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# Emission of hybrid organic-inorganic exciton/plasmon mixed states

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In this letter the authors experimentally demonstrate the strong coupling regime at room temperature between a surface plasmon and an exciton from an auto-organized quantum well. The sample is formed by a two dimensional layered perovskite-type semiconductor:  $s(\text{C}_6\text{H}_5\text{C}_2\text{H}_4-\text{NH}_3)\text{PbI}_4$ , spin coated onto a silver film. The dispersion lines resulting from reflectometry experiments performed at room temperature in the Kretschmann geometry present an anticrossing with a Rabi splitting of 167 meV. The emission of the low energy polariton is presented. © 2007 American Institute of Physics. [DOI: 10.1063/1.2695682]

Self-assembled quantum wells based on organic-inorganic perovskite materials have been of growing interest during the past decade due to their promising optical and electrical properties. In particular, lead halide based two dimensional layered perovskite-type semiconductors have been used to realize electroluminescent heterostructures<sup>1,2</sup> or field-effect transistors.<sup>3</sup> In this type of auto-organized quantum wells, a lead halide inorganic layer is sandwiched between two organic layers. Because the band gap of the inorganic layers is smaller than that of the organic layers, excitons are confined in the inorganic layers. Due to the large dielectric constant difference between the inorganic and organic layers, these compounds exhibit large exciton binding energy and oscillator strength.<sup>4</sup> They are therefore good candidates to achieve strong coupling regime with photon modes, and they were used for this purpose in distributed feedback cavity<sup>5</sup> and recently in Fabry-Pérot microcavity<sup>6</sup> configurations. In this particular regime of the light-matter interaction, the cavity photon mode and the quantum well exciton are not eigenmodes of the system any more; the new eigenmodes are two mixed states called polaritons.<sup>7</sup> The study of the polaritonic emission properties, and particularly of their optical nonlinearities, is interesting for fundamental physics and also for optoelectronic devices. In particular, these systems may lead to Bose-Einstein condensation<sup>8</sup> and to the realization of low-threshold polariton lasers.<sup>9</sup>

Strong coupling has recently been obtained between an exciton and a surface plasmon (SP) mode, which are waves propagating at a metal dielectric interface. In this configuration, polaritonic emission has been demonstrated with exciton from cyanine dye J-aggregate, as well as a Rabi splitting of several hundreds of meV at room temperature.<sup>10</sup> Besides the fundamental interest of studying strong coupling in this configuration, strong coupling with SP presents various advantages, such as the few technological steps necessary to realize the samples or the possibility to benefit from the tools of the emerging field of the plasmonic in order to manipulate the polaritons. Because of these advantages, a promising development of plasmon/exciton strong coupling is the possi-

bility to study the interaction between organic and inorganic polaritons.<sup>11</sup> Indeed, the SP related to the upper and lower interfaces of a thin metal film can interact in given configurations, and a transfer of excitation between the two surroundings layers has been demonstrated in the weak coupling regime.<sup>12</sup> Due to the optical properties versatility of perovskite-type materials, which can be tuned by changing, for example, the halide composition,<sup>13</sup> the study of polaritonic emission from perovskite inorganic exciton is of particular interest in order to achieve organic-inorganic polariton interaction.

In this letter we experimentally demonstrate the strong coupling regime at room temperature between a SP from a silver layer and an exciton from a two dimensional layered perovskite-type semiconductor:  $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4-\text{NH}_3)\text{PbI}_4$ . Polaritonic emission is also achieved in this configuration.

The sample consists of a two dimensional layered perovskite-type semiconductor deposited onto a silver film. The structure of the sample is sketched in the inset of Fig. 1. The 50 nm thick silver film is first thermally evaporated onto a Pyrex glass substrate at room temperature under a pressure of  $10^{-6}$  mbar. A 10 nm  $\text{SiO}_2$  layer is then evaporated on the metal, in order to prevent deterioration of the silver layer induced by the contact with the perovskite material. The perovskite active layer is obtained by spin coating onto the silver- $\text{SiO}_2$  stack a 10 wt % solution of  $\text{C}_6\text{H}_5\text{C}_2\text{H}_4-\text{NH}_3\text{I}$  and  $\text{PbI}_2$  dissolved in stoichiometric amounts in *N,N*-dimethylformamide. The thickness of this layer is 15 nm, as deduced from plasmon simulation (see hereunder). Figure 1 shows the absorption and emission spectra at room temperature of a perovskite layer deposited onto a glass substrate without silver. The absorption presents a clear peak at 2.402 eV attributed to the excitons formed in the inorganic layers.<sup>4</sup> The emission spectrum presents a Stokes shift of 31 meV compared to the absorption, which is coherent with previous measurements on this type of materials.<sup>13</sup>

In order to investigate the interactions between SP and perovskite excitons, reflectometry experiments at room temperature have been performed in the Kretschmann geometry.<sup>14</sup> For this purpose, the Pyrex side of the sample is set on a hemispherical glass prism with glycerol to ensure

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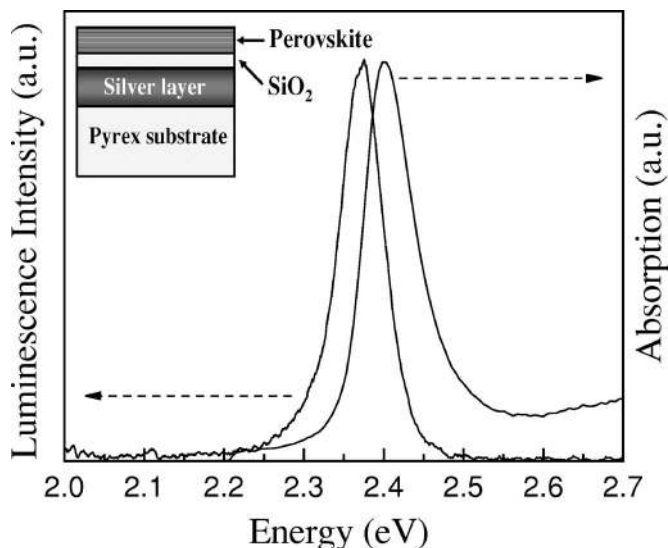


FIG. 1. Absorption and emission spectra at room temperature of a perovskite layer deposited onto a glass substrate. The inset shows a layout of the sample.

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 coupled with a charge coupled device detector. The incident light through the prism is coupled to the SP when the projection of its wave vector on the silver plane matches the wave vector of the SP located at the silver-perovskite interface, resulting in lack of the reflection intensity at the SP energy.

The reflected intensity as a function of the light energy has been measured for angles of incidence ranging from  $51^\circ$  to  $60^\circ$ , as presented in Fig. 2. Each spectrum exhibits two dips, whose positions in energy depend on the incidence angle. For an incidence angle of  $59^\circ$ , the two dips are equidistant from the noncoupled absorption energy (2.402 eV). In this case the energy separation between the two dips pre-

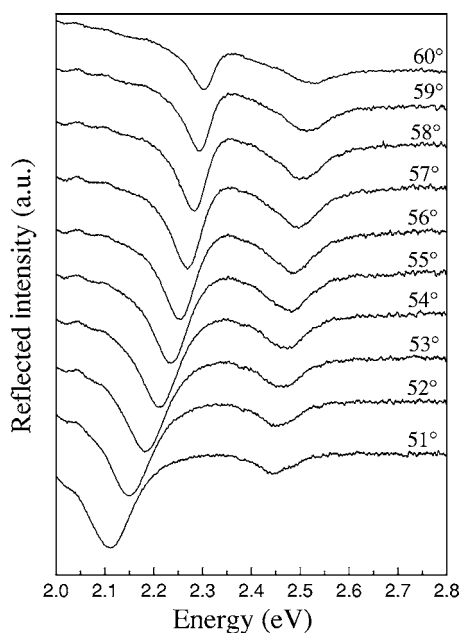


FIG. 2. Reflectivity spectra recorded for detection angles from  $51^\circ$  to  $60^\circ$ . The spectra are arbitrarily translated for the clarity of the figure.

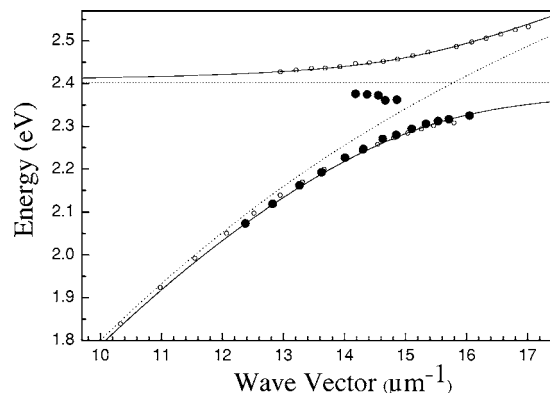


FIG. 3. Reflectometry energy dips (small empty circles) as a function of the wave vector. The dotted lines represent the calculated energy of the uncoupled plasmon and exciton, and the solid lines are the calculated polaritonic dispersion branches. The black circles represent the positions in energy of the luminescence peaks.

sents a minimal value of 220 meV. Figure 3 shows the energies of the dips as a function of the in-plane wave vector. A clear anticrossing between the two lines appears, characteristic of the strong coupling occurring between the SP and the perovskite 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 energy separation between the two polaritonic states has a minimum value of 167 meV around  $k = 15.9 \mu\text{m}^{-1}$ . This minimal energy separation, called Rabi splitting energy, is characteristic of the strength of the coupling. The theoretical dispersion relation of the uncoupled SP is shown in dotted line in Fig. 3. It has been calculated using a conventional transfer matrix method. By adjusting the calculated curve to the experimental data far from the resonance, that is to say, when the polariton is plasmonlike, a thickness of 15 nm is obtained for the perovskite layer. This thickness is the only adjustable parameter, the refractive index of the perovskite layer far from the resonance being obtained by ellipsometry measurement ( $n = 2.30$  at 632 nm). The absorption energy of the uncoupled states is also represented in dotted line in Fig. 3. The dispersion relations of the polaritonic branches are calculated using a two-level model:<sup>15</sup>  $E_{U,L}(k) = [E_{\text{pl}} + E_0] / 2 \pm \sqrt{\Delta + [E_{\text{pl}} - E_0]^2 / 4}$  where  $E_U$  and  $E_L$  are the energies of the upper and lower polariton states,  $E_0$  is the energy of the perovskite exciton given by the absorption measurement (Fig. 1),  $E_{\text{pl}}$  is the noninteracting plasmon mode energy calculated previously,  $k$  is the in-plane wave vector, and  $\Delta$  is an energy related to the interaction between the plasmon and the exciton. This formula is the same as the formula obtained for two coupled oscillators with a Rabi splitting of  $2\Delta$ . The dispersion relations of the high and low energy polaritonic branches were calculated using the Rabi energy of 167 meV obtained experimentally and are plotted in solid lines in Fig. 3. The calculated and experimental data are in very good agreement.

In order to observe the emission of the plasmon/exciton mixed state, luminescence experiments have been performed. As for the reflectometry experiment, the sample is set on a hemispherical prism and positioned at the center of the rotating holder. A 405 nm diode laser beam is focused on the perovskite side of the sample at normal incidence, and the photoluminescence spectra are recorded in TM polarization for various detection angles. Figure 4(a) shows the pho-

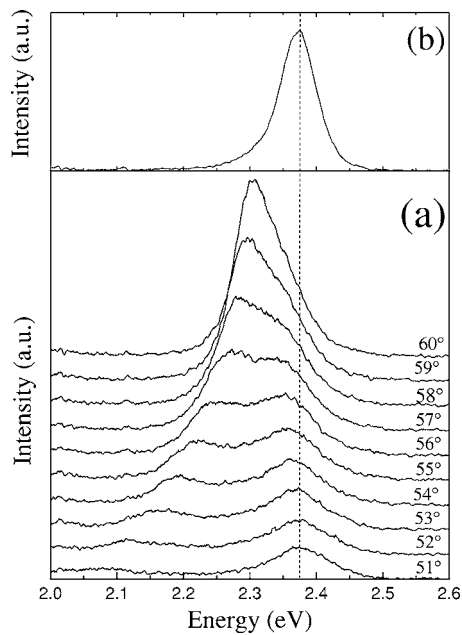


FIG. 4. (a) Luminescence spectra recorded for detection angles varying from  $51^\circ$  to  $60^\circ$ . (b) Luminescence spectra recorded in a region of the sample where no silver layer was deposited.

toluminescence spectra obtained for different angles of detection, ranging from  $51^\circ$  to  $60^\circ$ . For the lower angles, two peaks are present in the spectra. The position of the high energy peak is independent of the detection angle, whereas the position of the low energy peaks clearly varies as the detection angle is tuned. For the higher angles, the two peaks cannot be discriminated due to their own width that becomes larger than their separation in energy.

The energy positions of the luminescence peaks as a function of the in-plane wave vector have been reported as black circles in Fig. 3. The dispersionless data correspond to the noncoupled part of the perovskite exciton, emitting by transparency through the silver layer. The energy position of this peak corresponds to the one of the photoluminescence spectrum of the perovskite layer, recorded in a zone of the sample where no silver layer was deposited [Fig. 4(b)]. The variation of the low energy photoluminescence peak as a function of the detection angle coincides with the experimental dispersion relation of the low energy polaritonic branch.

Moreover, the low energy luminescence is clearly visible down to 2.11 eV, in a region where the uncoupled perovskite layer shows no emission [Fig. 4(b)]. This clearly indicates that this photoluminescence arises from the polaritonic emission, resulting from the surface plasmon/perovskite exciton mixed states.

In summary, we have demonstrated the strong coupling regime between a surface plasmon and an inorganic exciton from two dimensional layered perovskite-type semiconductor. Emission of the low energy polariton resulting from these mixed states has been presented. These results may lead to the coupling between organic and inorganic polaritons via surface plasmon.

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