Energy transfer from InGaN quantum wells to Au nanoclusters via optical waveguiding

G. W. Shu,[1] C. C. Lin,[1] H. T. Lin,[1] T. N. Lin,[1] J. L. Shen,[1] C. H. Chiu,[2] Z. Y. Li,[2] H. C. Kuo,[2] C. C. Lin,[2] S. C. Wang,[2] C. A. J. Lin,[3] and W. H. Chang[3]

[1]Department of Physics and Center for Nanotechnology at CYCU, Chung Yuan Christian University, 32023 Chung-Li, Taiwan

[2]Department of Photonic and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsin-chu, Taiwan

[3]Department of Biomedical Engineering, Chung Yuan Christian University, Chung-Li 32023, Taiwan

** jlshen@cycu.edu.tw*

Abstract: We present the first observation of resonance energy transfer from InGaN quantum wells to Au nanoclusters via optical waveguiding. Steady-state and time-resolved photoluminescence measurements provide conclusive evidence of resonance energy transfer and obtain an optimum transfer efficiency of ~72%. A set of rate equations is successfully used to model the kinetics of resonance energy transfer.

OCIS codes: (300.6470) Spectroscopy, semiconductors; (260.2160) Energy transfer; (160.4236) Nanomaterials.

References and links

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1. Introduction

Förster resonance energy transfer (FRET), in which a fluorescent donor transfers energy via nonradiative dipole-dipole interaction to a fluorescent or nonfluorescent acceptor, is a powerful technique to measure distance-dependent interactions [1]. This technique can be utilized for determination of molecular binding events, the structure and dynamics in organic molecules, and macromolecular assemblies such as biological membranes and proteins [2–4]. For the past years, fluorescent organic dyes have been widely used as donors and acceptors in the field of FRET-based research and applications [2]. FRET involving of organic dyes as the donor-acceptor complexes are often limited by the need for overlap between the emission and absorption spectra as well as the minimum direct excitation of acceptors. Colloidal quantum dots have recently been employed as the donor fluorophores to participate in FRET [5–7]. The broad excitation spectra and large absorption cross section of quantum dots paired with the narrow excitation spectra of acceptor dyes permit flexibility in the selection of the donor excitation wavelength which reduces unwanted direct excitation of the acceptor and enables an efficient FRET [5].

An alternative type of FRET is the electronic energy transfer between a quantum-well donor slab and an overlay of acceptors, which has been theoretically predicted at the late 1990s [8]. The resonant dipole-dipole interaction between the two layered materials in combination with the fast dephasing can lead to the non-radiative transfer of semiconductor excitation energy to the acceptors [9]. Several years later, resonance energy transfer via such a prototype structure has been implemented experimentally between semiconductor quantum wells and colloidal quantum dots [10]. Resonance energy transfer between the quantum wells and the layered organic materials has also been demonstrated [11–14], which provides an alternative pumping technique for hybrid inorganic-organic light emitters. In this type of energy transfer, the nonradiative transfer rate can exceed the radiative rate by one or two orders of magnitude, leading to high energy transfer efficiencies. An energy transfer efficiency as high as 55% has been reported [10]. By improving the quality of the quantum wells and/or by optimizing the geometry of acceptors/donors structure the efficiency of energy transfer in the layer-to-layer structure has been suggested to achieve nearly 100% [10].

In this FRET scheme, however, acceptors are still excited directly by the excitation light. This limitation reduces the transfer efficiency and/or sometimes leads to an ambiguousness of the obtained efficiency.

Here we develop a new energy transfer configuration to create FRET through light waveguiding, avoiding unwanted excitation of the acceptors. The resonance energy transfer was demonstrated by the steady-state and time-resolved photoluminescence (PL) using an InGaN quantum-well donor paired with an Au nanocluster (NC) acceptor. The acceptor in this configuration is excited solely by energy transfer from the donor (Fig. 1), leading to an improvement of energy transfer rate and an accurate energy transfer efficiency. To our knowledge, very few studies on the Au NC-based FRET have been reported before. One possible cause is that severe damage of Au NCs might happen when the NCs are photoexcited by the incident laser directly. However, using this new configuration, the Au NCs can avoid direct illumination of the excitation laser and prevent damage of the Au NCs.

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2. Experiment

The donor used for the present study is a single InGaN/GaN quantum-well structure grown by metal-organic chemical vapor deposition on a sapphire substrate. After a 200μm thick GaN buffer layer on the substrate, a single InGaN quantum-well layer with thickness of 2 nm was grown. The growth is terminated by a 2 nm thick GaN cap layer. The acceptor in this study is the Au NCs capped with dihydrolipoic acid (DHLA). The details of the growth method for Au NCs are described in literature [15]. Briefly, the gold precursor solution was prepared by dissolving $AuCl_3$ in the dihydrolipoic acid bromide solution. Decanoic acid was then combined with didodecyldimethylammonium bromide in toluence, followed by gold precursor solution. The synthesized Au colloids were further fragmented by adding the precursor solution, leading to formation of the Au NCs (mean diameter ~2 nm). To perform the FRET experiment, an Au NC (acceptor) was incorporated on the top of an InGaN quantum well (donor) by the drop-casting method upon evaporation of the solvent. The steady-state and time-resolved PL was measured at 15 K, using a cold finger of a closed-cycle helium cryostat. A pulsed laser with a wavelength of 260 nm, a repetition frequency of 20 MHz, and a duration of 250 fs was used as the excitation source. The collected luminescence was projected into a spectrometer and detected with a high-speed photomultiplier tube (PMT). Time-resolved PL were performed using the technique of time-correlated single-photon counting (TCSPC). The instrument response of the time-correlated single photon counting system is about 250 ps.

3. Results and discussion

Figure 2 (a) and 2 (b) shows the PL and PL excitation spectra of the Au NC, respectively. The PL spectrum of the single quantum well is shown in Fig. 2 (c), revealing a narrow PL band that peaks at around 420 nm. This wavelength is in the range of strong absorption for Au NCs, which allows strong coupling between donors and acceptors and efficient energy transfer from

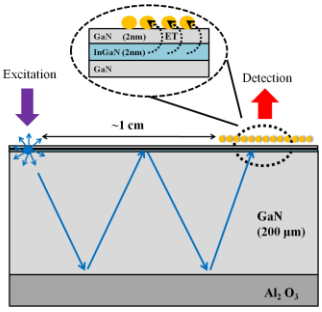

Fig. 1. Schematic representation of the resonance energy transfer from the InGaN quantum well to Au NCs via optical waveguiding.

the quantum well to Au NCs. In this study, a particular geometry was designed to observe FRET via optical waveguiding. The excitation was done by using normal incidence, while the luminescence was collected at the position about 1 cm away from the excitation spot (Fig. 1). Multiple total internal reflections occur within the GaN layer if the angle of incidence is above 48° (resulting from the refractive indices n_s = 1.64 for the sapphire and n_{GaN} = 2.42 for the GaN layer). Thus, some of the PL light exiting from the quantum well can totally internally reflect at the GaN/sapphire and GaN/air interfaces, creating a waveguide mode within the GaN layer. The waveguide mode propagates inside the GaN layer until the light looses all of its energy or it reaches the edge of the sample. This configuration avoids direct excitation of the acceptors, but allows transfer of energy before the donor is deexcited by some other competing processes.

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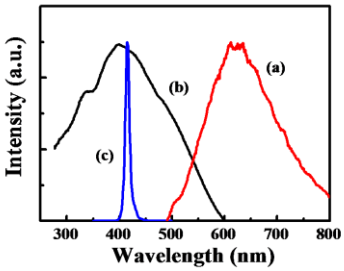

Fig. 2. (a) PL spectrum of Au NCs (b) PL excitation spectrum of Au NCs (c) PL spectrum of the InGaN quantum well.

The top-view photograph of the investigated sample is depicted in the inset of Fig. 3 upon optical excitation according to the configuration in Fig. 1. Clear red light from acceptors can be seen in the region where the acceptors was drop-casted (marked by the open ellipse), about 1-2 cm away from the laser excitation spot (marked by an arrow). Based on this configuration, the solid and dashed line in Fig. 3 shows the PL spectrum in the presence and absence of acceptors, respectively. A decrease of the relative donor PL intensity and a simultaneous increase in the acceptor PL emission was observed in the presence of acceptors. This observation demonstrates the energy transfer from InGaN quantum wells to Au NCs. However, it is important to distinguish between radiative pumping of the Au NCs from the quantum-well emission and nonradiative FRET from quantum wells to Au NCs.

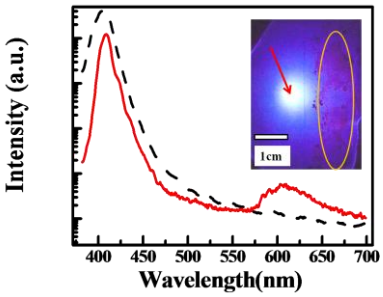

Fig. 3. PL spectra of the InGaN quantum well in the presence (the solid line) and absence (the dashed line) of Au NCs. The inset displays the photograph of the investigated sample under laser excitation (the spot marked by an arrow), showing the red emission of Au NCs (the region marked by the open ellipse).

The existence of FRET can be further identified by measuring the time-resolved PL. If the energy transfer is mediated through a nonradiative process, a decrease of the donor lifetime and a simultaneous increase of the acceptor lifetime should be observed. On the other hand, if the acceptor is pumped radiatively by the emission of donors, its lifetime should remain unchanged. The open circles in Fig. 4 (a) display the PL decay of the InGaN quantum well in the absence of Au NCs. The PL decay can be well fitted by a stretched exponential function [16]:

$$n_D(t) = n_D(0)e^{-(k_D t)^{\beta_1}}, \quad (1)$$

where $n_D(t)$ are carrier densities in donors (in the absence of acceptors) and k_D is the decay rate of carriers in donors and β_1 is a dispersive exponent. The dashed curve in Fig. 4(a) shows the fitted result, which is in good agreement with experimental results. The stretched exponential decay is often used to describe the dynamics in the disordered systems. The

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indium phase segregation and the associated spatial fluctuations of the local indium concentration have been suggested to be the origin of the disorder causing the stretched exponential kinetics in InGaN quantum wells [16]. The PL decay time of the InGaN quantum well in the presence of the Au NCs is displayed as the open squares in Fig. 4 (a). Evidently, the decay time from quantum wells in the presence of the Au NCs decreases considerably, in agreement with the behavior of FRET.

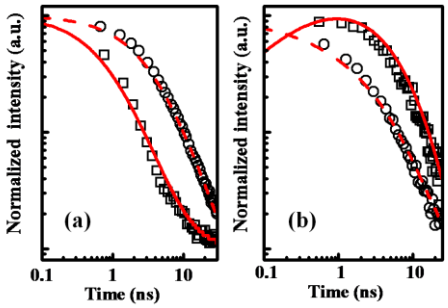

Fig. 4. (a) PL decay profile of the InGaN quantum well in the absence (open circles) and present (open squares) of Au NCs. The dashed line (solid line) is the fitted curve using Eq. (1) (Eq. (5)). (b) PL decay profile of Au NCs in the absence (open circles) and present (open squares) of InGaN quantum wells. The dashed line (solid line) is the fitted curve using Eq. (2) (Eq. (6)).

The open circles in Fig. 4 (b) display the PL decay of the Au NCs on a glass substrate. The PL decay of Au NCs can also be fitted by a stretched exponential function:

$$n_A(t) = n_A(0)e^{-(k_A t)^{\beta_2}}, \tag{2}$$

where $n_A(t)$ are carrier densities in acceptors (in the absence of donors) and k_A is the decay rate of carriers in acceptors and β_2 is a dispersive exponent. The dashed curve in Fig. 4(b) shows the fitted result using Eq. (2). The stretched exponential function has been used to describe the PL decays of Au NCs recently [17]. The open squares in Fig. 4 (b) display the PL decay of the Au NCs placed on top of the quantum well. A pronounced risetime of Au NCs roughly corresponding to the decay time of the donor PL was observed, providing clear evidence for FRET from the InGaN quantum well to Au NCs.

To quantitatively account for the FRET on the transient PL, it is necessary to determine the type of electronic excitations in the quantum well since the energy transfer mechanism is strongly dependent on whether the electronic excitations are unbound carriers (free electrons and holes) or bound electron-hole pairs (excitons) [10,14]. The excitation-density dependence of PL in an isolated quantum well was investigated to find out the type of carriers. The close squares in Fig. 5 shows the dependence of the integrated quantum-well PL on excitation density. A least square fit of the experimental data is displayed as the solid line in Fig. 5, revealing a slope value of 0.98. Such linear scaling suggests that the excitations in our case is excitons, but not the unbound electrons and holes. Based on this result, the rate of exciton density in FRET processes can be written as [18]:

$$\frac{dn_{DA}(t)}{dt} = -k_D n_{DA}(t) - k_{ET} n_{DA}(t), \tag{3}$$

where $n_{DA}(t)$ is the donor density in the presence of acceptors, and k_{ET} is the characteristic Förster transfer rate from donors to acceptors. The last term in Eq. (3) describes the additional

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relaxation channel for energy transfer. The $\propto t^{-1/2}$ corresponding rate equation for acceptors is then written as [18]:

$$\frac{dn_{AD}(t)}{dt} = -k_{NC} n_{AD}(t) + k_{ET} n_{AD}(t), \tag{4}$$

where $n_{AD}(t)$ is the acceptor density in the presence of donors. Assuming an initial population for the resonantly excited quantum well and the transfer rate is associated with the long-range resonance transfer ($\propto t^{-1/2}$) [19], the solution of the combined set of Eqs. (3)–(4) can be represented by

$$n_{DA}(t) = n_{DA}(0) e^{-(k_D t)^{\beta_1}} \times e^{-(k_{ET} t)^{1/2}}, \tag{5}$$

$$n_{AD}(t) = A e^{-(k_A t)^{\beta_2}} - B e^{-(k_D t)^{\beta_1}} \times e^{-(k_{ET} t)^{1/2}}, \tag{6}$$

where *A* and *B* are fitting parameters. Using Eq. (5) and Eq. (6), the solid lines in Fig. 4 (a) and 4 (b) are fits of the measured PL decays for donors and acceptors, respectively. The parameters used in the fits are listed in Table 1. The best fit curves well reproduce the experimental data, reconfirming that the energy from the quantum well indeed transfer to Au NCs and the configuration proposed in Fig. 1 is a new possibility for the creation of FRET in the layer-to-layer configuration.

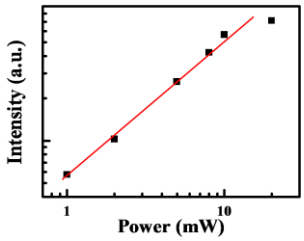

Fig. 5. The dependence of the PL intensity in InGaN quantum wells on excitation density. The nearly linear dependence reveals that recombination is dominated by excitons.

Table 1. The parameters used in the fits according to Eqs. (5) and (6)

k_A (ns^{-1})	k_D (ns^{-1})	k_{ET} (ns^{-1})	β_1	β_2	A	B
0.77	0.33	0.8	0.7	0.53	4.6	4.8

The energy transfer efficiency from donors to acceptors can be obtained experimentally and is commonly defined as [6]:

$$E = 1 - \frac{I_{DA}}{I_D}, \tag{7}$$

where I_{DA} and I_D is the PL intensity of the donor in the presence and absence of the acceptor, respectively. According to Eq. (7), the energy transfer efficiency obtained from Fig. 3 is 0.72. On the other hand, the energy transfer efficiency can also be calculated from the time-resolved PL measurements. The transfer efficiency is given by the donor decay rate in the absence and presence of acceptors. In the stretched exponential function the average decay time is represented by [20]

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$$< \tau >= \frac{1}{k\beta}\Gamma(\frac{1}{\beta}), \tag{8}$$

where Γ is the mathematical Gamma function. Considering $\langle k \rangle = \langle \tau \rangle^{-1}$, the energy transfer efficiency can be defined by

$$E = \frac{\langle k_{ET} \rangle}{\langle k_{ET} \rangle + \langle k_D \rangle}. \tag{9}$$

According to the fits in Fig. 4 (a) and the calculations from Eqs. (8) and (9), the energy transfer efficiency obtained from PL decay rates is ~0.70, in agreement with that from the change in PL intensities (0.72). The high efficiency in this configuration can be expected to be useful for providing FRET-pumping of organic gain media in optoelectronic devices and bio-analytical applications.

In summary, the resonant electronic energy transfer from InGaN quantum wells to Au NCs via optical waveguiding was investigated. Steady state and time-resolved PL were used to understand the FRET process. There is a decrease of the PL intensity and a shortening of PL decay time for the InGaN quantum well in the presence of Au NCs. A simultaneous increase in PL intensity and the PL rise time was observed at the acceptor sites. A set of rate equations for the kinetics of energy transfer from InGaN quantum wells to Au NCs has been used to understand the kinetics of energy transfer. The transfer efficiency obtained from the PL intensity is as high as 72%, in good agreement with the value extracted from the PL decay dynamics (70%). The observed FRET via optical waveguiding may be promising for their applications to the development of FRET-based bio-analytical and optoelectronic devices.

Acknowledgments

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