G. 2D materials: valley polaritons. *Nat Photonics* 2017;11:455–6.
- [29] Mak KF, Shan J. Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides. *Nat Photonics* 2016;10:216–26.
- [30] Mak KF, Lee C, Hone J, Shan J, Heinz TF. Atomically thin MoS₂: a new direct-gap semiconductor. *Phys Rev Lett* 2010;105:136805.
- [31] Splendiani A, Sun L, Zhang Y, et al. Emerging photoluminescence in monolayer MoS₂. *Nano Lett* 2010;10:1271–5.
- [32] Xenogiannopoulou E, Tsiapas P, Aretouli KE, et al. High-quality, large-area MoSe₂ and MoSe₂/Bi₂Se₃ heterostructures on AlN(0001)/Si(111) substrates by molecular beam epitaxy. *Nanoscale* 2015;7:7896–905.
- [33] Zhang Y, Chang T-R, Zhou B, et al. Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe₂. *Nat Nanotechnol* 2014;9:111–5.
- [34] Rossi A, Büch H, Di Rienzo C, et al. Scalable synthesis of WS₂ on graphene and h-BN: an all-2D platform for light-matter transduction. *2D Mater* 2016;3:031013.
- [35] Liu X, Galfsky T, Sun Z, et al. Strong light-matter coupling in two-dimensional atomic crystals. *Nat Photonics* 2015;9:30–4.
- [36] Dufferwiel S, Schwarz S, Withers F, et al. Exciton-polaritons in van der Waals heterostructures embedded in tunable microcavities. *Nat Commun* 2015;6:8579.
- [37] Chen Y-J, Cain JD, Stanev TK, Dravid VP, Stern NP. Valley-polarized exciton-polaritons in a monolayer semiconductor. *Nat Photonics* 2017;11:431–5.
- [38] Schneider C, Glazov MM, Korn T, Höfling S, Urbaszek B. Two-dimensional semiconductors in the regime of strong light-matter coupling. *Nat Commun* 2018;9:2695.
- [39] Low T, Chaves A, Caldwell JD, et al. Polaritons in layered two-dimensional materials. *Nat Mater* 2016;16:182–94.
- [40] Dufferwiel S, Lyons TP, Solnyshkov DD, et al. Valley-addressable polaritons in atomically thin semiconductors. *Nat Photonics* 2017;11:497–501.
- [41] Sun Z, Gu J, Ghazaryan A, et al. Optical control of room-temperature valley polaritons. *Nat Photonics* 2017;11:491–6.
- [42] Chakraborty B, Gu J, Sun Z, et al. Control of strong light-matter interaction in monolayer WS₂ through electric field gating. *Nano Lett* 2018;18:6455–60.
- [43] Król M, Lekenta K, Mirek R, et al. Valley polarization of exciton-polaritons in monolayer WSe₂ in a tunable microcavity. *Nanoscale* 2019;11:9574–9.
- [44] Zhang L, Gogna R, Burg W, Tutuc E, Deng H. Photonic-crystal exciton-polaritons in monolayer semiconductors. *Nat Commun* 2018;9:713.
- [45] Barachati F, Fieramosca A, Hafezian S, et al. Interacting polariton fluids in a monolayer of tungsten disulfide. *Nat Nanotechnol* 2018;13:906–9.

- [46] Rosenberg I, Liran D, Mazuz-Harpaz Y, West K, Pfeiffer L, Rapaport R. Strongly interacting dipolar-polaritons. *Sci Adv* 2018;4:eaat8880.
- [47] Rosenberg I, Mazuz-Harpaz Y, Rapaport R, West K, Pfeiffer L. Electrically controlled mutual interactions of flying waveguide dipolaritons. *Phys Rev B* 2016;93:195151.
- [48] Togan E, Lim H-T, Faelt S, Wegscheider W, Imamoglu A. Enhanced interactions between dipolar polaritons. *Phys Rev Lett* 2018;121:227402.
- [49] Flatten LC, Coles DM, He Z, et al. Electrically tunable organic-inorganic hybrid polaritons with monolayer WS₂. *Nat Commun* 2017;8:14097.
- [50] Rivera P, Yu H, Seyler KL, Wilson NP, Yao W, Xu X. Interlayer valley excitons in heterobilayers of transition metal dichalcogenides. *Nat Nanotechnol* 2018;13:1004–15.
- [51] Saparov B, Mitzi DB. Organic-Inorganic perovskites: structural versatility for functional materials design. *Chem Rev* 2016;116:4558–96.
- [52] Sutherland BR, Sargent EH. Perovskite photonic sources. *Nat Photonics* 2016;10:295–302.
- [53] Fu Y, Zhu H, Chen J, Hautzinger MP, Zhu X-Y, Jin S. Metal halide perovskite nanostructures for optoelectronic applications and the study of physical properties. *Nat Rev Mater* 2019;4:169–88.
- [54] Smith MD, Connor BA, Karunadasa HI. Tuning the luminescence of layered halide perovskites. *Chem Rev* 2019;119:3104–39.
- [55] Herz LM. Charge-carrier dynamics in organic-inorganic metal halide perovskites. *Annu Rev Phys Chem* 2016;67:65–89.
- [56] Akkerman QA, Bladt E, Petralanda U, et al. Fully inorganic Ruddlesden-Popper double Cl-I and Triple Cl-Br-I lead halide perovskite nanocrystals. *Chem Mater* 2019;31:2182–90.
- [57] Stoumpos CC, Cao DH, Clark DJ, et al. Ruddlesden-Popper hybrid lead iodide perovskite 2D homologous semiconductors. *Chem Mater* 2016;28:2852–67.
- [58] Kumagai M, Takagahara T. Excitonic and nonlinear-optical properties of dielectric quantum-well structures. *Phys Rev B* 1989;40:12359–81.
- [59] Hong X, Ishihara T, Nurmikko AV. Dielectric confinement effect on excitons in PbI₄-based layered semiconductors. *Phys Rev B* 1992;45:6961–4.
- [60] Miyata A, Mitoglu A, Plochocka P, et al. Direct measurement of the exciton binding energy and effective masses for charge carriers in organic-inorganic tri-halide perovskites. *Nat Phys* 2015;11:582.
- [61] Yang Y, Ostrowski DP, France RM, et al. Observation of a hot-phonon bottleneck in lead-iodide perovskites. *Nat Photonics* 2015;10:53.
- [62] Ishihara T, Hong X, Ding J, Nurmikko AV. Dielectric confinement effect for exciton and biexciton states in PbI₄-based two-dimensional semiconductor structures. *Surf Sci* 1992;267:323–6.
- [63] Straus D, Kagan CR. Electrons, excitons, and phonons in two-dimensional hybrid perovskites: connecting structural, optical, and electronic properties. *J Phys Chem Lett* 2018;9:1434–47.
- [64] Niu W, Eiden A, Prakash GV, Baumberg JJ. Exfoliation of self-assembled 2D organic-inorganic perovskite semiconductors. *Appl Phys Lett* 2014;104:171111.
- [65] Yaffe O, Chernikov A, Norman ZM, et al. Excitons in ultrathin organic-inorganic perovskite crystals. *Phys Rev B* 2015;92:045414.
- [66] Giovanni D, Chong WK, Dewi HA, et al. Tunable room-temperature spin-selective optical Stark effect in solution-processed layered halide perovskites. *Sci Adv* 2016;2:e1600477.
- [67] Walters G, Wei M, Voznyy O, et al. The quantum-confined Stark effect in layered hybrid perovskites mediated by orientational polarizability of confined dipoles. *Nat Commun* 2018;9:4214.
- [68] Fujita T, Sato Y, Kuitani T, Ishihara T. Tunable polariton absorption of distributed feedback microcavities at room temperature. *Phys Rev B* 1998;57:12428–34.
- [69] Lanty G, Lauret JS, Deleporte E, Bouchoule S, Lafosse X. UV polaritonic emission from a perovskite-based microcavity. *Appl Phys Lett* 2008;93:081101.
- [70] Niu W, Ibbotson LA, Leipold D, Runge E, Prakash GV, Baumberg JJ. Image excitons and plasmon-exciton strong coupling in two-dimensional perovskite semiconductors. *Phys Rev B* 2015;91:161303.
- [71] Fieramosca A, Marco LD, Passoni M, et al. Tunable out-of-plane excitons in 2D single-crystal perovskites. *ACS Photonics* 2018;5:4179–85.
- [72] Brehier A, Parashkov R, Lauret JS, Deleporte E. Strong exciton-photon coupling in a microcavity containing layered perovskite semiconductors. *Appl Phys Lett* 2006;89:171110.
- [73] Lanty G, Bréhier A, Parashkov R, Lauret JS, Deleporte E. Strong exciton-photon coupling at room temperature in microcavities containing two-dimensional layered perovskite compounds. *New J Phys* 2008;10:065007.
- [74] Wenus J, Parashkov R, Ceccarelli S, et al. Hybrid organic-inorganic exciton-polaritons in a strongly coupled microcavity. *Phys Rev B* 2006;74:235212.
- [75] Pradeesh K, Baumberg JJ, Prakash GV. Strong exciton-photon coupling in inorganic-organic multiple quantum wells embedded low-Q microcavity. *Opt Express* 2009;17:22171–8.
- [76] Zhang S, Shang Q, Du W, et al. Strong exciton-photon coupling in hybrid inorganic-organic perovskite micro/nanowires. *Adv Opt Mater* 2017;6:1701032.
- [77] Wang J, Su R, Xing J, et al. Room temperature coherently coupled exciton-polaritons in two-dimensional organic-inorganic perovskite. *ACS Nano* 2018;12:8382–9.
- [78] Su R, Wang J, Zhao J, et al. Room temperature long-range coherent exciton polariton condensate flow in lead halide perovskites. *Sci Adv* 2018;4:eaau0244.
- [79] Su R, Diederichs C, Wang J, et al. Room-temperature polariton lasing in all-inorganic perovskite nanoplatelets. *Nano Lett* 2017;17:3982–8.
- [80] Du W, Zhang S, Shi J, et al. Strong exciton-photon coupling and lasing behavior in all-inorganic CsPbBr₃ micro/nanowire Fabry-Pérot cavity. *ACS Photonics* 2018;5:2051–9.
- [81] Evans TJS, Schlaus A, Fu Y, et al. Continuous-wave lasing in cesium lead bromide perovskite nanowires. *Adv Opt Mater* 2018;6:1700982.
- [82] Fieramosca A, Polimeno L, Ardizzone V, et al. Two-dimensional hybrid perovskites sustaining strong polariton interactions at room temperature. *Sci Adv* 2019;5:eaav9967.
- [83] Lerario G, Fieramosca A, Barachati F, et al. Room-temperature superfluidity in a polariton condensate. *Nat Phys* 2017;13:837–41.
- [84] Plumhof JD, Stöferle T, Mai L, Scherf U, Mahrt RF. Room-temperature Bose-Einstein condensation of cavity exciton-polaritons in a polymer. *Nat Mater* 2013;13:247–52.
- [85] Vladimirova M, Cronenberger S, Scalbert D, et al. Polarization controlled nonlinear transmission of light through semiconductor microcavities. *Phys Rev B* 2009;79:115325.
- [86] Walker PM, Tinkler L, Skryabin DV, et al. Ultra-low-power hybrid light-matter solitons. *Nat Commun* 2015;6:8317.