Chemical Tuning on Resonance Coupling in Gold Nanorod–Monolayer WS$_2$ Heterostructures

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Resonance coupling between plasmonic resonances in metallic nanostructures and excitons in two-dimensional (2D) semiconductors has attracted much recent attention. The 2D semiconductor excitons are sensitive to external stimulus, enabling active tuning on the resonance couplings by physical, such as applying electrostatic gating, thermal scanning, etc., or chemical approaches. Among the others, chemical tuning approach has the advantage of facile implementation, high efficiency, and being capable of large-area tuning. Here, we report on chemical tuning of resonance coupling in heterostructures consisted of individual gold nanorods integrated with monolayer WS$_2$. We showed that by incubating the heterostructures into a bis (trifluoro-methane) sulfonimide (TFSI) solution, the exciton transition strength of the WS$_2$ will be enhanced significantly. As a result, the resonance coupling in the heterostructures evolved from a weak coupling regime to a strong coupling one, with the mode splitting energy increases from 94.96 to 105.32 meV. These findings highlight the potential of chemical treatment as an efficient technique for tailoring the interactions between plasmonic nanostructures and 2D semiconductors.

Keywords: WS$_2$, resonance couplings, gold nanorods, plasmon resonances, chemical tunings

INTRODUCTION

Resonance coupling refers to interactions between quantum emitters and optical cavity with spectrally overlapped resonances, which has great potentials in a variety of applications such as low-threshold lasers, ultrafast optical switches, as well as quantum information processings (Chen et al., 2013; Sanvitto and Kéna-Cohen, 2016; Baranov et al., 2018; Zheng et al., 2020; Huang et al., 2021). Basically, the resonance coupling is usually characterized by the coupling strength $g$ (Liu et al., 2017).

$$g = \frac{\hbar \omega_c}{\sqrt{2 \hbar \varepsilon_0 \varepsilon_a V_{\text{eff}}}} \mu_c \cdot \hat{F}_d (r_c)$$

where $V_{\text{eff}}$ is the effective mode volume of the cavity, $\mu_c$ and $r_c$ are the dipole moment and location of the emitter, respectively, and $\hat{F}_d (r_c)$ is the normalized electric field of the optical cavity at the emitter. A small effective mode volume and a strong transition dipole moment are therefore necessary for initiating strong resonance coupling of the system. Accordingly, resonance coupling between plasmonic metal nanostructures and 2D transition-metal dichalcogenides (TMDCs) has recently attracted considerable attention. On one hand, the metal nanostructures, such as nanospheres, nanorods, nanowires, are optical nanocavities exhibiting localized surface plasmon resonances (LSPRs) (Kleemann et al., 2017; Wen et al., 2017; Zheng et al., 2017; Jiang et al., 2020). The LSPRs can...
confine the free-space electromagnetic fields down to the nanoscale and generate ultrasmall mode volumes. On the other hand, many TMDCs sustain excitons with strong binding energies and transition dipole moments at room temperature. Furthermore, their excitons are sensitive to external stimulus (Ramasubramaniam, 2012; Chernikov et al., 2014; Schneider et al., 2018). Therefore, the resonance coupling between LSPR and excitons in TMDCs can be remarkably enhanced as well as actively controlled (Zheng et al., 2019; Sun et al., 2021; Yang et al., 2021). In particular, in comparison to other types of TMDCs, the monolayer WS$_2$ is a direct bandgap semiconductor with strong spin–orbit coupling, making their exciton binding energy and transition dipole moment large at room-temperature. Moreover, with high surface-to-volume ratio and tunable electrical properties, the monolayer WS$_2$ has a wide range of applications in sensor and photodetector (Han et al., 2019; Han et al., 2021; Luo et al., 2021). It has therefore been widely employed as quantum emitters for studying of strong light–matter interactions in different types of micro- and nanocavities (Supplementary Table S1).

Currently, the control over resonance coupling between LSPRs and TMDCs excitons focuses on two aspects. The first one is by adjusting the LSPRs characteristics through tuning the composition, size, morphology, and the surrounding dielectric environment of the metal nanostructures (Liu et al., 2016; Lee et al., 2017; Kleemann et al., 2017; Wen et al., 2017; Zheng et al., 2017; Han et al., 2018; Stührenberg et al., 2018; Wen et al., 2018; Wang et al., 2019a; Chen et al., 2019; Geisler et al., 2019; Hou et al., 2019; Jiang et al., 2020; Yankovich et al., 2019; Qin et al., 2020) (see the summary on resonance coupling in different LSPR nano-/microcavity–TMDCs hybrid systems, Supplementary Table S1). The other one is by applying external stimulus to modulate the exciton behaviors of the TMDCs (Supplementary Table S1). In both ways the spectral overlap between the LSPRs and exciton transitions will be modified, and consequently the resonance coupling strengths can be tailored. In comparison with the first one, modulating resonance coupling by tuning the 2D excitons are more favorable, because the exciton transitions can be dynamically controlled in response to the external fields. For example, previous studies were able to demonstrate control of the resonance coupling strength by electrical gating and thermal scanning (Liu et al., 2016; Wen et al., 2017; Lee et al., 2017; Abid et al., 2017; Cuadra et al., 2018) (Supplementary Table S1). Chemical tuning by incubating the heterostructures into the TFSI solution, the transition dipole moment of the WS$_2$ exciton can be strongly enhanced. This will strengthen the resonance coupling and give rise to a mode splitting energy of 105.32 meV. Such a value suggests that the resonance coupling has approached the strong coupling regime. The observed increments in mode splitting and associated enhancement of exciton transition dipole moment are in good agreement with calculated results using coupled oscillator model (COM).

**EXPERIMENTAL**

**Chemicals and Materials**

H$\text{AuCl}_4$·3H$_2$O (Au > 99.9%) was purchased from Aladdin (Shanghai, China). TFSI (95%) was purchased from Macklin (Shanghai, China). Cetyltrimethylammonium bromide (CTAB: >99%), silver nitrate (AgNO$_3$; >99%), sodium oleate (NaOL; >97%), and t-ascorbic acid (AA; >99%) were purchased from Sigma-Aldrich. Sodium borohydride (NaBH$_4$; >96%) was purchased from Acros Organics (Shanghai, China). The HCl (37 wt% in water) is of analytical grade, which was purchased from Aladdin (Shanghai, China). Monolayer WS$_2$ was grown directly onto a silicon substrate capped with a 300-nm thick oxide layer (Nanjing MKNANO Tech. Co., Ltd.). All chemicals were used without further purification. Deionized water (18.2 MΩ cm) was used during the preparations of the gold nanorods and heterostructures.

**Sample Preparations**

Gold nanorods were grown using a seed-mediated method with binary surfactant mixture (Ye et al., 2013; Zhuang et al., 2018; Xu et al., 2020). The seed solution was prepared by mixing 2.5 ml HAuCl$_4$ (0.5 mM) and 2.5 ml CTAB (0.2 M) solution in a 30-ml glass vial. Then 0.3 ml NaBH$_4$ solution (0.01 M) was added to the mixture under vigorous stirring for 2 min until the color of the solution changed from yellow to brownish yellow. The seed solution was aged at room temperature for 30 min before use. To prepare the growth solution, 0.9 g of CTAB and 0.1234 g of NaOL was dissolved in DI water (~50°C) in a 25 ml glass conical flask, kept undisturbed for 15 min at 27°C after adding AgNO$_3$ solution (2.4 ml, 4 mM). Subsequently, HAuCl$_4$ (25 ml, 1 mM) was added to the solution and stirred for 90 min. A certain amount of HCl solution was added to the growth solution and stirred for 15 min to adjust the PH. Afterwards the AA solution
(0.125 ml, 0.064 mM) was added with vigorous stirring for 30 s. A certain amount of the prepared seed solution was injected into the growth solution under vigorous stirring for 30 s. The mixture was then left undisturbed for 12 h for the growth of the gold nanorods. The aspect ratio of the nanorods can be continuously adjusted by varying the amounts of the seed solution as well as pH of the growth solution (Jiang et al., 2020).

To fabricate the heterostructures, the monolayer WS₂ was first transferred onto another SiO₂ substrate for releasing the stress (Gurarslan et al., 2014; Xu et al., 2015; McCreary et al., 2016). Specifically, a layer of poly styrene (PS) was spin-coated (3,300 rpm, 1 min) onto the as-grown WS₂, followed by a baking process at 120°C for 1 h. After scribing the PS film with a scalpel, the sample was placed into DI water to lift off the PS film adhered with the WS₂ monolayer from the SiO₂/Si substrate. The PS film was then placed onto the target SiO₂ substrate. Afterwards, the PS film was removed with toluene solution after baking the sample at 120°C for 1 h. The heterostructures were formed by drop-casting gold nanorod aqueous solutions with different nanorod aspect ratios onto the transferred monolayer WS₂ flake.

**Chemical Treatment**

Certain amounts of TFSI were dissolved into 20 ml acetone to make TFSI solutions with different concentrations. The SiO₂ substrates with the gold nanorods and heterostructures were incubated into the TFSI solutions for different 30 s. Afterwards, the substrate was taken out from the TFSI solution and annealed on a hot plate at 50°C for 1 min.

**Characterizations**

Raman and photoluminescence (PL) spectra were measured using a micro-Raman spectrometer (inVia Reflex, Renishaw). The samples were excited by a laser of 532 nm. Extinction spectra of the aqueous gold nanorod samples with different aspect ratios were measured on a UV/visible/near-infrared spectrophotometer (U-4100, HITACHI). Atomic force microscopy (AFM, NTegra Spectra, NT-MDT) was employed to characterize the morphologies and thicknesses of the samples. The scattering spectra of the various individual gold nanorods and heterostructures were recorded on a home-built dark-field microscope. The microscope consists of an optical microscope (Olympus BX51) integrated with a broadband white light source, a monochromator (Acton SpectraPro 2,360), and a charge-coupled device camera (Princeton Instruments Pixis 400BR_eXcelon). During the measurements, the CCD was coupled device camera (Princeton Instruments Pixis 400BR_eXcelon). During the measurements, the CCD was employed to both illuminating the heterostructures and collecting the scattered light.

**Numerical simulations**

Scattering spectra of the individual gold nanorods and heterostructures were simulated using the finite-difference time-domain (FDTD) method. A single gold nanorod was modeled as a cylinder capped with a hemisphere at each end. The monolayer WS₂ was modeled as dielectric layer with a thickness of 1 nm. An individual heterostructure is constructed by placing a gold nanorod onto the WS₂ layer, with a gap of 1 nm in between (Wen et al., 2017; Jiang et al., 2020). The bulk dielectric function of the gold was used (Johnson and Christy, 1972). The dielectric function of the pristine and TFSI treated monolayer WS₂ was modeled using the Lorentzian model (Yilei et al., 2014), with parameters determined from their PL spectra (see the discussion below). A dielectric constant of 2.25 was used for the SiO₂ substrate. The diameters of the gold nanorods were set from 34.48 to 61.93 nm, and the lengths were varied from 77.26 to 125.60 nm. These parameters correspond to nanorod aspect ratios ranging from 1.47 to 2.66. All of the nanorods and heterostructures were excited by a linearly polarized plane wave, with the polarization along the longitudinal axes of the nanorods. Mesh size of 0.5 nm was set around the nanorods.

**RESULTS AND DISCUSSION**

The as-prepared gold nanorods have uniform size and shape distributions (Figure 1A; Supplementary Figure S1), where two types of LSPR modes can be observed from their extinction spectra (Figure 1B; Supplementary Figure S1M). They are the transverse (TPM) and longitudinal (LPM) LSPR modes, which are associated with electron oscillations along the transverse and longitudinal directions of the nanorods, respectively. In our study, the LPM is considered because its resonance wavelengths (frequencies) can be synthetically tuned by tailoring the aspect ratio of the gold nanorods (Figure 1B; Supplementary Figure S1M), which is defined as the nanorod length divided by the diameter (Chen et al., 2013). The commercial monolayer WS₂ flake was grown by chemical vapor deposition (CVD) method, where an intrinsic tensile strain exists between the flake and SiO₂ substrate (McCreary et al., 2016). Such a strain can significantly suppress the exciton transition of the WS₂. Therefore, the monolayer WS₂ was first transferred to another SiO₂ substrate to release the tensile strain (Figure 1I) (Gurarslan et al., 2014; Xu et al., 2015). The thickness of the transferred WS₂ flake can be determined by AFM topography, which is 1.0 nm as shown in Figures 1C,D. The monolayer WS₂ exhibits two evident Raman peaks at 352 cm⁻¹ and 419 cm⁻¹ (Figure 1E), which correspond to the E₂g and A₁g modes of WS₂, respectively (Cong et al., 2014). In addition, 2D Raman intensity mapping (monitored at 352 cm⁻¹) across the entire flake is uniform, indicating a good crystallinity of the monolayer WS₂ (Figure 1F). The exciton luminescence of the monolayer WS₂ was characterized by PL spectroscopy. As shown in Figure 1G, the pristine monolayer WS₂ exhibits a PL peak at 2.016 eV (615 nm), with a linewidth (hυ/ex) of 95.1 meV. The PL intensity mapping across the entire flake reveals excellent uniformity of the exciton transition (Figure 1H).

To construct the heterostructures (Figure 1I), gold nanorods were centrifuged twice to remove the capping agents CTAB and redispersed into deionized water. Afterwards, gold nanorods with different aspect ratios were mixed and drop-casted respectively onto a clean SiO₂ substrate and the monolayer WS₂ flake that was transferred onto another SiO₂ substrate (Figure 1I). The concentration of the nanorod solution was controlled to
ensure sparse nanorod distribution onto the SiO$_2$ substrate and WS$_2$ flake (Figure 1K), enabling subsequent characterizations of an individual heterostructure (Figure 1L). Due to the organic residues surrounding the nanorod, the spacing between the nanorod and WS$_2$ surface (or the clean SiO$_2$ substrate surface) is ~1 nm.

Chemical treatment was realized by incubating the heterostructures into TFSI solutions (Figure 1I). To ascertain
the optimum TFSI concentration \( C_{\text{TFST}} \) for the incubation, a typical monolayer WS\(_2\) flake was subjected to chemical incubation with different \( C_{\text{TFST}} \), whereby its PL spectra was measured and compared. The incubation time is set as 30 s. In comparison with the pristine WS\(_2\) monolayer, those experiencing TFSI incubations exhibit evidently enhanced PL intensity (Supplementary Figure S2A–S2F). In addition, the chemical treatment also affects the PL spectral shape of the WS\(_2\) (Supplementary Figure S2G). The modifications of the PL intensity and spectra are dependent on the \( C_{\text{TFST}} \). Specifically, the peak intensity of the PL increases steadily and reaches a maximum at a \( C_{\text{TFST}} \) of 3 mg/ml (Supplementary Figure S2H). Afterwards, the PL intensity reduces as the \( C_{\text{TFST}} \) is further increased. To quantify the exciton emission of the monolayer WS\(_2\) upon TFSI incubation, the PL spectra were fitted using a lineshape of,

\[
I = F \frac{h\gamma}{4(h\omega - h\omega_{\text{ex}})^2 + (h\gamma)^2}
\]

where \( F \) and \( h\gamma \) are respectively scale factor and the PL spectrum linewidth. In particular, \( F \) is proportional to exciton transition dipole moment, while \( h\gamma \) is proportional to the damping rate of the exciton. \( h\omega_{\text{ex}} \) is the exciton transition energy. As shown in Supplementary Figure S2I, the PL spectra of the pristine WS\(_2\) and WS\(_2\) flake incubated in TFSI solution of 0.1 mg/ml can be well described using \text{Eq. 2}. By applying \text{Eq. 2} to fit the spectra shown in Supplementary Figure S2G, it can be clearly seen that the extracted \( h\omega_{\text{ex}} \) (\( h\gamma \)) first increases (decreases) and then
Figure 3 | Resonance coupling in individual gold nanorod–WS₂ heterostructures. (A) Scattering spectra of an individual gold nanorod (upper), PL spectra of the monolayer WS₂ (middle), and scattering spectra of an individual heterostructure (lower). (B) DF scattering spectra from different individual heterostructures. Left panel: pristine heterostructures. Right panel: heterostructures upon 0.1 mg/ml-TFSI incubation. Numbers next to the curves indicate the aspect ratios of the gold nanorods in the heterostructures. (C) Scattering peaks as a function of the detuning energy between the LPM and exciton transition energy. Upper panel: pristine heterostructures. Lower panel: heterostructures upon 0.1 mg/ml-TFSI incubation. The horizontal and diagonal black dashed lines indicate the exciton transition energy and LPM energy, respectively. The colored symbols are extracted from the scattering spectra shown in (B). The colored dashed lines are polynomial fittings.

The resonance coupling in the various individual plasmonic nanostructures was characterized using single-particle DF scattering spectroscopy, which can rule out the average effect from the ensemble measurements (Zengin et al., 2015; Santhosh et al., 2016; Cuadra et al., 2018; Stührenberg et al., 2018). Figure 3A (upper panel) shows DF scattering spectrum from a typical gold nanorod with an aspect ratio of 1.75, where a well-defined peak centering at 2.03 eV can be observed. The scattering maximum corresponds to LPM of the nanorod, which is in resonance with the exciton emission of the WS₂ (2.016 eV) (Figure 3A, green curve in middle panel). Upon formation of the heterostructure, the DF scattering spectrum was modified significantly due to the resonance coupling between the LPM and exciton transition. Two scattering maxima separated by a spectral dip corresponding to the exciton transition energy of WS₂ can be observed (Figure 3A, blue curve in the lower panel). Moreover, the two scattering peaks are strongly dependent on the detuning energy defined as \( \Delta = \hbar \omega_{\text{pl}} - \hbar \omega_{\text{ex}} \), with \( \omega_{\text{pl}} \) the LPM energy. Specifically, when \( \Delta < 0 \), i.e., the LPM energies is smaller than the exciton transition energy, the low-energy peak is stronger than the high-energy one (Figure 3B, left panel). As \( \Delta \) is increased and larger than 0, the high-energy peak becomes dominated. In addition, both of the two peaks blue-shifted with increasing LPM energies (reducing aspect ratios), where an anti-crossing behavior can be clearly observed on the scattering spectra from heterostructures with different nanorod aspect ratios (Figure 3B, left panel).
Numerical FDTD simulations were then employed to verify the experimental findings. To that end, simulation architectures were set according to the SEM images of the individual gold nanorods and various heterostructures. A pivotal parameter employed in the simulations is the dielectric function of the pristine and TFSI treated monolayer WS₂. In our study, the Lorentzian model was used to describe the dielectric functions of the pristine and TFSI treated monolayer WS₂. Specifically, the dielectric function can be expressed as (Yilei et al., 2014),

\[
\varepsilon = \varepsilon_{\infty} - \frac{f \omega_{ex}^2}{\omega^2 - \omega_{ex}^2 + i\omega\gamma_{ex}}
\]

(3)

where \(\varepsilon_{\infty} = 18.1\) is the high-frequency permittivity (Yilei et al., 2014). For the pristine and TFSI treated WS₂ flakes, \(\omega_{ex}\) and \(\gamma_{ex}\) are respectively adopted from the fittings of the corresponding PL spectra using Eq. 2 (Supplementary Figure S4 and Supplementary Table S2). Parameter \(f\) is the oscillator strength that is related to the exciton transition dipole moment. For the pristine WS₂, \(f\) is set as 0.523 (Yilei et al., 2014), while for the TFSI treated WS₂, it is calculated according to \(f = 0.523 F'/F_0\), with \(F_0\) and \(F'\) the scale factors of the WS₂ before and after incubation in 0.1 mg/ml TFSI solution (Supplementary Table S2). The dielectric functions of the pristine and TFSI-treated WS₂ calculated by Eq. 3 are shown in Supplementary Figure S4, which exhibit similar lineshapes. However, due to the strengthened exciton transition dipole moment by the chemical treatment, the \(f\) is enlarged by 1.53 times, giving rise to enhancement of the magnitudes for both of the real and imaginary parts (Supplementary Table S2).

With the knowledge of \(\varepsilon\), the scattering spectra of the various structures are readily calculated. As shown in Figure 4A (upper and middle panels), the simulated scattering spectra of an individual gold nanorod (with an aspect ratio of 2.04) and the associated heterostructure can well-reproduce the experimental spectra (Figure 3A, upper and lower panels). Additionally, the simulated spectral evolutions against the \(\Delta\) for the various heterostructures agree well with the experimental ones (Figure 4B, left panel). Anti-crossing behavior can also be identified from the simulated scattering spectra. It should be noted that there is a discrepancy on the scattering dip position between the experimental measurements and simulations. This can be understood because the dielectric function of the WS₂ used in the simulations was measured on samples obtained by mechanical exfoliation, while the monolayer WS₂ employed in the measurements was grown by the CVD method. It is known that the \(\omega_{ex}\) can vary between the CVD-grown and exfoliated samples (Amani et al., 2014; Krustok et al., 2017), giving rise to differences in the corresponding dielectric functions.

The dependence of the two scattering peaks on the \(\Delta\) was further investigated. As shown in Figure 3C (upper panel), the two peaks always exist when the \(\Delta\) is tuned from negative to positive values. In addition, the two peaks show a distinct anti-crossing behavior against \(\Delta\) (Figure 3C, upper panel), featuring the occurrence of the resonance coupling. The energy difference (\(\hbar\Omega\)) between the two scattering maxima at zero detuning characterizes the coupling strength (see the following discussion) (Baranov et al., 2018; Törnä and Barnes, 2015). With the knowledge of \(\hbar\Omega\), the regime of the resonance coupling (i.e., weak coupling, moderate coupling, or strong...
coupling) can be ascertained. As shown in Figure 3C (upper panel), the $\Omega$ can determined as 94.96 meV. Such a value is smaller than $(h\gamma_{pl}+h\gamma_{ex})/2$ (123.78 meV) (Supplementary Table S3), suggesting that the resonance coupling between the LPM and WS$_2$ exciton is a Fano interference process, i.e., a weak coupling regime (Wu et al., 2010; Leng et al., 2018).

The TFSI treatment can enhance the excition transition dipole moment as well as reduce the damping of the exciton (middle panel of Figure 3A and Supplementary Figure S4A). These can in turn affect the dielectric function and thereafter the resonance coupling between the LPM and WS$_2$ exciton. As shown in Figure 3A (lower panel), the intensity ratio between the two scattering maxima in the incubated sample (orange) is distinctly different from that of the pristine sample (blue). The chemical tuning on the resonance coupling can be manifested more evidently from the evolution of the scattering spectrum against the nanorod aspect ratio. As shown in Figure 3B (right panel), for the incubated heterostructures, the energy differences between the two scattering peaks become larger for the incubated sample as compared to those of the pristine counterparts (Figure 3B, left panel). In addition, the spectral dip corresponding to the excition transition also becomes deeper. The experimental spectral shapes and evolvements of the incubated heterostructures agree well with the simulated results (Figure 4A, lower panel and Figure 4B, right panel).

Most importantly, the $h\Omega$ deduced from the anti-crossing curves increases to 105.32 meV after the chemical treatment. Such a value is a bit larger than $(h\gamma_{pl}+h\gamma_{ex})/2$ (104.6 meV) (Supplementary Supplementary Table S3), indicating that the resonance coupling has approached the strong coupling regime (Liu et al., 2015; Törmä and Barnes, 2015). The two scattering peaks can thereafter be ascribed to occurrence of mode splitting.

To further discuss the underlying physics governing the chemical tuning of the resonance coupling, mode analyses on the simulated scattering spectra were performed using a coupled oscillator model (COM). The COM is widely employed for analyzing resonance coupling between quantum emitters and plasmonic nanostructures (Wu et al., 2010; Leng et al., 2018; Wang et al., 2019b). Specifically, the scattering spectrum of an individual gold nanorod–monolayer WS$_2$ heterostructure can be written as (Wu et al., 2010; Wang et al., 2019b),

$$
\sigma_{\omega}\propto \omega^2 \frac{\left(\omega^2 - \omega_{pl}^2 + i\omega\gamma_{pl}\right)\left(\omega^2 - \omega_{ex}^2 + i\omega\gamma_{ex}\right) - 4\omega^2 g^2}{\left(\omega^2 - \omega_{pl}^2 + i\omega\gamma_{pl}\right)\left(\omega^2 - \omega_{ex}^2 + i\omega\gamma_{ex}\right) - 4\omega^2 g^2}
$$

where $g$ is the coupling strength between LPM and WS$_2$ exciton. For zero detuning, i.e., $\omega_{pl} = \omega_{ex}$, the heterostructure exhibits two eigenstates with energies (frequencies) as,

$$
\omega_{\pm} = \omega_{ex} \pm \frac{i\gamma_{pl} + i\gamma_{ex}}{2} \pm \sqrt{g^2 - \frac{(\gamma_{pl} + \gamma_{ex})^2}{16}}
$$

The two eigenstates are manifested as the two scattering peaks in the DF scattering spectra. Therefore, the energy difference between the two scattering peaks at $\Delta = 0$ can be expressed as,

$$
h\Omega = 2\sqrt{g^2 - \frac{(h\gamma_{ex} - h\gamma_{pl})^2}{16}}
$$

Eq. 6 provides the direct relationship between the energy difference $\Omega$ and coupling strength $g$. When $2g < (h\gamma_{pl}+h\gamma_{ex})/2$, Fano interferences between the exciton transition and LPM takes place, while for $2g > (h\gamma_{pl}+h\gamma_{ex})/2$, mode splitting occurs (Wu et al., 2010; Itoh et al., 2014; Dufferwiel et al., 2015; Wang et al., 2019b). As shown in Figures 4A,B (dashed lines), Eq. 4 can well-describe the FDTD simulated scattering spectra. Moreover, for both the pristine and chemically-treated heterostructures, the scattering peaks extracted from the fitting spectra using Eq. 4 follow clear anti-crossing behaviors (Figure 4C). The obtained $\Omega$ at zero detuning are respectively 57.58 and 73.48 meV (Supplementary Table S4). Although these values are both smaller than the corresponding experimental ones, the enhancement of $\Omega$ by chemical treatment agrees well with the experimental measurements. Most importantly, the COM results indicate that for the pristine heterostructure the two scattering peaks are due to the Fano interference because the 2 g (57.58 meV) is smaller than $(h\gamma_{pl}+h\gamma_{ex})/2$ (86.93 meV). In contrast, for the chemically-treated heterostructure, the 2 g = 73.48 meV > $(h\gamma_{pl}+h\gamma_{ex})/2$ = 65.84 meV can be observed. Therefore, the chemical treatment can tune the heterostructure from a weak coupling regime into a strong coupling one, which is corroborated with the experimental findings.

With the COM fitting results, the mechanisms on the chemical tuning of resonance coupling can be understood. Specifically, TFSI solution can effectively passivate/repair the defects and impurities on the monolayer WS$_2$. This can enhance the exciton transition dipole moment and reduce the damping rate. A larger transition dipole moment can generate a stronger oscillator strength, and a smaller damping rate can lead to a longer exciton lifetime. These two outcomes will both enhance the resonance coupling between the LPM and exciton transition, making the system transfer from a weak coupling regime into a strong coupling regime.

We need to point out that the chemical tuning approach reported in our current study is very slow, which is a main drawback in our proposal. The tuning speed is about 30 s, because the monolayer WS$_2$ has to be incubated into the TFSI solution for such a long time to remove and repair the surface defects. Currently, it is a challenge to accelerate the chemical tuning on the resonance coupling, which is limited by the intrinsic materials properties in the monolayer WS$_2$. We anticipate that the tuning speed can be improved by increasing the incubation temperature, which can help accelerate the chemical reactions responsible for defects repair. Another issue is the stability of the chemical tuning approach. Generally, the defects removed by surface passivation will be recovered after exposure to water and commonly used organic solvents. Therefore, to improve the stability of the chemical tuning, preservation and encapsulation of the heterostructure should be considered. Previous studies have demonstrated that some polymer with environmental stability and high optical transparency, such as CYTOP and amorphous perfluorinated polymer, have been applied to encapsulate the TMDCs (Kim et al., 2017). They can therefore be employed to encapsulate the incubated heterostructures to extend the tuning effect on the resonance coupling.
CONCLUSION

In summary, we successfully demonstrate chemical tuning on the resonance coupling between LSPR in individual gold nanorod and 2D excitons in monolayer WS2 flake. By incubating the heterostructures into TFSI solution, defects and impurities in WS2 will be reduced, which can enhance the exciton transition dipole moment and reduce the damping rate. These will lead to stronger coupling strengths between the LSPR and 2D excitons. Consequently, the splitting energies between the two DF scattering peaks become larger for the incubated individual heterostructures. The mode splitting energy increases from 94.96 to 105.32 meV, indicating that the resonance coupling evolves from a weak coupling regime to a strong coupling one. These results can be verified with those obtained from FDTD simulations and COM analyses. We believe that the findings in our study can on one hand provide an efficient approach for tailoring the interactions between plasmonic nanostructures and 2D semiconductors, and on the other hand help to improve our understanding on light–matter interactions at nanoscale.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article supplementary material, further inquiries can be directed to the corresponding author.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2021.744275/full#supplementary-material

AUTHOR CONTRIBUTIONS

HC and SD conceived the study and supervised the project. SW prepared the heterostructures, characterized the resonance coupling, conducted the FDTD simulations, and performed the COM analyses. SD helped prepare the samples and characterizations. SW, SD, KC, HC, and SD. analyzed the data and discussed the results. The article was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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