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Exciton Polaritons in 1D Organic Nanocrystals

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Today's computers, using the movement of electrons in and out of transistors to do logics, are rapidly approaching fundamental limits caused by interconnect delay and large heat generation. Optical or photonic computing, which is intended to use photons produced by lasers or diodes, in place of electrons, has been pursued as a potential strategy for advancing beyond these limitations. Relative to electrons, photons are greatly superior in many aspects; they are faster, and have higher bandwidth, larger information-carrying capacity, and greater resistance to electromagnetic-wave interference.[1] However, the diffraction limit of light hinders the miniaturization of integrated photonic devices. Among diverse strategies developed to break the bottleneck, polaritons, arising from the strong coupling of electromagnetic waves with an electric or magnetic dipole-carrying excitation, are now being actively investigated as the most promising one. Polaritons have interesting hybrid photonic–electronic features, including reduced effective mass when compared to excitons, bosonic particle statistics, and long temporal and spatial coherence length.[2] Surface plasmon polaritons (SPPs), that is, quanta collective electron oscillations strongly coupled to photons in metals, afford a possibility to control light at the nanoscale and become an important subfield in nanophotonics.

Takazawa et al. recently described the realization of micrometer-scale photonic circuits based on the propagation and coupling of another kind of polaritons, exciton polaritons (EPs) in 1D organic dye nanocrystals.[3] EPs, which have generally been regarded as cavity polaritons in the past, are formed by strong coupling between a photon and an exciton,[4] which is a migratory electron–hole bound pair. **Figure 1**A illustrates the formation of EPs. When an exciton and a photon are placed in a cavity, and the cavity resonance is tuned to the exciton absorption line, they can strongly couple to form a new eigenstate called an EP.[5] Compared with uncoupled light, EPs show remarkable propagation properties,[6] such as anomalously low group velocity,[7] which leads to a substantially large refractive index of the media,[8] enabling nanowires with subwavelength width to propagate the EPs and steer them at wavelength scale. This opens up potential applications of nanowires in highly miniaturized EP-based photonic devices, and paves the way to a new generation of integrated photonic circuits.

To realize such nanowire devices, EPs must be stable enough to propagate over macroscopic distances. The stability is governed by the exciton binding energy E_{ex} and the longitudinal–transverse exciton splitting energy ΔE_{L-T}, which is proportional to the strength of the photon–exciton interaction. When E_{ex} and ΔE_{L-T} are greater than the thermal energy kT, where k is the Boltzman constant and T is temperature, EPs can be stable in medium. For inorganic materials, EPs have generally been observed at cryogenic temperatures[8b,9] because of the intrinsic limitation posed by the weakly bounded Wannier excitons, which break apart as the temperature rises, thus destroying the polaritons.[10] In contrast, materials used in this work[3] possess

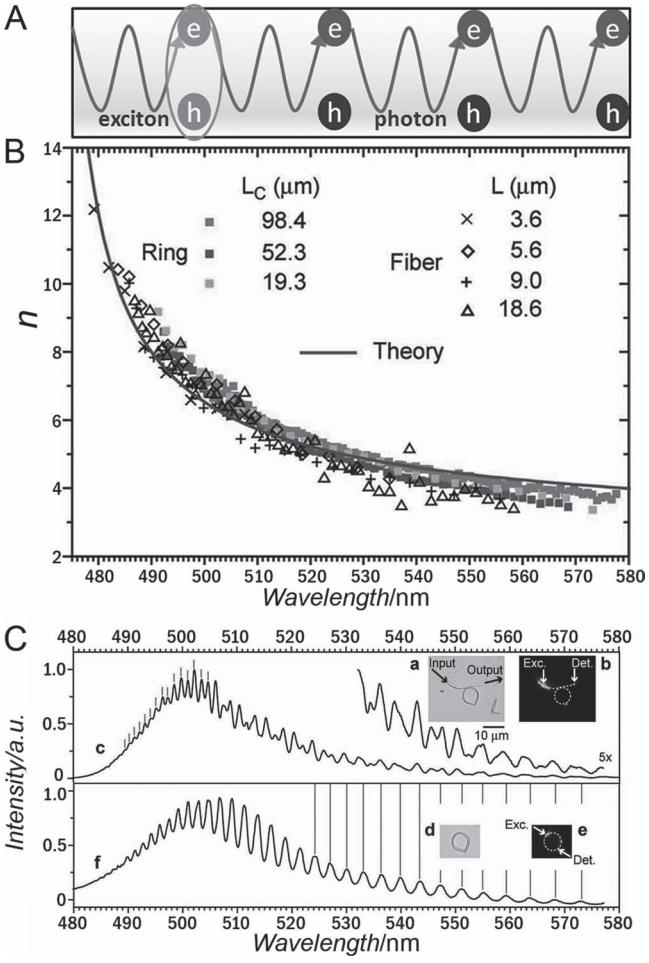

Figure 1. A) Graphic expression of the formation of EPs, which results from the strong coupling of photons and excitons. B) The refractive index $n(\lambda)$ obtained from the resonance peaks of microring cavities and the Fabry–Pérot (FP) modes of straight nanofibers agree well with each other. C) Ring-resonator component and coupling properties: The left upright bars indicate the FP modes of the I/O bus, while the right upright lines indicate the coupling EP ring modes with a slight constant shift to ordinary ring modes. Reproduced with permission.[3]

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inherent advantages, that excitons in organic materials are Frenkel type with larger E_{ex} and transition oscillator strength.[11] Since both E_{ex} and ΔE_{L-T} of Frenkel excitons are on the order of eV and much larger than kT (30 meV)[12] at room temperature, EPs in a wide variety of organic molecules are far less fragile than their inorganic counterparts.

Strong exciton–photon coupling in organic materials was first demonstrated in an organic-based microcavity by David Lidzey and co-workers by using a porphyrin-based compound blended in a polystyrene film.[13] This pioneering work has ignited intense interest in EPs in organic systems. The cyanine dye nanowires prepared by Takazawa and colleagues showed efficient propagation of EPs over a millimeter scale at room temperature,[11] indicating that the energy is well confined in the nanowire, and the scattering into the surrounding medium is quite limited. Shown in Figure 1B is the refractive index $n(\lambda)$ obtained from the resonance peaks of microring cavities and the FP modes of straight nanofibers.[3,11] The $n(\lambda)$ curves obtained independently from the rings and the straight fibers agree well with each other, confirming that the rings also functioned as EP cavities. Such a long-distance transmission suggests a new strategy to manipulate EPs through singlet–singlet, triplet–triplet, or singlet–triplet energy transfers in doped nanowires during propagation. In our recent work, we found that the fluctuation of singlet and triplet excitons allowed doped EP waveguides to behave as a kind of optical modulator,[14] which represents a new way to achieve stable white-light sources and novel multicomponent waveguides for miniaturized photonic devices.

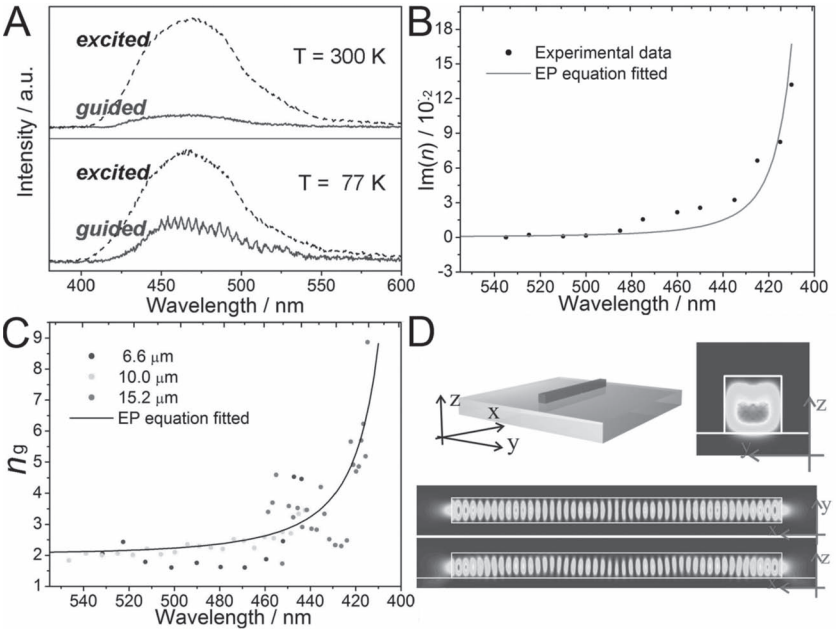

Figure 2. A) Fluorescence spectra of the excited spots and the guided spots at room temperature (300 K) and liquid nitrogen temperature (77 K), respectively. B) Imaginary part $\kappa_{||}(\lambda)$ and C) real part $n_{||}(\lambda)$ of the complex refractive index versus wavelength. The dramatic increase of $\kappa_{||}(\lambda)$ and $n_{||}(\lambda)$ reflects the presence of EPs. D) Simulated electric-field intensity distribution in a nanowire EP resonator. Reproduced with permission.[19] Copyright 2011, American Chemical Society.

The excellent flexibility of organic nanowires facilitates the preparation of annular EP channels with varying circumference. All cyanine loops in Takazawa's work function as EP-ring resonators, and the bending loss is negligibly small for loops with average curvature radius of 3.1 μm and above.[3] That is to say, EPs can be propagated in either straight or curved organic nanowires in a near-lossless way. As curved waveguides are indispensable in photonic circuits, the propagation loss of EPs resulting from continuous or discontinuous bending becomes an important parameter in evaluating the performance of devices. These findings ensure the microminiaturization of EP-based photonic circuits. This may be a powerful basis for the development of long-distance interactions, such as remote control and sensing.

Takazawa and co-workers also constructed a practical photonic circuit by manipulating two organic nanowires: one serves as an I/O bus and the other as a ring resonator. The EPs propagating along the bus can be loaded into the ring if the ring and the wire are sufficiently close (Figure 1C).[3] Since the EPs have an unusual dispersion relationship, the refractive index of the nanowires increases rapidly with photon energy at the high-energy region. The great divergence in refractive index between the wire and surrounding dielectric leads to the tight restrainment of EPs in the wire. This opens the door to ultracompact integration with low crosstalk between adjacent EP routes. A coupling coefficient of 0.8 was achieved,[3] which implies an efficient split and combination for fabricating various types of interferometers. In addition, the monotonic rise of refractive index with photon energy induced by the EP effect leads to a wavelength-dependence of the coupling, which will find a great number of applications in multiplex circuit components.

In a typical microcavity, two facets serve as imperfect reflectors during EP propagation that reflect a small portion of EPs to travel back and forth while the residuals leak out of the cavity radiatively. Due to the bosonic nature of polaritons,[15] EPs can lase at a low threshold because the process does not need a population inversion; this provides a solution to the contradiction between the conventional relatively high lasing threshold and the low damage threshold of organic crystals.[16] EP lasing at room temperature has been demonstrated in both an organic microcavity composed of a melt-grown anthracene single nanocrystal sandwiched between two dielectric mirrors,[17] and a single GaN nanowire microcavity that consists of a SiO_2 λ cavity sandwiched by top and bottom-distributed Bragg reflectors.[18] The clear observation of a threshold for nonlinear emission is accompanied by a significant line narrowing, a collapse of the emission lifetime, a change in the modal structure, and a redistribution of the EP population.[10]

1D crystalline nanostructures with optically flat surfaces can be regarded as natural FP resonators with high Q-factors to realize the EP lasing. Recently, we obtained EP lasing with low lasing threshold under two-photon pumping in a single nanowire.[19] It can be seen in **Figure 2**A that the modulated fluorescence spectrum from nanowire tips exhibits characteristic FP modes at 77 K, which indicates enhanced EP stability at

low temperature. As shown in Figure 2B, $\kappa_{||}(\lambda)$ is nearly zero up to 2.65 eV and then sharply increases at ≈2.7 eV, which implies that the attenuation of guided EPs is very low below 2.65 eV but rapidly increases above ≈2.7 eV. The $n_{||}(\lambda)$ values shown in Figure 2C increase dramatically with energy, exceeding 8.0 at energies of ≈3.0 eV, which is an unusually large value for dielectric waveguides. This anomalous behavior of $n_{||}(\lambda)$ strongly suggests that the guided fluorescence propagates as EPs. The well-confined EP energy in the resonator (Figure 2D) is of great significance for lowering the lasing threshold. We observed UV lasing in a single nanowire and found that the resonance of EPs is highly sensitive to the dimensions of the nanowire resonator,[20] which reveals a way to modulate the modes of EP lasing. Though the thresholds are currently not as low as expected, EP lasing—propelled by the enormous progress in function-oriented molecular design and synthesis—may eventually lead to electrically pumped near-zero threshold sources working at room temperature, which are sought after for photonics.

Aside from the technological importance of making progress towards applications, these results are also a step forward in understanding and utilizing EPs. Considering the vast number of optically and electronically active organic molecules, the properties of which can be easily tailored by using rational design, and considering the diverse construction strategies, as well as the outstanding optoelectronic properties of 1D nanostructures,[21] organic nanowires are expected to have equally great potential as their inorganic analogues, which have proved to be workhorses[22] of nanoscale science and engineering. The EP effect brings additional advantages to the organic version of the nanowires, including the ability to break through the diffraction limit, an ultralow propagation loss, a high coupling efficiency, and an extremely low lasing threshold and so on, all of which points toward a bright, promising future.

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