

CHAPTER 3

Photonics and Plasmonics

3.1 Introduction

Electronic circuits provide us with the ability to control the transport and storage of electrons. However, their performance is now becoming rather limited when digital information needs to be sent from one point to another. Photonics offers an effective solution to this problem by implementing optical communication systems based on optical fibers and photonic circuits. Unfortunately, the micrometer-scale bulky components of photonics have limited the integration of these components into electronic chips, which are now measured in nanometers. Surface plasmon-based circuits, which merge electronics and photonics at the nanoscale^[1], may offer a solution to this size-compatibility problem. So, plasmonics can be considered as a kind of nanophotonics. In this chapter, we introduce the excitation kinds of plasmons and plasmonics, which are mainly focused on the exciton and polariton.

3.2 Exciton

3.2.1 Brief introduction of excitons

In 1931, Frenkel (Fig. 3-1) first proposed the concept about excitons, he indicated that it was possible for neutral excitation of a crystal through light

where electrons remained bound to the holes generated at the lattice sites, the lattice positions were determined to be quasiparticles, i. e. exciton^[2]. Excitons were electrically neutral and were mostly found in insulators, semiconductors and certain liquids^[2,3]. When photons were absorbed by a semiconductor, excitons were generated, causing electrons to transition from the valence band to the conduction band. The decay of exciton, in other words, the recombination about hole



Fig. 3-1 Yakov Il'ich Frenkel

and electron, was limited by the resonance stability owing to the overlap of hole and electron wave functions, causing a prolonged lifetime about the exciton.

Since the discovery of the excitons, their lifespan has been very short, only 10 microseconds, and the energy extremely low, which made the study of exciton movement very difficult. However, due to the development of laser, low-temperature and electronic technologies, extremely favorable conditions had been provided for the study of surface excitons. Because the laser could emit a monochromatic beam of intense energy with a large intensity, the intensity of the light indicated that the number of photons contained in the beam increases, which caused a large number of excitons to be generated in the crystal. In 1966, Haynes first observed electron-hole droplets, that is, a large number of exciton condensates, which led to a new phase of exciton research. Later, the researchers studied fluid quantum mechanics. In addition, the formation of crystal defects and motion and exciton were linked, and certain results had been achieved. Therefore, the study of excitons was currently a hot area in solid state physics. Moreover, in addition, excitons were divided into many types, such as the Frenkel^[4-14], the Wannier-Mott^[15], the charge-transfer^[16-23], the surface^[24-26], and the atomic and molecular excitons^[27,28], as well as the self-trapping of excitons^[29, 30].

3. 2. 2 Exciton classification

Frenkel excitons

The Frenkel excitons named after him, has a binding energy of 0.1 eV to 1 eV. And it had considerable interaction cross sections having molecular vibrations. Particularly, about coherently coupled Frenkel excitons, the rate of exciton scattering was significantly enhanced. Furthermore, the application of Frenkel excitons was very extensive. For example, in previous study, the *J* band in the PIC aggregates in the glass and Langmuir-Blodgett (LB) films could be described by the disordered Frenkel exciton band, it was proved that resonance light scattering was an important tool for studying exciton dynamics in polymers and aggregates. And in organic semiconductor microcavities, the studies of photon-mediated hybridization of Frenkel excitons was demonstrated. Microcavities were artificial structures of wavelength dimension in which coupling could be excited by their mutual interaction with restricted photon modes. Energy storage, capture and transfer between excitations of coherently coupled molecules could be studied. Studies had shown that it was possible to generate mixed exciton materials consisted of coherently coupled excitons in a microcavity. These novel hybrid exciton-photon structures had probable research interests as model systems for studying energy capture and storage and energy transfer between excitations of coherently coupled molecules was of great help. Especially the bright and dark states might allow for the study of energy capture and storage functions. If energy transfer was indeed feasible, the Frenkel-Wannier hybrid exciton device will be more widely used.

There had some progress in the study about the interference between the charge-transfer (CT) state and the Frenkel exciton for the perylene pigments crystallochromy. For compounds having smaller holes and electron transfer, such as diindenoperylene (DIP) and 3, 4, 9, 10-perylene tetracarboxylic dianhydride (PTCDA), their molecular structural formulas were shown in

Fig. 3-2. For materials with relatively large electron and hole transport, the exciton model allowed the energy about the CT transition to be determined down the stacking direction with an accuracy better than 0.05 eV, which was much lower than the systematic deviations produced by the general calculation. In addition, for the breakdown about the Frenkel exciton model, the exciton band structure about pentacene molecular solids was applied here. Studies had shown that the exciton dispersion behavior of pentacene measured from electron energy-loss spectroscopy (EELS) was inconsistent with Frenkel-like electron-hole pairs, and further research is needed. And, there were of course many other applications, such as in-band relaxation about the fluorescence decay time about 1 D Frenkel excitons, and low-energy spectra about 1D local Frenkel excitons of Hidde structures.

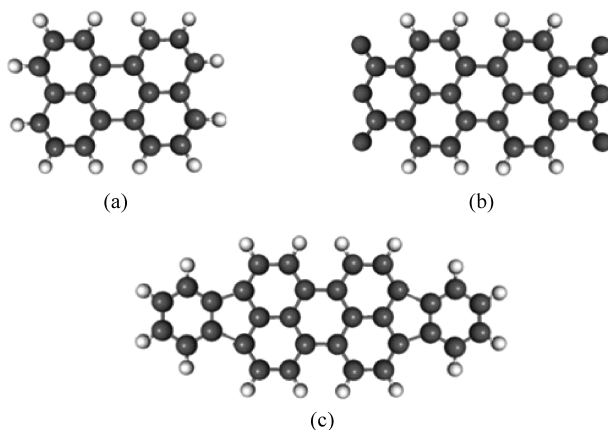


Fig. 3-2 The structures of (a) Perylene, (b) PTCDA and (c) DIP^[8]
(For colored figure please scan the QR code on page 1)

Wannier-Mott excitons

Excitons were the basic optical excitation of dielectric solids. Two excitons were created in nature, namely the Frenkel exciton with smaller radius and the Wannier exciton with larger radius. Among them, Wannier excitons were formed in materials used in semiconductor technology. Because of the

different radii of the two excitons, they had completely different properties. Wannier exciton interaction density is low, resulting in a multi-particle effect which is related to laser action and optical nonlinearity; while the Frenkel excitons, due to their small radius, barely saw each other but produce huge features in the spectrum^[15].

Wannier-Mott excitons had a large dielectric constant, therefore, the electric field shielding effect weakened the Coulomb interaction between holes and electrons, i. e., Wannier excitons, whose radius was greater than the lattice spacing. The small effective electron mass typical for semiconductors favors excitons with larger radii. Compared with hydrogen atoms, owing to its small mass and Coulomb interaction, its binding energy was small, about 0.01 eV.

In recent years, inorganic and organic semiconductor nanostructures had been the subject of much research. There was a need to synthesize composite inorganic or organic semiconductor heterostructures for using in the synthesis of novel nanostructures of optics, electrons, and transport to further understand their size-dependent physical properties. Hybrid excitons could be generated from the resonant mixing about Frenkel-Wannier-Mott excitons in inorganic or organic quantum wells, which was a new elementary state produced by optical excitation. This hybrid exciton exhibited unique physical properties while providing a foundation for new electro-optic technology. This unique mixed exciton had the properties of two excitons. In addition, the resonator of the Frenkel exciton was quite strong, and the Wannier-Mott exciton had a large radius and was delocalized.

In previous studies, the authors had researched the nonlinear and linear optical properties about inorganic-organic nanostructure caused by resonance interactions between Wannier-Mott excitons in semiconductor quantum wells (QWs) and Frenkel excitons in organic QWs. For the Coulomb dipole-dipole interaction and through the cavity photons in the microcavity, this coupling resulted in the mixing of Frenkel-Wannier excitons. Studies had shown that enhancement of resonance optical nonlinearity, relaxation processes, and the

fluorescence efficiency could be achieved by adjusting this hybrid state and the plotted dispersion curve.

It was known that in the physical system, there were two quantum wells, the inorganic semiconductor and the molecular solid. Therefore, the authors considered a novel kind of electronic excitation owing to Frenkel and Wannier exciton hybridization. The physical system contained a 2D layer separated by a distance z_0 , which was a tightly bound Frenkel excitons (FE) and a loosely bound Wannier excitons (WE), and they had the same energy. These two were referred to as organic quantum wells and inorganic quantum wells, respectively, and it was worth noting that this model was equally applicable to any heterostructure having a layer that maintains large and small radius resonant excitons. The real excitation in the physical system was a hybrid exciton (HE) owing to the dipole-dipole interaction between WE and FE. When EF and WF were almost completely mixed, 2D HE were most likely to display strong optical nonlinearities in some fields. For example, excitons with smaller radii had larger oscillator strength, and excitons with larger radii had a smaller saturation density.

In 1998, the authors had proposed a new type of HF in organic-inorganic heterostructures, and had researched some nonlinear optical properties in theory. For ordinary semiconductor quantum wells, it could be predicted that the linear and nonlinear portions of the susceptibility coefficient will produce strong enhancement. Studies had shown that the above results were consistent with FE with larger oscillator strength and WE with smaller saturation densities, both of which were hybrid resonances. If the above structure could be synthesized successfully, it will show significant nonlinearity. In addition, hE were also important systems for studying the properties of electro-optical and magneto-optical properties. To further demonstrate the above experimental results, the authors also studied resonant inorganic and organic quantum wells in microcavities. Although only a hypothesis, the authors believed that in this structure the exciton relaxation time could be reduced to a

state with a larger radiation width and a shorter fluorescence decay time. The authors also hypothesized that the combination of the electrical pumping about excitons with fast relaxation in inorganic quantum wells and the fluorescence about excitons in organic quantum wells would provide new ways to study the exciton process in microcavities, which will also be applied to more devices.

Charge-transfer excitons

Between the WE and the FE, there was a special excitons called charge-transfer excitons (CT excitons)^[16]. When an electron and a hole separately occupy adjacent molecules, the exciton was generated. CT excitons were mainly present in ionic crystals. Unlike the WEs and the FE, they were capable of exhibiting electrostatic dipole moments. CT excitons could be generated at the organic semiconductor surface and interface, i.e. the donor and acceptor interfaces in an organic heterojunction solar cell. According to the classic dielectric constant about organic semiconductors and the size about conjugated molecules, it was estimated that the binding energy about CT excitons at the acceptor and donor interfaces will be an order of magnitude larger than $k_B T$ in condition of room temperature, where T was temperature and k_B was the Boltzmann constant.

The use of CT excitons was widespread. For example, in organic photovoltaic (OPV) devices, the generation of photocurrents relied on the dissociation about excitons into free electrons and holes at the acceptor/donor heterointerface. Since the organic semiconductors dielectric constant was low, the strong interaction between electrons and hole pairs effectively prevented the generation of free charges, and electrons and holes will overcome the capture of Coulomb interactions to some extent. Studies had shown that thermal CT excitons played a key role in this process. The authors used femtosecond nonlinear spectroscopy and non-adiabatic hybrid quantum mechanics to generate thermal CT excitons using the phthalocyanine-fullerene model OPV system. Studies had shown also that when the reaction was carried out for 10—

13 seconds, that is, the phthalocyanine just started to excite, it will generate thermal CT excitons, then reduce the energy and shorten the distance between electron-holes. At the same time, as mentioned above, for typical molecular size and dielectric constant, the interfacial CT exciton binding energy of several hundred millivolts of electrons was estimated to be an order of magnitude higher than the thermal energy at the condition of room temperature.

Another important application was the use of the FE with the lowest energy and CT excitons in the quasi-1D structure for *N,N'*-dimethylperylene-3,4,9,10-dicarboximide (MePTCDI) and PTCDA crystals. The authors proposed a Hamiltonian that included some vibrating FE and a nearest neighbor CT exciton that could describe the polarization direction, peak intensity, and energy position of a 1D crystal for a molecule that contained only one molecule. The intrinsic oscillator strength of crystal and CT excitons was very small. Electro-absorption measurement was the most ideal direct observation tool. It proved that CT excitons had large internal transition dipole moments in quasi-1D crystals having strong orbital overlap, which seriously affected the polarization direction about the mixed excitons. However, the CT transition dipole reached a polarization ratio for a three-dimensional (3D) crystal containing two molecules and having a weak coupling between 1D stacks. This mechanism directly demonstrated the mixing about Frenkel and CT excitons in MePTCDI, which was not directly related to electroabsorption measurements^[17].

Other applications of CT excitons included polymer/fullerene mixtures, bulk heterojunctions of polyfluorene copolymers and fullerene derivatives, van der Waals interfaces, polymer semiconductor heterojunctions, organic solar cells, narrow band gap polymer-based volume heterojunctions, and organic solids in first principle^[18-22]. Among them, the molecular donor/acceptor and the van der Waals interface of the graphene-based 2D semiconductor were the key to the photo-electrical mutual conversion, including photodetectors, light-emitting diodes and solar cells. A distinguishing characteristic of the two van der Waals

interfaces was the poorly shielded Coulomb potential, resulting in bound electron-hole pairs, i. e. CT excitons. For organic solar cells, the dissociation efficiency about the CT state of the weakly bonded interface was very significant for organic heterojunction solar cells. And the authors examined a variety of donor polymers and acceptors through photoluminescence (PL) quenching to observe that the dissociation is not different from CT excitons and FE. Studies had shown that the field-dependent photocurrent about pure polymers was related to the quenching effect. However, the correlation between CT exciton quenching and photocurrent was not significant. It was worth noting that for pure polymers, PL and electroluminescence were the same, but red shift of blend electroluminescence could still be observed. The above indicated that the energy in the blending was low and was not visible in PL. Thus, the luminescent state of the PL-detected blend was produced by photocurrent^[23].

Surface excitons^[24-26]

In previous studies, the theory about surface excitons in molecular crystals showed that the presence of surface excitons and their states on or below the exciton state were based on the nearest neighboring environmental displacement term and the exciton transfer term determines. In addition, the surface exciton's localization energy was not sensitive to the thickness of crystal.

Surface excitons were widely used. For example, ionic crystals and rare gases. Here was a brief introduction to the application of surface excitons in ZnO crystals, which were n-type semiconductors with upwardly band bending on the surface, and generated by negative acceptor-like surface states. When the light was excited, the surface electric field separated the photocarrier from the surface, and the photocarrier was accompanied by movement to the bulk of the electrons and holes. Note that the surface excitons studied here had very specific time behaviors. For bound excitons, their decay time was very short.

The study of the radiation and non-radiative decay mechanisms about surface excitons needed to require more in-depth research. Therefore, the authors suggested that the surface-bound excitons decay might be related to low temperatures.

Surface excitons could still be observed in rare gases. The first evidence showed that surface excitons were observed only under ultrahigh vacuum (HHV) conditions, and their strength was quickly reduced even in very small ranges, such as 10^{-10} Torr. More than twice as much as half an hour. The residual gas adsorbed by the single layer causes the surface excitons to disappear. When covering different rare gas films, the surface excitons will disappear, while the surface excitons of the overlay will emerge.

For studying the dependence of surface excitons on film thickness, since the transmittance of each film was constant, the transmittance of the multilayer film decreased with increasing thickness. The authors speculated that surface excitons caused the sample to be limited to 1 layer to 2 layers. In addition, studies had shown that the position of excitons, splitting, and the strength of the oscillator needed to be considered. Compared to bulk excitation, surface excitation was caused by changes in the spatial environment close to the surface.

Another important application was volume and surface excitons in solid neon. Rare gas solids (RGSs) were prototype materials for insulators because RGS had a relatively simple electronic structure at the ground state. The valence band was produced by the relatively weak van der Waals force in the crystal and the outermost closed p-shell electron^[24].

Atomic and molecular excitons

In previous studies, molecular exciton models were used to deal with excited-state resonance interactions in weakly coupled electronic systems, which was seen as an important tool for studying the photochemistry and spectroscopy of complex molecules. For composite molecules, loosely bound light absorbing