Particularities of surface plasmon–exciton strong coupling with large Rabi splitting

C Symonds\textsuperscript{1,4}, C Bonnand\textsuperscript{1}, J C Plenet\textsuperscript{1}, A Bréhier\textsuperscript{2}, R Parashkov\textsuperscript{2}, J S Lauret\textsuperscript{2}, E Deleporte\textsuperscript{2} and J Bellessa\textsuperscript{3}

\textsuperscript{1} Laboratoire de Physique de la Matière Condensée et Nanostructures, Université Lyon I, CNRS UMR 5586, Domaine Scientifique de la Doua, F-69622 Villeurbanne Cedex, France
\textsuperscript{2} Laboratoire de Photonique Quantique et Moléculaire de l’Ecole Normale Supérieure de Cachan, CNRS UMR 8537, 61 Avenue du Président Wilson, 94325 Cachan Cedex, France
\textsuperscript{3} Groupe d’Etude des Semiconducteurs, Université Montpellier II, CNRS, Case Courrier 074, F-34095 Montpellier Cedex 5, France
E-mail: clementine.symonds@lpmcn.univ-lyon1.fr

New Journal of Physics 10 (2008) 065017 (11pp)
Received 31 January 2008
Published 30 June 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/6/065017

Abstract. This paper presents some of the particularities of the strong coupling regime occurring between surface plasmon (SP) modes and excitons. Two different active materials were deposited on a silver film: a cyanine dye J-aggregate, and a two-dimensional layered perovskite-type semiconductor. The dispersion relations, which are deduced from angular resolved reflectometry spectra, present an anticrossing characteristic of the strong coupling regime. The wavevector is a good parameter to determine the Rabi splitting. Due to the large interaction energies (several hundreds of milli-electron-volts), the calculations at constant angle can induce an overestimation of the Rabi splitting of more than a factor of two. Another property of polaritons based on SP is their nonradiative character. In order to observe the polaritonic emission, it is thus necessary to use particular extraction setups, such as gratings or prisms. Otherwise only the incoherent emission can be detected, very similar to the bare exciton emission.

\textsuperscript{4} Author to whom any correspondence should be addressed.
Contents

1. Introduction ........................................... 2
2. Strong plasmon–exciton couplings ................. 3
   2.1. Samples and experimental set-up ............. 3
   2.2. Reflectometry results ......................... 4
3. Determination of the Rabi splitting ............... 5
4. Polaritonic emission ................................ 7
   4.1. Extraction of the luminescence ............... 7
   4.2. Sample and experiments in the Kretschmann configuration .................. 7
   4.3. Samples and luminescence experiments with a corrugated sample ....... 9
5. Conclusion ........................................... 11
References ............................................. 11

1. Introduction

During the past decade, many studies have been devoted to the interactions between organic and metallic materials. In particular, when the emitter is very close to the surface, the contribution of surface plasmon (SP) modes to the light emission becomes predominant [1]. The SP modes have, for example, been used recently to enhance the spontaneous rate emission of doped polymer layers [2], or to create an energy transfer channel across a metallic thin film [3]. These studies, which aim at improving organic light emitting devices, were performed under a weak coupling regime.

Due to their high oscillator strength, organic materials are good candidates to reach the strong coupling regime at room temperature. In this particular light–matter interaction regime, an optical mode and an organic exciton form hybrid states, so-called polaritons [4]. The study of the polaritonic emission properties, and particularly their optical nonlinearities, is of great interest in fundamental physics but also in order to realize optoelectronic devices. The strong coupling regime has been intensively studied in planar microcavities, with organic [5] or hybrid organic/inorganic materials [6] under optical or electrical pumping [7].

When a light emitter exhibiting a high oscillator strength is located close to a metallic surface, strong coupling can also occur between the exciton and the SP mode [8]–[11]. This configuration is of particular interest because of the possibility of using the plasmonic emerging tools in order to control and manipulate the polaritons. The plasmon/organic exciton polaritons present particularities related to the optical properties of plasmon modes and to the high oscillator strength of organic materials.

It this paper, we will present the particularities of the strong coupling regime obtained between SP modes and organic or hybrid organic/inorganic excitons. Two kinds of active layered materials were used: a cyanine dye J-aggregate, and a perovskite-type quantum well. In the first section, we present the samples and the reflectometry experiments used to investigate the strong coupling regime. In the second part, we discuss how to estimate the Rabi splitting in the case of the very strong coupling regime obtained with organic materials. In the last part, we present two possible experimental ways to extract the otherwise nonradiative polaritonic emission.
Figure 1. (a) Absorption spectra of (i) the TDBC monomer and (ii) TDBC J-aggregates in water. (b) Absorption and emission spectra of a perovskite layer deposited on a glass substrate. The insets of (a) and (b) present a sketch of the TDBC and the perovskite samples, respectively.

2. Strong plasmon–exciton couplings

2.1. Samples and experimental set-up

Two types of active layers were used to prepare the samples. We used first a J-aggregated cyanine dye (5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-di(4-sulfobutyl)-benzimidazolocarbocyanine (TDBC)). This material is well suited for the observation of strong coupling due to the aggregation of the monomers that occurs when their concentration in water is sufficient, which induces a redshift and a narrowing of the absorption band. Figure 1(a) presents the monomer absorption band of TDBC in water, as well as the J-band of aggregated TDBC in water. The J-aggregate absorption spectrum is characterized by a single, narrow and intense band lying at about 2.1 eV.

Self-assembled quantum wells based on organic–inorganic perovskite materials were also used to obtain plasmon–exciton strong couplings. The absorption and emission spectra of the two layered \((C_6H_5C_2H_4-NH_3)_2-PbI_4\) quantum wells are shown in figure 1(b). The absorption presents a clear peak at 2.402 eV, attributed to the excitons formed in the inorganic layers [12]. The emission spectrum presents a Stokes shift of 31 meV compared to the absorption, which is coherent with previous measurements on this type of material [13].

The samples studied were constituted of a 50 nm thick silver film produced by thermal evaporation under a pressure of \(10^{-7}\) mbar. A 10 nm SiO\(_2\) layer was then evaporated on the metal, in order to prevent deterioration of the silver layer induced by the contact with the active layer. The active layer is then spin-coated onto this stack. In the case of the TDBC active layer, we used a solution of pure TDBC diluted in water. This sample will be referred to as the TDBC sample. In the case of the perovskite-type active layer, a 10 wt.% solution of \(C_6H_5C_2H_4-NH_3I\) and PbI\(_2\) dissolved in stoichiometric amounts in DMF (N,N-dimethylformamide) was used. This sample will be referred to as the perovskite sample. Sketches of the TDBC and perovskite samples are presented in figure 1.
In order to investigate the interactions between silver SPs and excitons from the active layer, reflectometry experiments at room temperature have been performed in the Kretschmann geometry [14]. For this purpose, the Pyrex side of the sample is set on a hemispherical glass prism with glycerol to ensure optical index continuity, and positioned at the center of a rotating holder. A transverse-magnetic (TM) polarized white light beam is then focused on the sample, and the reflected light is detected by a spectrometer associated with a CCD detector. The incident light through the prism is coupled to the SP mode when the projection of its wavevector on the silver plane matches the wavevector of the SP located at the silver–active layer interface, resulting in a lack of the reflection intensity at the SP energy. The value of the SP wavevector is \( k = \frac{2\pi}{\lambda} n_p \sin(\theta) \), where \( n_p \) is the refractive index of the prism and \( \theta \) is the incident angle of the light in the prism. The SP energy depends on its wave vector and can be changed by modifying the incident light angle, which enables the SP resonance to be tuned and thus cross the exciton energy.

2.2. Reflectometry results

The reflected intensity as a function of the light energy for the TDBC and perovskite samples is presented in figure 2 for different incidence angles. In both cases, the spectra exhibit two dips, whose positions are angle-dependent. For the perovskite sample (figure 2(b)), at the smaller angles the low energy dip presents an important blue shift as the angle is increased, then its position in energy remains almost constant for the higher angles. The high energy dip has the opposite behavior: its energy position remains constant at the smaller angles and shifts toward the higher energy.

\[ Figure 2. \] Reflected intensity as a function of the incident light energy for various detection angles in the case of (a) the TDBC sample and (b) the perovskite sample.
higher energies for higher angles. For the TDBC sample (figure 2(a)), the behavior is roughly the same, except that for the smaller angles of detection presented the position of the high energy dip does not remain constant. In this case, the angle dependence is more clearly illustrated by the dispersion curves shown in figure 3(b), which include more data than the spectra presented in figure 2(a).

As a consequence, the two dips present an anticrossing and a minimum value of their separation energy. In the case of the TDBC sample, for an incident angle of 48° the two dips are equidistant from the noncoupled absorption energy (2.1 eV), and have a minimum energy separation of 695 meV. In the case of the perovskite sample, the two dips are equidistant to the noncoupled absorption (2.4 eV) for an incident angle of 50°, and present a minimum energy separation of 142 meV.

3. Determination of the Rabi splitting

In order to calculate the interaction energies for the TDBC sample, the position in energy of the dips as a function of the in-plane wavevector $k$ is presented in figure 3(a). The data present a clear anticrossing between the two lines, characteristic of the strong coupling regime occurring between the SP mode and the TDBC exciton. This strong coupling regime leads to the formation of mixed plasmon–exciton states, that is to say the high- and low-energy polaritonic branches. The polariton energies can be calculated using a coupled oscillator model, $E_{U,L}(k) = \left[ E_p(k) + E_0 \right]/2 \pm \sqrt{\Delta/2 + \left[ E_p(k) - E_0 \right]^2/4}$, where $k$ is the in-plane wavevector, $E_U$ and $E_L$ the energies of the upper and lower polariton states and $E_0$ the energy of the TDBC exciton. $E_p(k)$ is the noninteracting plasmon mode energy, calculated using a conventional transfer matrix method with thicknesses of 10 nm for the TDBC layer ($n = 1.74$ from ellipsometry measurements) and 50 nm for the silver film. $\Delta$ is the interaction energy between the plasmon and exciton, also called Rabi splitting, and corresponds to the minimum energy separation between the two branches. The solid black lines in figure 3(a) represent the calculated polariton dispersion, and give a Rabi splitting energy of 310 meV. In order to adjust the experimental data, a value of 2.05 eV was used for the uncoupled exciton energy.

Figure 3(b) presents the energy positions of the reflectometry dips as a function of the incident angle for the TDBC sample. Replacing the wavevector by the angle, the previous formula gives $E_{U,L}(\theta) = \left[ E_p(\theta) + E_0 \right]/2 \pm \sqrt{\Delta/2 + \left[ E_p(\theta) - E_0 \right]^2/4}$. The adjustment of the data leads to an interaction energy of 695 meV. In order to explain the mismatch between this value and the one obtained previously, it has to be noticed that in the spectra recorded at constant angle the wavevector ($k = (2\pi/\lambda) \sin \theta$) is not constant. As a consequence, the upper and lower polaritons presenting an energy separation close to the minimum at an angle of 46° (stars in figure 3(b)) have a wavevector of $k = 13.2$ and 9.2 $\mu$m$^{-1}$, respectively (stars in figure 3(a)). The minimum energy splitting in angle thus does not correspond to the energy splitting at the resonance ($k = 11$ $\mu$m$^{-1}$). Using the angle as the parameter to determine the Rabi splitting results in an important overestimation of the strength of the coupling (more than a factor 2 in the present case).

In addition to the dispersion relation anticrossing, an inversion of the dip linewidths is associated with the strong coupling regime. At resonance, the polariton states are formed by an admixture of equal weight of plasmon and exciton, and the widths of the two peaks should be the same. We plotted the width of the reflectometry dips for the TDBC sample as a function of the wavevector (figure 3(c)) and the angle (figure 3(d)). In figure 3(c), for the wavevector
Figure 3. Panels (a) and (b) represent the reflectometry dip energy positions (black circles) as a function of the wavevector and the angle, respectively. The stars correspond to the dip energy positions recorded at an angle of 46°. The dotted lines represent the calculated energy of the uncoupled plasmon and exciton. The solid black lines represent the calculated upper and lower branches of the polaritonic dispersion, and the solid gray line the energy difference between the two branches. Panels (c) and (d) represent, respectively, the full width at half minimum (FWHM) of the reflectometry dips as a function of the wavevector and the angle.

corresponding to the minimal energy separation between the polariton branches \((k = 11 \mu m^{-1})\), the dip widths are roughly the same. In figure 3(d), however, at the resonance angle, the polariton widths are very different, confirming that the use of the wavevector is appropriate to calculate the Rabi splitting energy \([15, 16]\).

Finally, we plotted the energy position of the reflectometry dips for the perovskite sample as a function of the wavevector (figure 4(a)) and the angle (figure 4(b)). As previously, the dotted lines represent the non-dispersive perovskite exciton and the uncoupled plasmon dispersion, calculated using a thickness of 8 nm for the perovskite layer \((n = 2.30\) at 632 nm from ellipsometry measurements). Using the coupled oscillator model given previously, the data adjustment leads to an interaction energy of 87 meV when using the wavevector, and 142 meV when using the incident angle. The Rabi splitting energy is thus 87 meV. Note that the discrepancy between these two values is particularly significant when the interaction energies are high.
Figure 4. Reflectometry dip energy of the TDBC sample (black circles) as a function of (a) the wavevector and (b) the detection angle. The dotted lines represent the calculated energy of the uncoupled plasmon and exciton, and the solid black lines the calculated upper and lower branches of the polaritonic dispersion.

4. Polaritonic emission

4.1. Extraction of the luminescence

The polaritons resulting from the strong coupling between a SP mode and an exciton present the same properties as the SP, i.e. they are TM polarized and nonradiative. This last point is due to the fact that, for a given energy, their wavevector is always larger than the wavevector of the light. Consequently, the polariton and the light tangential wavevector components cannot match, and thus the polariton cannot couple to radiative modes. In order to excite and extract the polaritonic emission, one possible method is to use a prism in the Kretschmann geometry described in the previous section, the prism refractive index leading to an enhancement of the tangential component of the light wavevector.

Another method, more compact than the use of a hemispherical prism, is to create a periodic corrugation on the sample surface. In this case, the wavevector of the polariton diffracted at the order $m$ is given by $k = \pm k_{\text{pol}} + \frac{2\pi m}{a}$, where $k_{\text{pol}}$ is the polariton wavevector at a similar planar interface, and $a$ is the period of the corrugation. In these conditions, the polariton wavevector can match the light wavevector, and the polaritonic emission can be extracted [17, 18]. In the following subsections, we will present the luminescence results obtained with the two types of configurations, i.e. using a prism for a perovskite sample, and with a metallic grating for the TDBC sample.

4.2. Sample and experiments in the Kretschmann configuration

The sample studied in this subsection is the perovskite sample described previously (see figure 5(a)). In order to observe the emission of the plasmon–perovskite exciton mixed state, luminescence experiments have been performed using a prism in the Kretschmann configuration. The sample is excited on the perovskite using a 405 nm laser diode. The luminescence at various angles is detected in TM polarization through the prism, using a cooled...
Figure 5. Sample and luminescence detection set-up for (a) the perovskite sample in the Kretschmann configuration and (b) an imprinted TDBC sample.

Figure 6. Polaritonic emission of the perovskite sample. (a) Luminescence spectra recorded through the silver layer (detection 1) for detection angles varying from 48° to 51°. (b) Luminescence spectrum detected at an angle of 50° on the top of the sample (detection 2). (c) Energy positions of the luminescence peaks (open circles) and polariton dispersion (full circles).

CCD detector associated with a spectrometer (detection 1 in figure 5(a)). The luminescence was also detected directly in the air on the perovskite side (detection 2 in figure 5(a)).

Figure 6(a) presents the luminescence spectra recorded in detection 1 for angles ranging from 48° to 51°. Each spectrum exhibits two intensity peaks. The high-energy one (around
2.37 eV) is angle-independent, whereas the one at lower energy presents a clear dependence on the detection angle. For the higher angles the peaks can no longer be discriminated, due to their own width that becomes larger than their separation energy. The high-energy peak corresponds to the noncoupled part of the perovskite exciton, emitting by transparency through the silver layer, whereas the other one can be attributed to the lower branch of the plasmon–perovskite exciton polariton. Indeed, its position in energy, reported as a function of the wavevector in figure 6(c), follows the lower branch of the polariton-dispersion curve obtained by reflectometry. As previously observed in the literature for microcavities in the strong coupling regime, the high-energy polaritonic branch is not present in the luminescence spectra. This could be explained by the nonradiative decay of the upper polaritonic states towards uncoupled excitonic states [15], or by the emission of optical phonons between the two polaritonic branches [19].

Finally, figure 6(b) presents the luminescence spectrum of this sample recorded directly on the perovskite side (detection 2 in figure 5(a)). In this spectrum, obtained at an angle of 50°, a single line appears at 2.37 eV, corresponding to the incoherent emission of the perovskite exciton. This emission is very similar to the emission of a perovskite layer without silver (see figure 1(b)). This shows that strong plasmon–exciton coupling can occur in a structure without being noticed if the detection set-up is not adapted.

4.3. Samples and luminescence experiments with a corrugated sample

The sample studied in this subsection contains a spatially modulated silver film deposited onto a TDBC active layer. To obtain this structure, a several microns thick polyvinyl alcohol (PVA) layer is spin-coated onto a pyrex glass substrate. This thick layer will ensure a good imprint of the silver layer. In order to protect this layer and improve the adhesion of the following layers, a 20 nm TiO$_2$ film is deposited onto the PVA. The TDBC active layer is then spin-coated onto this stack, and a 45 nm thick silver layer evaporated onto the active layer. Finally, a TiO$_2$ layer is deposited by spin-coating onto the silver film (see figure 5(b)). In order to create a spatial modulation on the silver film, we used an anvil grating with a periodicity of 417 nm. This anvil grating is pressed onto the sample ($P = 2 \times 10^8$ Pa) at a temperature of 60°C in order to soften the PVA layer. The measured height of the resulting sample corrugation is around 45 nm.

Luminescence experiments were performed on this sample, by exciting its grating side with the 488 nm line of an argon laser and by collecting the emitted signal on this same side through a spectrometer at various detection angles. The luminescence spectra obtained for angles ranging from 8° to 20° are presented in figure 7(a). Three intensity peaks are present in these spectra. The peak around 2.8 eV is angle-independent, whereas the two peaks at lower energy present a blueshift and a redshift respectively, as the detection angle increases. In order to attribute the origin of these peaks, it is necessary to study the dispersion relations of the plasmons present in this type of sample. Indeed, the surface corrugation gives access to the plasmons of both sides of the metallic layer, that is to say in our case the silver/TiO$_2$ plasmon and the silver/TDBC polariton. For this purpose, reflectometry experiments have been performed on both sides of the sample, and the dip positions deduced from these spectra are reported in figure 7(c). The gray line corresponds to the diffracted orders of the silver/TiO$_2$ plasmon. The black line, which presents an anticrossing with a Rabi splitting energy of 180 meV, corresponds to the silver/TDBC polariton diffracted on the grating. The energy positions of
Figure 7. Polaritonic emission of the corrugated TDBC sample. (a) Luminescence spectra for detection angles varying from 8° to 20°. (b) Luminescence spectrum detected in a noncorrugated area of the sample. (c) Energy positions of the luminescence peaks (open circles). The black lines represent the silver/TDBC polariton dispersion and the gray lines the silver/TiO$_2$ plasmon dispersion. (d) Luminescence spectra recorded at an angle of 15° in TM polarization (full line) and in TE polarization (dotted line).

The luminescence peaks as a function of the wavevector are also presented in figure 7(c) (open circles). The blueshift luminescence peak follows the dispersion relation of the polaritonic lower branch, while the redshift luminescence peak follows the dispersion relation of the silver/TDBC plasmon. Moreover, luminescence spectra were recorded in TE polarization at an angle of 15° (see figure 7(d)). It appears that the high energy peak is not polarized (polarization rate of 3%), whereas the low energy ones are strongly TM polarized (polarization rate of 68%). This indicates that the high energy peak corresponds to the emission of incoherent exciton states by transparency through the silver layer, while the other ones can be attributed to the lower branch of the plasmon–perovskite exciton polariton. As discussed in the previous subsection, the emission of the upper polaritonic branch is not observed in the luminescence spectra.
The luminescence spectrum of a noncorrugated area of the sample (figure 7(b)) presents no particular feature except the peak due to the noncoupled part of the TDBC emission, indicating that the grating produces an efficient way to extract polaritonic emission.

5. Conclusion

In summary, we obtained a strong coupling regime between the SP mode and exciton from organic and hybrid organic/inorganic materials. The use of these materials leads to high values of the plasmon–exciton interaction, and it is thus necessary to use the wavevector as the quantum number to estimate the value of the Rabi splitting. We obtained Rabi splitting values of 310 and 87 meV for the TDBC and the perovskite-type samples, respectively. Polaritonic emission with these two active layers was also demonstrated, using a prism and a grating in order to extract the luminescence of the otherwise non-radiative plasmon–exciton hybrid states. We have shown that strong coupling with SPs can be present and modify the emitters’ properties without appearing in conventional luminescence experiments.

References

[1] Worthing P T, Amos R M and Barnes W L 1999 Phys. Rev. A 59 865
[2] Neal T D, Okamoto K and Scherer A 2005 Opt. Express 13 5522
[3] Andrew P and Barnes W L 2004 Science 306 1002
[4] Weisbuch C, Nishioka M, Ishikawa A and Arakawa Y 1992 Phys. Rev. Lett. 69 3314
[5] Lidzey D G, Bradely D D, Skolnick M S, Virgili T, Walker S and Whittaker D M 1998 Nature 395 53
[6] Brehier A, Parashkov R, Lauret J S and Delpeurere E 2006 Appl. Phys. Lett. 89 171110
[7] Tischler J R, Bradely M S, Bulovic V, Song J H and Nurmikko A 2005 Phys. Rev. Lett. 95 036401
[8] Bellessa J, Bonnand C, Plenet J C and Mugnier J 2004 Phys. Rev. Lett. 93 036404
[9] Dintinger J, Klein S, Bustos F, Barnes W L and Ebbesen T W 2005 Phys. Rev. B 71 035424
[10] Sugawara Y, Kelf T A, Baumberg J J, Abdelsalam M E and Bartlett P N 2006 Phys. Rev. Lett. 97 266808
[11] Symonds C, Bellessa J, Bonnand C, Plenet J C, Brehier A, Parashkov R, Lauret J S and Deleporte E 2007 Appl. Phys. Lett. 90 091107
[12] Ishihara T, Takahashi J and Goto T 1990 Phys. Rev. B 42 11099
[13] Kitazawa N, Enomoto K, Aono M and Watanabe Y 2007 J. Mater. Sci. 39 749
[14] Kretschmann E and Raether A 1968 Z. Naturf. a 2135
[15] Agranovich Y M, Litinskaia M and Lidzey D G 2003 Phys. Rev. B 67 85311
[16] Houdré R, Weisbuch C, Stanley R P, Oesterle U, Pellandini P and Ilegems M 1994 Phys. Rev. Lett. 73 2043
[17] Wedge S, Hooper I R, Sage I and Barnes W L 2004 Phys. Rev. B 69 245418
[18] Bonnand C, Bellessa J, Symonds C and Plenet J C 2006 Appl. Phys. Lett. 89 231119
[19] Lidzey D G, Fox A M, Rahn M D, Skolnick M S, Agranovich Y M and Walker S 2002 Phys. Rev. B 65 195312

New Journal of Physics 10 (2008) 065017 (http://www.njp.org/)