

CdTe and Au quantum-dot bioconjugated super-molecules: light emission and energy transport

Jaebeom Lee[†], Alexander O. Govorov[‡] and John Dulka[‡], Nicholas A. Kotov^{†,*}

[†] Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, 48109

[‡] Department of Physics and Astronomy, Ohio University, Athens, OH, 45701

This paper reports photoluminescence enhancement of CdTe nanoparticles from hybrid semiconductor-metal bioconjugated supermolecules. In the presence of metallic nanoparticles, excitonic light emission of nanoparticles is strongly enhanced. The enhancement effect is explained in terms of plasmon-assisted absorption of incident light and plasmon-induced increase of nanoparticle dipole moments. The supermolecules and bioconjugates can be used to build efficient photonic devices and biological sensors utilizing the light-harvesting effect.

1. INTRODUCTION

Metallic nanoparticles (NPs) such as Au or Ag are widely observed as attractive candidates for inorganic-organic or biological assemblies because of their unique optical and electronic properties.¹⁻⁵ These assemblies may be a potential key technique to construct further complicated applications for spectroscopy, chemical and biological sensing, microelectronic devices.

Here we present the energy transfer between Au NPs and CdTe NPs in solution state. Two NPs were bioconjugated by streptavidin and *d*-biotin. It was investigated that the emission intensity of CdTe NPs was 5 times increased after bioconjugation with Au NPs. Following electron microscopic and lifetime spectroscopic experiments proved that the PL enhancement of CdTe NPs would be originated from collective response of an ensemble of interacting Au-NPs.

2. EXPERIMENTAL

All chemicals such as Cd(ClO₄)₂H₂O, Mercaptoacetic acid (thioglycolic acid: TGA), Al₂Te₃ and NaOH were purchased from Aldrich and used without further purification. Since Al₂Te₃ was a high oxidizing and toxic agent it was stored in N₂ glove box. *D*-biotin and streptavidin were gained from Aldrich. 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), and N-hydroxy-sulfosuccinimide (NHS) were purchased from Aldrich and Merck for bio-conjugation, respectively.

CdTe NPs were prepared as mentioned precisely elsewhere.⁶ The diameter of Au NPs was measured as 3.7 nm using transmission electron microscopy (TEM). Two separated solutions with Au and CdTe NPs are prepared for bioconjugation. Au NPs were conjugated with streptavidin (SA) while CdTe NPs with *d*-biotin. Then the solution with Au NPs was mixed with another solution. SA and *d*-biotin demonstrate strong

* Corresponding Author: kotov@umich.edu, 734-763-8768

biological binding from ligand-receptor reaction, which is well-known as one of the strongest noncovalent biological interaction. Bond formation between d-biotin and streptavidin is very rapid and this binding is less affected by wide extremes of pH, temperature, or organic solvents or other denaturing agents.⁷ Au NPs were conjugated with streptavidin.

Two solutions that were bioconjugated Au-SA and CdTe-biotin were mixed in an optical cuvette of 3ml with a gentle stirring. The final volume of each solution was 10~400 μ l as the ratio 1:1 of Au-SA and CdTe-biotin remained. The UV-Vis spectrum of each sample was measured. The photoluminescences of samples were investigated using a fluorescence photometer (Fluoromax-3, Jovin Yvon Horiba, NJ). The PL intensity enhancement from the reaction between two solutions was chronically measured every 2- 10 min up to 2 hrs.

3. RESULTS

Fig. 1A depicts the UV-Vis spectra of individual bioconjugated NPs. CdTe NPs with *d*-biotin conjugation still remained strong and narrow emissions at each wavelength even though their quantum efficiency (QE) was decreased. The QE of CdTe NPs was calculated as 18%, compared with the QE of Rhodamine 6G as 95%. The QE of bioconjugated CdTe NPs was various in the range of 1.6 ~ 6.7 %. It can be seen that the surface plasmon peak of Au NPs is broaden after conjugation with CdTe NP and *d*-biotin because it is probable that the aggregation of Au NPs as well as Au-NP and CdTe-biotin would induce broadening.⁸

PL enhancement of CdTe NP-biotin system is presented in fig. 1B. The photoluminescence of CdTe NPs was enhanced twice for the first 20 min. The enhancement was then saturated at 80 min and the maximum wavelength of each spectrum shifts gradually toward higher energy range (blue shift) at the beginning of reaction.

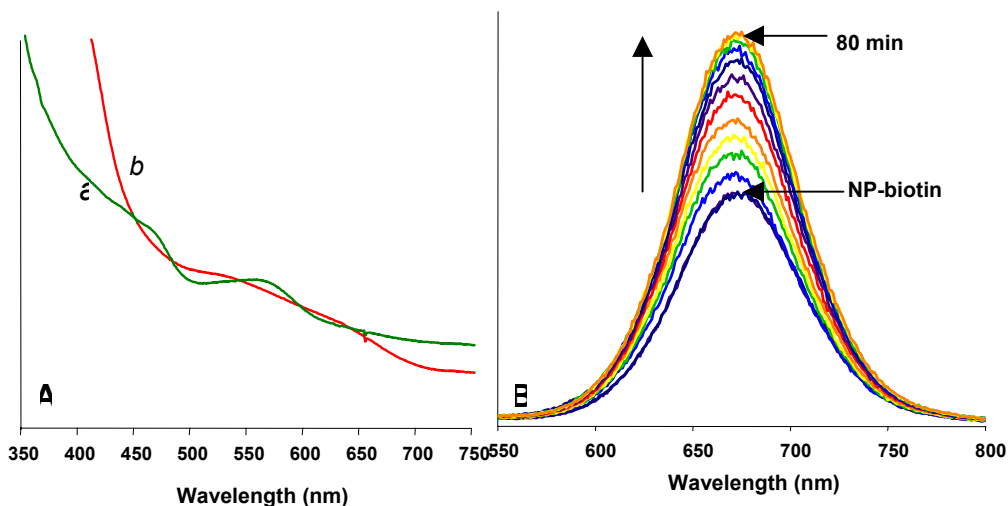


Fig. 1: UV-VIS Spectra of (A) mixed solution of two bioconjugated NPs. The spectra of *a – g* depict as follows: *a*: Au-SA with CdTe NP (570nm)-d-biotin, and *b*: Au-SA with CdTe NP (650nm)-d-biotin (B) Chronical PL spectra of CdTe NP (673nm)-Biotin between conjugated with Au-STV for 80 min (every 5~10 min observation).

4. Discussion

The observed blue shift of the CdTe NP emission peak as already presented about similar effects elsewhere can be explained that it comes from the interaction between the excitons in NP and plasmons in Au-NPs.⁹ In the presence of Au-NPs, the plasmon-assisted electromagnetic fields enhanced excitonic absorption and emission of CdTe NPs. The bond of *d*-biotin and SA assisted to maintain appropriate distance between two NPs.

The conjugation between CdTe NP and Au NP presents the enhancement of PL in CdTe NPs. It can be explained that the surface plasmon energy of Au NP would assist the acceleration of PL enhancement in CdTe NP. This enhancement was consistent for over an hour with similar reproducibility. A possible reason for this enhancement would be collective surface plasmons around CdTe NPs.

5. Conclusion

CdTe and Au NPs were conjugated using streptavidin and *d*-biotin. We found that the PL enhancement was conducted when two semiconductor and metal NPs are linked through ligand-receptor interactions. The wavelength of emission band moved to higher energy (blue shift) due to the energy transfer of surface resonance plasmon on Au NPs that assist to enhance the PL of CdTe NPs as well. It is known from SERS and previous experiments on PL that the random fields induced by a rough metallic surface result in a strong electric-field enhancement.

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