Out-of-plane trion emission in monolayer WSe₂ revealed by whispering gallery modes of dielectric microresonators

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The manipulation of light emitted by two-dimensional semiconductors grounds forthcoming technologies in the field of on-chip communications. However, these technologies require from the so elusive out-of-plane photon sources to achieve an efficient coupling of radiated light into planar devices. Here we propose a versatile spectroscopic method that enables the identification of the out-of-plane component of dipoles. The method is based on the selective coupling of light emitted by in-plane and out-of-plane dipoles to the whispering gallery modes of spherical dielectric microresonators, in close contact to them. We have applied this method to demonstrate the existence of dipoles with an out-of-plane orientation in monolayer WSe₂ at room temperature. Micro-photoluminescent measurements, numerical simulations based on finite element methods, and ab-initio calculations have identified trions as the source responsible for this out-of-plane emission, opening new routes for realizing on-chip integrated systems with applications in information processing and quantum communications.

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The race to develop high-performance photonic and optoelectronic devices which take advantage of the distinctive properties and versatility of two-dimensional (2D) semiconductors^{1–3} has already given rise, for example, to high-speed and high-responsivity waveguide-integrated photodetectors⁴, plasmonic nanocavities^{5–7}, and optical resonators with enhanced light-matter interactions^{8–10}, as the basis to construct nanolasers operating at room temperature^{11,12}. Most of the optoelectronic and photonic devices developed so far are based on 2D transition-metal dichalcogenide (TMD) semiconductors such as MoS₂, MoSe₂, WS₂, and WSe₂. Consequently, the characteristics of the performance of these devices strongly depend on the in-plane (IP) dipolar nature of the robust free excitons of the 2D TMDs^{13–15}. Light from IP excitons can be easily extracted in stacked (vertical) devices. However, some emerging applications in the generation of radially polarized light in 2D TMDs¹⁶ and integrated photonic chips can be efficiently enabled when out-of-plane (OP) excitons mediate light-matter interactions^{17–24}. Although rare, OP excitons can be found in 2D semiconductors. For instance, atomically thin layers of Indium Selenide (InSe) have demonstrated, as 2D TMDs, potential applications for next generation electronics and optoelectronics^{25–27} due to their highly tuneable bandgap^{28–30} and high electron mobility³¹. Nevertheless, unlike 2D TMDs, 2D layers of InSe have revealed to sustain luminescent free excitons with an intrinsic OP orientation¹⁴. This panorama puts into evidence the necessity of identify, among the different excitonic complexes existing in 2D semiconductors, those with a suitable dipole orientation for their optimal application in the emerging field of integrated photonic circuits based on 2D materials^{32–37}. This question is particularly relevant for the development of novel devices based on monolayer TMDs, since strong spin-orbit coupling makes these materials offer, apart from bright and long-lived dark excitons^{38,39}, high-order charge-complexes with unexplored dipolar characteristics, such as bound excitons, trions^{40–44}, and biexcitons⁴⁵. These complexes are technologically promising as they can manifest even at room temperature^{46–48}, have an intrinsic charge and spin degrees of freedom that facilitate their manipulation by the application of an electric or a magnetic field^{45,49}, possess a valley degree of freedom (as free excitons), permit new optical gain mechanisms at extremely low carrier densities⁵⁰, and can be further used as entangled photon sources^{51–55}.

Back focal plane imaging is usually considered the method-of-choice to discern the orientation of the dipole responsible for the luminescent signal emitted^{13,14,56}. However, it is challenging to use this technique to discriminate contributions from different sources to the luminescent signal that may eventually have a different dipolar orientation. To overcome this limitation, more sophisticated methods have been proposed, but their application is rather limited as they require an efficient excitation of surface plasmon polaritons⁵⁷.

In this work, we propose a versatile and simple method to spectroscopically elucidate the existence of an OP component in the photoluminescent response of a dipole which, at the same time, puts into evidence its feasibility to promote light coupling to a planar device. The proposed method relies on the different selective ability of IP and OP dipolar emission to excite whispering gallery modes of SiO₂ microspheres deposited on top of the emitting layers. We have applied this method to study the orientation of dipoles related to the different light contributions observed in monolayer WSe₂ at room temperature, these from trions and excitons. By microphotoluminescence (μ -PL) measurements, numerical simulations based on the finite element method (FEM), and ab initio calculations of the excitonic states we have found a non-negligible OP dipolar component of trions

in monolayer WSe₂, which contrasts to the well-established IP nature of its free bright excitons. These results establish that exciton complexes are excellent candidates for light manipulation in planar optoelectronic devices and photonic chips.

Results and discussion

Light-coupling effects in 2D-semiconductor/microsphere systems. Figure 1 puts into evidence pronounced lensing and strong light-coupling effects when, as is illustrated in Fig. 1a, dielectric microspheres are deposited on top of 2D semiconductors. Figure 1b shows μ -PL spectra acquired in a bulklike (16 nm thick) InSe nanosheet deposited on a SiO₂/Si substrate and partly covered with SiO₂ microspheres (see optical image at the inset of Fig. 1b). The μ -PL spectrum measured in a bare region of the InSe nanosheet shows an emission peak located at 1.24 eV, corresponding to the radiative free-exciton recombination processes occurring at energies reported for bulk InSe^{14,30}. Although it is almost negligible in this spectrum, it is worth mentioning that a weak broad emission is detected at energies higher than 1.45 eV, which stems from the amorphous SiO₂ substrate. Compared to the μ -PL spectrum measured in the bare InSe nanosheet, the one acquired in a point of sample covered with SiO₂ microspheres shows a strong enhancement of the signal intensity (see Fig. 1b and the μ -PL map in its inset) that makes visible even the weak luminescence coming from the SiO₂ substrate. This lensing effect, promoted by the microspheres, is not restricted to bulklike InSe nanosheets. In fact, the use of dielectric microspheres seems to provide for a tool to enhance the usually low-intensity PL signal of atomically thin InSe nanosheets without damaging the sample, as it has been demonstrated for a 2D InSe nanosheet 6.5-nm-thick with an noticeable blueshift of its PL signal due to quantum-confinement effects (See Supplementary Fig. 1)³⁰.

A similar lensing effect is observed in other 2D semiconductors. Figure 1c shows the μ -PL spectra acquired in a monolayer of WSe₂ deposited on a SiO₂/Si substrate, on which a SiO₂ microsphere has been placed (see the optical image at the inset of Fig. 1c). In the bare region of the monolayer of WSe₂, the PL spectrum shows a double-peak structure whose deconvolution has been performed by assuming gaussian-like components^{48,58}. In this way, deconvolution processes have allowed to resolve a main PL peak centered at 1.666 eV, coming from optical recombination of the X⁰ neutral exciton, and a second and broad PL peak centered at 1.640 eV. Such low-energy feature has been usually attributed to recombination of trions, whose observation is hard at room temperature but possible in doped samples (as those used in this work) due to the higher probability of forming charged excitons in these samples than in intrinsic ones^{48,57,59,60}. In line with that observed for InSe nanosheets, the μ -PL spectrum measured in the region of the WSe₂ nanosheet under the SiO₂ microsphere (see also the PL map inserted in Fig. 1c) shows an enhanced intensity signal, compared to that of the bare monolayer.

Clearly, the lensing effect described above is promoted by the difference between air and the microsphere refractive index^{61–63}, increasing the excitation power density on the sample (Fig. 2a, top panel) and consequently enhancing the global PL signal intensity. The lensing effect is not only restricted to the excitation process but extends also to the light-collection process (Fig. 2a, bottom panel). Importantly, this effect tends to enhance the collection of light within the numerical aperture of our optical objective that would be eventually lost in the absence of the microsphere, as the far-field emission from OP dipoles³⁸.

Sensitivity of Whispering Gallery Modes to the orientation of radiating dipoles. Besides the lensing effect, the presence of the

Fig. 1 Photoluminescence response of 2D nanosheets partly covered with SiO_2 microspheres. **a** Illustration of the measurement process of the PL response of nanosheets partly covered by dielectric microspheres. **b** Micro-PL spectra acquired in two points of the 16-nm-thick InSe nanosheet deposited on a SiO_2/Si substrate, which is shown in the optical image in the inset. A certain number of microspheres can be observed in the optical image, as blurred spheres since the image was taking focusing on the nanosheet. The inset includes a PL map acquired in a region of the nanosheet delimited by the red dashed rectangle depicted on the optical image. The PL-signal integrated intensity of each point of the PL map follows the color-code indicated on the right side of the PL map, revealing a clear PL intensity enhancement in the region of the nanosheet covered with microspheres. The two μ -PL spectra shown in the main graph were acquired in each one of the two points marked in the PL map, one in a bare region of the nanosheet (A point) and the other in a point covered by a microsphere (B point). **c** Micro-PL spectra acquired in two points of a monolayer WSe_2 nanosheet deposited on a SiO_2/Si substrate, which is shown in the optical image in the inset. In this case, a microsphere was purposely pushed on top of the WSe_2 nanosheet, which appears on the optical image as a blurred bump. The inset includes a PL map acquired in a region of the nanosheet delimited by the red dashed rectangle depicted on the optical image. As before, the PL map reveals a clear PL intensity enhancement in the region of the nanosheet covered with the microsphere. The two μ -PL spectra shown in the main graph were acquired in each one of the two points marked in the PL map, one in a bare region of the nanosheet (C point) and the other on a point covered by a microsphere (D point). The μ -PL spectrum measured in the C point was deconvoluted into two gaussian components (shown on the graph), one attributed to the neutral exciton X^0 and the other to charged excitons X^C .

Fig. 2 Optical properties of whispering gallery modes in dielectric microspheres. **a** Illustration of the focusing effects of the incident (top panel) and emitted light (bottom panel) produced when a dielectric microsphere is placed on top of an emitting layer. **b** Illustration of an eventual WGM excited by the coupling of emitted light with the modes of the microspherical resonator. **c** Illustration of the two possible orientations of radiative dipoles that may excite WGMs in the dielectric microspheres on top. Red lobes illustrate dipolar far-field intensity in free space. **d** Micro-PL spectra measured in an amorphous SiO₂/Si substrate which contains native radiative centers spread within the SiO₂ overlayer. The μ -PL spectra of these centers have been recorded on points of the SiO₂/Si substrate with and without dielectric microspheres on top (see illustration depicted on the plot). Comparing these two μ -PL spectra, only the one measured in the point covered with a microsphere shows the presence of quasi-equally spaced peaks due to the coupling of the light emitted excitation of WGMs of the microsphere. The lower panel of the plot shows the spectral response response of the normalized power calculated for a dipolar emission coupled to the WGMs of a spherical dielectric microresonator of index of refraction 1.45 and 4.66 μ m in diameter, when these emitting dipoles are IP (purple curve) or OP (orange curve) oriented, as it has been illustrated in **c**. The TM or TE character of each WGMs has been indicated on each resonance peak, as referred to the radial component of the vector field.

microspheres also promotes the appearance of strong resonances in the PL spectrum (see Fig. 1 and Supplementary Fig. 1) which reveal a strong coupling of emitted light from dipoles existing under the dielectric microspheres to modes of the spherical microresonator (Fig. 2b, c). The spectral response of these resonances, called whispering gallery modes (WGMs)^{64–66}, mostly depends on the precise diameter of the microsphere (Supplementary Fig. 2), which may be used to fine-tune the relative weight of desired energy regions of the PL spectrum with respect to others. However, we would like to focus here on a photonic application of these microspheres on nanomaterials (See Supplementary Figs. 3 and 4), connected to the ability of WGMs of dielectric microspheres to provide for a tool to discriminate the OP component, from the IP one, of dipoles underneath (i.e., the luminescent dipoles of the 2D nanosheet), as illustrated in Fig. 2c.

Figure 2d shows the μ -PL spectra measured in the SiO₂/Si substrate, covering the 1.43–1.70 eV energy region where a weak emission from the amorphous SiO₂ overlayer has been detected (Fig. 1b). One of these spectra has been acquired in the bare SiO₂/Si substrate (black continuous line), whereas the other has been recorded in a point of the substrate covered by a SiO₂ microsphere (red continuous line). In this second PL spectrum, the emitted light appears to couple to the WGMs of the microsphere on top, which gives rise to resonances that consist in relatively intense peaks separated to each other every 60–70 meV. Besides, the spectra reveal the additional presence of weak but clear resonances (see, for instance, the one at 1.675 eV) in between the more intense lines. To understand the origin of this pattern of alternating intense and weak resonances, we have calculated the spectral response of a dipolar emission when coupled to the WGMs of a spherical resonator of 4.66 μ m in

diameter, a value close to the nominal diameter of the microspheres ($\sim 5 \mu\text{m}$, Methods section) that allows to nicely reproduce the experimental data. These numerical simulations are based on the treatment developed by Chew⁶⁷, which disregards the effects of the substrate. See Supplementary Fig. 3 for further details about the effects of a realistic environment in the coupled emitter-resonator, as obtained by FEM-based simulations. If we first consider that the dipole is oriented parallel to the z -axis -or OP- (Fig. 2c), its radiated field is expected to couple to a discrete set of transverse magnetic (TM) modes of the spherical resonator (Fig. 2d, orange curve), where the modal electric field is given in terms of the spherical vector wave functions $N_{lm}^{(1)}$, with polar mode number $l = 1, 2, \dots$ and azimuthal mode number $m = 0, \pm 1, \dots, \pm l$.⁶⁸ Note that the magnetic field of the vertical-dipole radiation is azimuthally oriented parallel to $\hat{\phi}$, allowing the electric field of the scattered signal set in terms of the spherical vector wave functions $N_{lm}^{(3)}$.⁶⁹ Peak resonances of the scattered field, labeled as $\text{TM}_{l,n}$ in Fig. 2d (orange curve), are characterized by the solutions to the so-called modal equation and are classified by a radial mode number $n = 1, 2, \dots$. They are thus characteristic from each l th-order TM mode, taking into account a generalized $2l + 1$ mode degeneracy when varying the azimuthal index m .⁶⁷ Nevertheless, due to the location of the electric dipole set along the z -axis, the highly-symmetric scattered fields lead to excitation of only one azimuthal mode $m = 0$ for each polar mode index. In addition, due to the relatively low Q factors associated with the dielectric microspheres, one can only observe peaks in Fig. 2d corresponding to the radial mode $n = 1$ (those with l between 20 and 23).

When tilting the dipole $\mathbf{p}$ from the OP configuration to have an IP dipolar component, excitation of transverse electric (TE) modes in the dielectric resonator starts to be allowed (see Supplementary Discussion 1). Now, the electric field in the resonator includes terms depending on the spherical vector wave functions $M_{lm}^{(1)}$. As a result, a new set of natural frequencies associated with the peaks labeled as $\text{TE}_{l,n}$ will also appear in the spectrum of the scattered electric field accompanied by their corresponding $\text{TM}_{l,n}$ ones, involving the spherical vector wave functions $M_{lm}^{(3)}$. The relative coupling strength of TM and TE modes depends on the tilting angle of the dipole. If the dipole is fully IP oriented (Fig. 2c), the coupling strength to $\text{TE}_{l,n}$ modes is significantly higher than to their corresponding $\text{TM}_{l,n}$ ones (Fig. 2d, purple curve). However, in comparison with the TM modes excited by the OP dipoles, both TM and TE modes excited by IP ones are less intense (Fig. 2d). In this case, note that the excited azimuthal modes with TE and TM polarization are now $m = \pm 1$ exclusively^{67,69}. On the contrary, the radial index $n = 1$ of the observed peaks is maintained unaltered here.

The nice match observed between experimental and simulation results summarized in Fig. 2d reveals a clear preference of WGMs in dielectric microspheres to couple to light emitted from OP dipoles in detriment of that from IP ones. Naturally, this selective behavior of WGMs provides for an easy, fast, and powerful method to detect the presence of OP dipoles in an emitting 2D layer. Furthermore, the observation of WGMs at a particular energy of the PL spectrum can be considered as a fingerprint of the ability of the emitted photons to propagate along a planar structure, somehow represented by a dielectric microsphere. Since each kind of radiative excitonic complex (free-exciton, trion, bi-exciton, etc) can be identified by its transition energy, the spectral distribution of WGMs in the PL spectrum would allow to identify and select, among all excitonic complexes of a system, the optimal candidates to be implemented in optoelectronic devices designed to operate in a particular planar configuration.

Out-of-plane component of luminescent dipoles in InSe nanosheets and WSe₂ monolayers evidenced by and Whispering Gallery Modes. The method proposed above, to disentangle the OP component of radiative excitonic complexes and detect their potential ability to couple its light to horizontal devices, has been applied to 2D materials with promising applications in optoelectronics, photonics, and quantum communications. InSe and WSe₂ can be considered as paradigm systems which give rise to 2D semiconductors and devices with a completely different orientation of their respective free neutral excitons. Luminescent free excitons of 2D InSe have been recently demonstrated to be OP whereas those of monolayer WSe₂ are IP^{13–15}. With the aim to emphasize the effects of the microspheres on the PL response of these kind of nanosheets, we show, in the middle panels of Fig. 3a, b, the ratio between the μ -PL spectra acquired in a point of the nanosheet under the microspheres and in another of the bare one, for the 16-nm-thick InSe nanosheet and the monolayer WSe₂ already described in Fig. 1, respectively. For the sake of clarity, top panels of Fig. 3a, b show again the original μ -PL spectra acquired in each one of these nanosheets and bottom panels display the spectral response calculated for IP and OP dipolar emission eventually coupling to the WGMs of a spherical resonator of $4.69 \mu\text{m}$ in diameter, within the energy range enclosed by the PL response of each nanosheet, respectively. Results summarized in Fig. 3 reveal a different behavior of the excitation of WGMs, depending on the nanosheet probed. The PL intensity ratio obtained for the 16-nm-thick InSe nanosheet (Fig. 3a, middle panel) shows an approximately constant enhancement factor of 4–5, in the energy range comprising the PL peak (1.20–1.35 eV), due to the lensing effect. Overlapped with this basement line, the spectrum shows clear and pronounced resonances at the energy positions expected for light coupling to the WGMs of the microspheres when the emitter is, precisely, an OP dipole (Fig. 3a, bottom panel). A similar behavior arises for thinner InSe nanosheets (Supplementary Fig. 1), although the microsphere used in this experience was slightly bigger (of $4.80 \mu\text{m}$ in diameter). These results support previous works reporting the OP orientation of radiative free excitons in InSe¹⁴, and allow us to conclude, by the relatively simple method used here, that radiative recombination processes of OP free excitons conform the whole room-temperature PL spectrum of InSe nanosheets. The dominant OP orientation of dipoles responsible for the room-temperature PL signal of InSe contrasts to these observed for monolayer WSe₂ (Fig. 3b). Unlike InSe, the magnification of the PL signal promoted by the microspheres as well as the excitation of WGMs resonances tend to concentrate in the low-energy side of the PL spectrum of monolayer WSe₂ (Fig. 3b, middle panel), being both effects strongly reduced at the energies of the main PL peak. In fact, the excitation of WGMs becomes particularly strong at light-emission energies as low as $\sim 1.50 \text{ eV}$ (see inset at the top panel of Fig. 3b), far beyond the energy range usually observed for radiative recombination of free excitons in monolayer WSe₂ at room temperature (Fig. 1c). Therefore, as occurs for InSe, WGMs resonances in the WSe₂ monolayer appear to be excited by its OP dipoles (Fig. 3b, bottom panel). These results reflect that, as reported, luminescent free-excitons of monolayer WSe₂ are strongly IP^{13–15}. However, light emitted from the recombination of trions, which notably contribute to the low-energy side of the PL spectrum of monolayer WSe₂ (Fig. 1c), has a relevant OP dipolar component that promotes its coupling to the WGMs of the microspheres.

Optical selection rules of in-plane and out-of-plane radiating dipoles. The electronic states at the bandgap of monolayer WSe₂ are majorly tungsten d-orbitals and the spin-orbit interaction is

Fig. 3 Revealing the OP orientation of dipoles by the excitation of WGMs of dielectric microspheres. Top panels: μ -PL spectra acquired in the **a** 16-nm-thick InSe nanosheet and **b** monolayer WSe₂ which have been already shown in Fig. 1b, c, respectively. Middle panels: intensity ratio between the PL spectra shown in their respective top plots, which evidence the coupling of emitted light to the WGMs of dielectric microspheres. Bottom panels: spectral response calculated for a dipolar emission coupled to the WGMs of a spherical microresonator of 4.69 μ m in diameter, when these emitting dipoles are IP (purple curve) or OP (orange curve) oriented. The TM or TE character of each WGMs has been indicated on each resonance peak.

strong, resulting in optical selection rules with IP and OP emission dipoles of distinct intensities (see the Supplementary Discussion 3 for discussion of the optical selection rules)^{38,55}. In order to quantify the luminescent dipoles in monolayer WSe₂ we have calculated the exciton states for IP and OP polarized light. Figure 4a, b show the band structure of monolayer WSe₂ calculated along the M-K- Γ high-symmetry directions, indicating the electronic transitions relevant for the absorption of IP and OP light and the optical absorption including excitonic effects, respectively. The dark X_z^0 and bright X^0 exciton transition energies are marked with blue and red vertical lines, separated by 69 meV. In contrast to InSe, the optical selection rules have the origin in the spin-orbit interaction^{70,71}. The strong effect of the spin-orbit interaction is evidenced by looking at the wave functions of excitons X_z^0 and X^0 in Fig. 4d. The excitonic wave function depends on the electron and hole position. In these calculations, we fix the hole position near the W atom and the resulting electronic density is displayed, with the X_z^0 excitonic configuration showing a higher electron density on the Se atoms that is responsible for its OP orientation component. Moreover, each exciton X^0 and X_z^0 has an associated trion family (X^c and X_z^c ,

respectively) that inherits the optical selection rules (see Fig. 4c)⁷², whose recombination results in a broad PL-band at the energy of the peak around 1.640 eV, as shown in Fig. 1c, due to the coupling of light to both to IP and OP dipoles. These facts arise trions as the main source of OP light able to excite WGMs of dielectric microspheres.

Conclusions

To summarize, we have demonstrated a spectroscopic method that enables the identification of the out-of-plane component of radiating dipoles. This would allow to identify, at any temperature, potential sources for radially polarized light in monolayer transition-metal dichalcogenides, which may have applications in imaging, phase modulation, and diffractive optics, due to the cylindrical symmetry of their light. Also, this method opens up new routes for the realization of planar devices efficiently exploiting the fundamental properties of atomically thin materials. The technique does not require magnetic fields and can be easily implemented, making it accessible, versatile, and technologically relevant. To evidence the effectiveness of this technique, we have performed a spectroscopical analysis of the luminescent

Fig. 4 Optical selection rules for excitons and trions. **a** Band structure of monolayer WSe₂ calculated by using LDA along the M-K-Γ high-symmetry direction. The color code indicates the spin projection of each band. The width indicates the contribution of each band, at the K-point, to the excitonic wavefunction of the excitons X⁰ (IP transition) and X_z⁰ (OP transition). **b** Optical absorption for IP and OP configurations, in logarithmic scale. The ground excitonic states of each spectra are denoted as X⁰ and X_z⁰. **c** Scheme of energy levels of excitons and trions. The trions X^c and X_z^c inherits the optical selection rules of the excitons X⁰ and X_z⁰, respectively. **d** Wave functions of the excitons X⁰ and X_z⁰. The position of the hole is fixed (pink sphere) near the W atom and we represent the electronic density. The maximum is set to 1 and we fix the isosurface value to 0.1 for both wave functions.

signal of InSe nanosheets and monolayers of WSe₂. This study evidences that excitonic complexes with binding energies larger than that of the room-temperature free-excitons by even 150 meV (such as trions) have an important out-of-plane dipolar orientation, which makes them suitable candidates for their incorporation into planar devices with potential applications for information processing and on-chip communications. Interestingly, the wide energy range observed here for optical transitions in monolayer WSe₂ at room temperature with an important out-of-plane dipolar component also corresponds to the region where quantum emitters are usually observed at low temperature. Results reported here suggest that quantum light from these emitters are expected to efficiently couple into photonic chips to develop optimal quantum devices based on two-dimensional semiconductors.

Methods

Sample Preparation. InSe and WSe₂ 2D nanosheets have been micromechanically exfoliated using the well-known scotch-tape technique. InSe monocrystals used here to prepare the nanosheets were cleaved perpendicular to the (001) direction from an ingot grown by the Bridgman method from a nonstoichiometric In_{1.05}Se_{0.95} melt. To act as n-dopant, tin, in a content 0.01%, was introduced previously to growth. From these ingots, thin n-doped InSe samples were cleaved and used to prepare atomically thin InSe nanosheets. InSe samples have been then directly transferred onto Si substrates coated with 285 nm of SiO₂, previously cleaned with acetone, ethanol and isopropanol in an ultrasound bath.

p-doped bulk WSe₂ (from HQgraphene) has been used here to obtain WSe₂ nanosheets, which were obtained by a micromechanical exfoliation method to a polydimethylsiloxane (PDMS) stamp. Monolayers of WSe₂ were distinguished from thicker ones by means of their PL emission at room temperature and then transferred onto the Si/SiO₂ (285 nm) cleaned substrates through the all-dry viscoelastic technique. The samples have been identified via optical contrast using a Zeiss Axio Scope.a1 microscope with an Axiocam ERc 5s camera.

SiO₂ microspheres solved in H₂O (from Sigma-Aldrich) have been used, with a nominal diameter of 5 μm (4.83 ± 0.19 μm). To have a sparse concentration of these microspheres in solution, different aliquots in ethanol were prepared, and dropped onto the exfoliated substrates via spin coating, after which high vacuum is applied to force evaporation and avoid H₂O residues. In the case of monolayer WSe₂ nanosheets, microspheres in their surroundings were shoved until precisely placed on top of the nanosheets, by using a tip probe attached to the transfer setup micromanipulators.

Micro-Photoluminescence measurements. Micro-Photoluminescence measurements have been performed in a Horiba Scientific Xplora micro-Raman system using a 532-nm CW excitation laser, not exceeding 70 μW of power in 7 s acquisition time measurements in InSe and 10 μW in 1 s acquisition time measurements in WSe₂ to prevent overheating. The optical excitation and collection spots are typically around 1 μm².

Numerical calculations. In order to calculate numerically the WGMs of the spherical microresonator, we used the COMSOL Multiphysics modeling software based on the FEM. A unit point dipole pointing to the center of the microsphere (OP dipole) or oriented perpendicularly (IP dipole) was introduced in our frequency-domain model through the RF module. To block troublesome reflections from outer boundaries of the computational domain, a perfectly matched layer of one-wavelength thickness surrounding the photonic structure was implemented. The power emitted by the electric point dipole in the presence of the sphere (P) and isolated dipole (P₀) were calculated by considering the power flux through a small-scale closed surface surrounding the emitter.

The optical absorption of monolayer WSe₂ has been computed within the framework of the Bethe-Salpeter Equation, as implemented in Yambo code⁷³. The input of the BSE are the electronic states of WSe₂, calculated using density functional theory within the local-density approximation with the code Quantum Espresso⁷⁴. We use fully relativistic pseudopotentials with semicore electrons for W. The simulations of the excitonic states have been performed in a 15 × 15 × 1 k-grid including 2 valence and 2 conduction bands. The vacuum distance between two periodic images is 30 Bohr.

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request. Correspondence and requests for materials should be addressed to J.F.S.R.

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Author contributions

J.P.M.P. and J.F.S.R. conceived the study. D.A.P. performed experiments and analysis of experimental data. M.K. and C.J.Z.R. performed computational analyses and simulations

on whispering gallery modes. A.M.S. performed ab initio computational analyses and simulations and contributed to theoretical descriptions. D.A.P. and J.F.S.R. wrote the manuscript, with extensive inputs from A.M.S., C.J.Z.R., and the rest of authors.

Competing interests

All authors declare no competing interests.

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