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Hybrid excitons in parallel organic and inorganic semiconducting quantum wires

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We study excited states in parallel neighboring organic and inorganic semiconducting quantum wires. Due to the resonance dipole-dipole interaction between the wires, the hybrid exciton is a mixture of Frenkel and Wannier-Mott excitons. For the transition dipole moments oriented perpendicular to the wires, the interwire hybridization strength is nonzero even for small exciton wave vectors along the wires and decays rather slowly with increasing interwire spacing. This is in contrast to two-dimensional quantum wells where the dipole-dipole coupling decays fast with increasing interwell distance and is nonzero only for nonzero excitonic wave vectors. The hybrid wire excitons possess both a large radius and a relatively large oscillator strength, which could be especially interesting with respect to applications in nonlinear optics.

There has been considerable progress in the preparation of organic and semiconductor nanostructures (see, e.g., Ref. 1). Therefore, in the near future the fabrication of composite organic-inorganic semiconductor heterostructures seems to be possible. We realize that the preparation of such systems might be a rather difficult problem. However, the expected unique physical properties of such systems would justify the efforts. As has been noted recently,[2] a new type of excitonic state in such heterostructures could be possible due to resonant mixing of Frenkel and Wannier-Mott excitons. The hybrid excitons would possess strong oscillator strengths (typical for Frenkel excitons) and high sensitivity to external perturbations (typical for Wannier-Mott excitons).

The heterostructure considered in Ref. 2 consists of a two-dimensional (2D) organic molecular layer and a neighboring semiconductor 2D quantum well. For such a system, the electrostatic coupling of Frenkel and Wannier excitons vanishes in the range of small two-dimensional exciton wave vectors. This is a consequence of the well-known fact that the electric field of a uniformly polarized layer vanishes outside the layer. Thus, the conditions for the manifestation of hybridization effects are not favorable just for the most interesting small wave-vector excitons that interact actively with light.

In the present paper we propose another organic-inorganic semiconductor system where the hybridization of Frenkel and Wannier-Mott excitons is especially effective just for excitons with small wave vectors. We consider a system of parallel organic and semiconductor quantum wires. The Frenkel $|F,k,l\rangle$ and Wannier-Mott $|W,k,l\rangle$ exciton states in the wires are characterized by a one-dimensional (1D) wave vector k and the label l counting quantized states of the transverse motion of excitons within the wires. To simplify the consideration, below we restrict ourselves to the lowest transverse state of excitons and omit the label l. The resonance coupling of the Frenkel and Wannier-Mott excitons is governed by the hybridization parameter

$$\Gamma(k)=\langle F,k|H_{\rm int}|W,k\rangle, \tag{1}$$

where the interaction Hamiltonian $H_{\rm int}$ for a pair of wires is given by

$$H_{\rm int}=-\int \mathbf{E}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r}. \tag{2}$$

Here the integration is carried out over the semiconductor wire; $\mathbf{P}(\mathbf{r})$ is the transition polarization operator for Wannier-Mott excitons

$$\mathbf{P}(\mathbf{r})=\mu^W\Psi_e(\mathbf{r})\Psi_h(\mathbf{r})+\text{H.c.}, \tag{3}$$

where $\Psi_{e(h)}(\mathbf{r})$ is the electron (hole) operator and μ^W the (intracell) optical transition dipole moment. In Eq. (2) $\mathbf{E}(\mathbf{r})$ is the operator of the electric field created in the semiconductor wire by the exciton in the organic wire

$$E_i(\mathbf{r})=-\sum_{\mathbf{n}}\left[\delta_{ij}-\frac{3(\mathbf{r}-\mathbf{r}_{\mathbf{n}})_i(\mathbf{r}-\mathbf{r}_{\mathbf{n}})_j}{|\mathbf{r}-\mathbf{r}_{\mathbf{n}}|^2}\right]\frac{\mu_j^F}{\epsilon|\mathbf{r}-\mathbf{r}_{\mathbf{n}}|^3}(A_{\mathbf{n}}^\dagger+A_{\mathbf{n}}), \tag{4}$$

where summation runs over sites $\mathbf{n}$ (with the radius vector $\mathbf{r}_{\mathbf{n}}$) of the molecular lattice, $A_{\mathbf{n}}^\dagger$ is the creation operator of the Frenkel exciton at the site $\mathbf{n}$, and μ^F the transition dipole moment for Frenkel excitons; ϵ is an effective dielectric function of the medium; indices i,j denote vector components in Cartesian coordinates with the z axis chosen along the wires, and the x and y axes perpendicular to the wires; and the y axis is perpendicular to the plane determined by the wires. The state corresponding to the Frenkel exciton is represented as

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$$|F,k\rangle = \frac{1}{\sqrt{N_F}} \sum_{\mathbf{n}} \exp(ikz_{\mathbf{n}}) A^{\dagger}_{\mathbf{n}} |0\rangle, \tag{5}$$

where N_F is the total number of molecular sites and $|0\rangle$ is the exciton vacuum state. For the state of the Wannier-Mott exciton we take the following representation:

$$|W,k\rangle = \frac{1}{\sqrt{L}} \int dz_e dz_h \exp\left(ik\,\frac{z_e+z_h}{2} \right) \Phi_0(z_e - z_h) \times \Psi^{\dagger}_{e0}(z_e) \Psi^{\dagger}_{h0}(z_h) |0\rangle. \tag{6}$$

Here L is the length of the wires. The operators $\Psi^{\dagger}_{e(h)0}(z)$ correspond to the lowest ($l=0$) state of the transverse motion in the operator expansion over transverse modes ϕ_l:

$$\Psi^{\dagger}_{e(h)}(\mathbf{r}) = \sum_{l} \Psi^{\dagger}_{e(h)l}(z)\, \phi^{*}_{e(h)l}(\boldsymbol{\rho}), \tag{7}$$

where $\mathbf{r}=(\boldsymbol{\rho},z)$. The function $\Phi_0(z_e-z_h)$ in Eq. (6) describes the relative 1D motion of the bound electron and the hole. We consider only the lowest transverse state; then the transition polarization operator Eq. (3) for the Wannier-Mott exciton becomes

$$\mathbf{P}(\mathbf{r}) = \mu^{W} \Psi_{e0}(z) \Psi_{h0}(z)\, \phi_{e0}(\boldsymbol{\rho})\, \phi_{h0}(\boldsymbol{\rho}) + \text{H.c.} \tag{8}$$

Using Eqs. (2)–(8) we obtain the following expression for the hybridization parameter Γ of Eq. (1):

$$\Gamma(k) = f_{eh} \Phi_0(0) \sqrt{\frac{N_F}{L}} \frac{\mu^F_i \mu^W_j}{\epsilon} C_{ij}, \tag{9}$$

where

$$f_{eh} = \int \phi_{e0}(\boldsymbol{\rho})\, \phi_{h0}(\boldsymbol{\rho})\, d^2\rho, \tag{10}$$

$$C_{ij} = \int \frac{\exp(ikz)}{(R^2+z^2)^{3/2}} \left[\delta_{ij} - \frac{3r_i r_j}{R^2+z^2} \right] dz = -2[(\nabla^{\perp}_i - ik\delta_{iz})(\nabla^{\perp}_j - ik\delta_{jz}) K_0(k\rho)]_{\boldsymbol{\rho}=(R,0)}. \tag{11}$$

The first line of Eq. (11) is obtained under the simplifying assumption that the interwire distance R is large in comparison with the thickness of the wires; $\nabla^{\perp}_i$ denotes the derivative with respect to the transverse variables ($i=x,y$); K_0 is the modified Bessel function of zeroth order with the following limiting behavior:[3]

$$K_0(x) = \begin{cases} \sqrt{\dfrac{\pi}{2x}} \exp(-x), & x \gg 1 \\ -\ln(x/2), & x \ll 1. \end{cases} \tag{12}$$

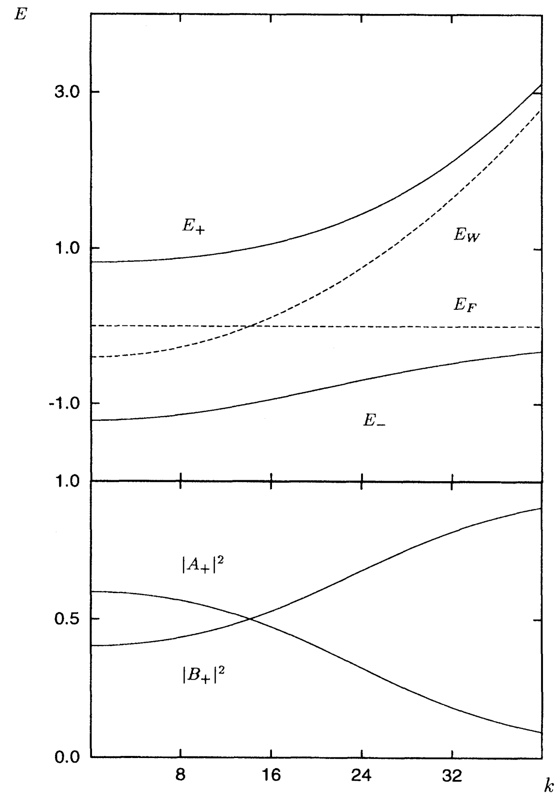

FIG. 1. Energies $E_{\pm}(k)$ of the hybrid excitons plotted as functions of the wave vector k on the upper part (solid lines). Dashed lines represent the energies of Frenkel $[E_F(k)]$ and Wannier-Mott $[E_W(k)]$ excitons. The latter is taken in the effective-mass approximation, the former is approximated by a constant that is taken as the origin of the energy axis. The figure corresponds to the following parameter values: $\Gamma=5$ meV, $E_F-E_W(k)=2$ meV, and Wannier-Mott exciton effective mass $M=0.3m_0$ (m_0 is the free electron mass). Energies are measured in units of Γ; wave vectors in units of 10^5 cm^{-1}. The lower part of the figure shows the behavior of the weights $|A|^2$, $|B|^2$ of Frenkel and Wannier-Mott counterparts for the hybrid state corresponding to the "+" sign in Eq. (16).

As follows from Eq. (12), the interwire coupling is suppressed exponentially for excitons with wave vectors $k \gtrsim 1/R$, i.e., for the major part of the Brillouin zone. On the other hand, coupling of excitons with relatively small wave vectors $k \lesssim 1/R$ is quite effective. This is in contrast to the case of a 2D system of quantum wells where the coupling at small wave vectors is suppressed because the electric field outside of a uniformly polarized layer vanishes. The range of small wave vectors $k \sim 1/\lambda \ll 1/R$ is of special interest, as excitations with such wave vectors may be created straightforwardly by light of wavelength λ. In the leading order in $kR \ll 1$, the hybridization parameter $\Gamma(k)$ Eq. (9) has the following form:

$$\Gamma(k) = \frac{f_{eh}}{\epsilon R^2} \sqrt{\frac{2S_F}{a_{1B} v_F}} (\mu^F_y \mu^W_y - \mu^F_x \mu^W_x), \tag{13}$$

where S_F and v_F are the cross section and the volume of an elementary lattice cell for the molecular wire; the 1D exciton ground state wave function $\Phi_0(0) = 1/\sqrt{2a_{1B}}$ in the strong-confinement limit has been expressed in terms of the 1D Bohr radius $a_{1B} = (a_0/2)\sqrt{E_0/E_1}$, with a_0 and E_0 being the Bohr radius and the ground-state energy of the bulk exciton, respectively; and E_1 is the ground-state energy of the 1D exciton (see Refs. 4 and 5).

Note that the excitonic polarization component along the wires does not contribute to Γ in the leading order in kR. This is due to the obvious fact that a uniform longitudinal polarization is not accompanied by the appearance of an electric charge. To estimate the value of Γ we use the following parameter values: $a_{1B}=30$ Å, $\mu^F=5$ D, $\mu^W=10$ D, $S_F=(50\ \text{Å})^2$, $v_F=100\ \text{Å}^3$, $R=50$ Å, $f_{eh}=1$, and $\epsilon=3$, and we obtain $\Gamma\approx 5.4$ meV.

The resonance coupling of Frenkel and Wannier-Mott excitons results in the appearance of hybrid excited states

$$|\Psi,k\rangle=A(k)|F,k\rangle+B(k)|W,k\rangle. \tag{14}$$

Here

$$|A(k)|=\frac{|\Gamma(k)|}{\sqrt{[E_F(k)-E(k)]^2+\Gamma^2(k)}},$$
$$B(k)=\frac{\Gamma(k)}{E(k)-E_W(k)}A(k), \tag{15}$$

where $E_{F(W)}(k)$ are the energies of Frenkel (Wannier-Mott) excitons and the energies $E(k)$ of the hybrid state (see Fig. 1) are given by the well-known expression

$$E_{\pm}(k)=[E_F(k)+E_W(k)]/2 \pm\sqrt{[E_F(k)-E_W(k)]^2/4+\Gamma^2(k)}. \tag{16}$$

The coupling is strong when the energies of Frenkel and Wannier-Mott excitons are in resonance: $|E_F(k)-E_W(k)| \sim|\Gamma(k)|$. In this case the size of the hybrid state is comparable with that for Wannier-Mott excitons, i.e., it is much larger than the radius of Frenkel excitons. This causes a high sensitivity of the hybrid states to external fields. Outside the resonance range, the coupling is governed by the parameter $\Gamma^2/(E_F-E_W)$ and is rather small. The condition of resonance is rather strict for the considered range of parameters and requires a careful choice of materials for both wires. Naturally, the exciton linewidths should be small as compared to Γ. In general, the excitonic linewidth is determined by the radiative decay and by other dephasing processes. For the transition dipole moment oriented perpendicular to the wire, the contribution γ_{rad} to the Frenkel exciton linewidth caused by the collective radiative decay in a 1D wire is given by

$$\gamma_{\text{rad}}(k)=\frac{(\mu^F)^2S_Fk^2}{4\pi v_F}, \qquad k\leqslant 2\pi/\lambda. \tag{17}$$

Even for $k=2\pi/\lambda$ and $\lambda=5000$ Å, we find $\gamma_{\text{rad}}\approx 0.1$ meV, which is significantly smaller than the above estimation of 5.4 meV for Γ. The quantity γ_{rad} decreases fast with decreasing k. In fact, the main contribution to the excitonic linewidth in quantum wires is of nonradiative nature and due to scattering processes on the structural imperfections, surface corrugation, etc. At low temperatures, the nonradiative linewidth may be ~ 1 meV for Wannier excitons, and even smaller for Frenkel excitons. These linewidths may be thus smaller than the resonant splitting $2\Gamma\approx 11$ meV of the hybrid excitations.

Up to now, the consideration has been restricted to the case of a pair of wires. The results obtained may be straightforwardly extended to the case of a 2D array of alternating organic and semiconductor wires. Due to the periodicity in the alternation (x) direction of the array, the excited states acquire an additional label, which is the wave-vector component k_x. Due to the fast decay of Γ with increasing interwire distance, the hybridization may be considered in the nearest-neighbor approximation. In this approximation $\Gamma(k,k_x) =2\Gamma(k)\cos(k_xR)$.

In conclusion, we have demonstrated the possibility of strong resonance hybridization of Frenkel and Wannier-Mott excitons in parallel organic and inorganic semiconductor wires. The new states possess the properties of both types of excitons. They have a large size like Wannier-Mott excitons, but they have also a large transition dipole moment that is typical for Frenkel excitons. Thus, one could expect strong nonlinear optical effects in such systems.

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