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Nanoassembly of CdTe nanowires and Au nanoparticles: pH dependence and reversibility of photoluminescence

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Abstract−Radial organized nanohybrids that are composed of Au nanoparticles (NPs) surrounding CdTe nanowires (NWs) via bioconjugation of streptavidin (SA) and D-biotin (B) were prepared to compare with the non-conjugated NWs. Two respective NW-containing hybrids with/without Au bioconjugation presented the same pH dependence except for photoluminescence (PL) reversibility. It would be explained that the chemical modification of NW surface can be retarded due to the geometric hindrance of acidic fluids in nanoscale regime and the loosely encapsulated Au NPs on NWs assisted to induce the luminescence recovery from collective resonance of excitons and plasmons in nanohybrids.

Key words: Nanowires, Nanoparticles Bioconjugates, Luminescence Enhancement, Collective Effects, pH Dependence

INTRODUCTION

The nanoscale hybrids are a fascinating access to make novel properties of composite materials and to control properties up to nanoscale via simple biological or polymeric conjugation methods [1-8]. Semiconductor nanoparticles or nanowires such as CdTe, CdS, and ZnS are considered to be a part of electronic and photonic devices. Loosely combined nanohybrids of semiconducting and metallic nanomaterials in solution state have presented unique optical properties like PL enhancement and blue shifts [9-12]. Nanocolloidal hybrids have merits in their spontaneous movements through nano/microfluids to increase their diffusivity, permitting their utilization in nanofluidic devices and in other strongly confined spaces where other sensors cannot reach.

In particular, one-dimensional fluorescent nanomaterials like CdTe NWs in colloidal state are beneficial to nano electronic circuits and biological sensing devices due to their easy synthesis and direct application to the aqueous state. Previously, it was reported that the combination of CdTe NWs and Au NPs presented a unique optical property, luminescence enhancement by collectively resonant interaction, which is similar to surface enhanced Raman scattering (SERS) of plasmons of Au NPs and excitons of CdTe NWs [12]. This SERS-like effect can be employed in fundamental research on non-linear optical properties in nano/micro regime and practical optical and biological sensing device applications. In a series publication on nanoscale assemblies using metallic and semiconductor nanomaterials, it was revealed that the collective interaction of exciton-plasmon in the nanomaterials interfaces was the main reason to observe the luminescence enhancement. However, less study on the surrounding factors was concerned even though it is quite crucial to comprehend the interaction of nanomaterials, in particular, when bio-moieties are employed.

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In this paper, we report that the PL intensity of CdTe NWs depends on the pH of aqueous solution. This pH dependence is different from that of the CdTe NPs used to synthesize the NWs. It is also shown that the PL intensity of the Au NP conjugated CdTe NW superstructures are totally recovered after their PL is decreased in acidic solution while the PL of the unconjugated NWs is not recovered. This effect is explained by the screening of pH effects on NWs due to the NP shell and the extra reinforcement for the PL recovery by plasmon-exciton resonance in solution state. The fundamental research on interfaces of different nanomaterials will be applicable to develop ultra-packed electric circuits as well as lab-on-a-chip (LOC) biosensors.

EXPERIMENTAL

$Cd(ClO_4)_2 \cdot H_2O$, Al_2Te_3, *L*-cysteine, thioglycolic acid (TGA), condensed H_2SO_4 and NaOH were purchased from Aldrich and used without further purification. In all experiments, 18 MΩ deionized water was used (Barnstead E-pure system, USA). Streptavidin (SA) was purchased from Rockland Immunochemicals, Inc. (Gilbertsville, PA) and *D*-biotin (B) was gained from Aldrich. 1-ethyl-3-(3-dimethlamino propyl) carbodiimide hydrochloride (EDC), and *N*-hydroxy-sulfosuccinimide (NHS) were purchased from Aldrich and Merck for bioconjugation, respectively.

CdTe NPs and NWs were prepared as mentioned elsewhere in detail [13,14]. Au NPs with trisodium citrate and $NaBH_4$ were synthesized based on the method of Jana et al. [15]. To link affinity bioligands on Au NPs and CdTe NWs, EDC/sulfo-NHS cross linking procedure was utilized in both cases [16]. Detailed preparation procedures are described in other publications [10-12,16-18]. Two solutions were prepared: Au NPs with B, and CdTe NWs with SA. Briefly, fresh solution of 0.2 M EDC in 2 mL of PBS buffer solution, 25 mM NHS in 2 mL of PBS, were respectively prepared at pH 7.2. Biotin (5 mg) was dissolved in 1 mL of PBS. The solutions of EDC, NHS, and biotin in the amounts of 1 mL each were

mixed together with gentle stirring for 30 min at room temperature. A 2 mL portion of cysteine stabilized CdTe NW dispersion was added into the resulting mixture and left to react for 2 h at room temperature with gentle stirring. The solution was stored at 4 °C and showed strong fluorescence for 2 weeks. These solutions were always freshly prepared before experiments to avoid quenching by precipitation of NWs and further oxidation in the solution. The luminescence spectra of NP-NW dispersions were registered in a 3 ml quartz cuvette in different pH solutions (adjusted by 1 M NaOH and 1 M HCl solution) with a Fluoromax-3 spectrofluorometer (Jobin Yvon/SPEX Horiba) every 2-10 min. The zeta potentials of the stabilizer on the NWs were measured by Zetasizer (nano-ZS, Malvern Instrument, United Kingdom).

RESULTS AND DISCUSSION

Atomic force microscopy (AFM) showed that the average diameter of CdTe NP was 3.7±0.37 nm and CdTe NWs had diameter of 5.8±1.1 nm, average length of 1,027±92 nm (the aspect ratio of 179) and PL at 670 nm. The diameter of Au NPs was measured as 3.7 nm by using transmission electron microscopy (TEM) images obtained with a JEOL 2010F TEM. It was shown that >98% of CdTe NPs was transformed into NWs. From the HRTEM examination in Fig. 1, the lattice parameter (d spacing) of the crystalline CdTe NWs was found to have lattice plane spacing of 0.398±0.01 nm that is typical for hkl (100) hexagonal wurtzite CdTe structures [14]. When Au NPs were conjugated to NWs, it was able to be distinguished by the specific crystal lattice fringes of Au NPs. The Au NPs had a lattice spacing of 0.23±0.008 nm, which corresponded to the (111) planes of Au crystal. From the image, one can clearly see that the NPs were attached to the CdTe NW surface. For longer conjugation time and for larger Au NPs amounts, dense layers of NPs were observed around NWs [12].

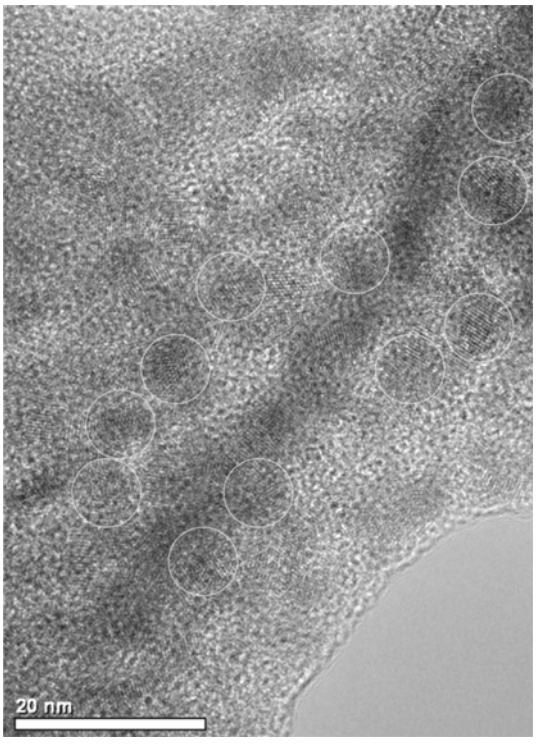

Fig. 1. a TEM image (300k×) of Au NP conjugated CdTe NWs; the gray circles indicate Au NPs.

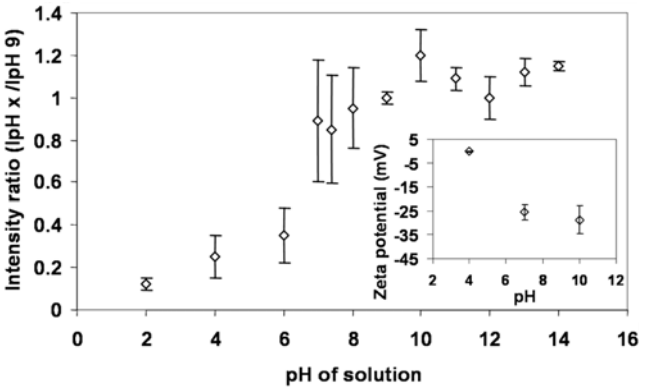

Fig. 2. pH dependence of CdTe NW at PL intensity ratio. The PL intensity is normalized at pH 9. (Insert) zeta potentials of the stabilizer at pH 4, 7, and 10.

Initially, we observed the pH dependence of NWs without any conjugation treatment. Fig. 2 shows a typical PL dependence of non-conjugated CdTe NW on the pH of solvents. The PL intensity of NW was stable in >pH 9 with narrow standard deviation. In <pH 7, the PL was strongly quenched. Gao et al. observed PL enhancement of CdTe NPs at acidic solution [1]. They explained that the formation of surface complexes with cadmium ions and thiolic stabilizers in acidic pH resulted in the PL enhancement. However, NWs, relatively bulky structures, induced aggregation and precipitation in the acidic solution due to the partial loss of stability in the stabilizer of the NW and the decrease of electrical repulsion energies between stabilizers of nanoparticles [14]. The insert in Fig. 2 shows the zeta potentials of the NWs depending on the pH of aqueous solution. The zeta potential varied from –28.7 mV to –0.17 mV with the change of high to low pH. For the synthesis of CdTe NWs, NPs with the negatively charged stabilizers like TGA or *L*-cysteine were utilized in basic solution (pH 11.2-5). The stabilizers in acidic solution led to the decrement of the surface charge due to the deionization of the stabilizers [19]. These stabilizers have two important chemical roles: to make the NWs soluble in organic or aqueous solvents, and for the dispersion of each nanomaterial to avoid aggregation in solution state by electronic repulsion of functional groups in the stabilizers. Deionized NPs and NWs in basic state reduced *inter*-electrostatic repulsion, forming agglomeration. In the NW solution, the aggregation of NWs may be more dominant than chemical modifications at NP surfaces because the surface/volume ratio was markedly decreased in NWs up to 37% from simple calculations based on geometric and structural data of AFM and TEM.

Fig. 3 presents examples of the PL changes in the superstructures of bioconjugated NP-NW in solutions at pH 7.4 and 11.1. Indeed, the conjugation process of NP-B and NW-SA induced gradual luminescence enhancement for up to two hours. The PL intensities of the conjugated NP-NW nanohybrids were dependent on the pH of the solution; e.g., higher at pH 11.1 (PL intensity=~ 2.5×10^5 cps) than at pH 7.6 (PL intensity=~1.3×10^5 cps) in the initial spectra of the bioconjugates. The PL intensity was different up to 5 times from the initial NW-SA solution at different pH. However, the enhance-

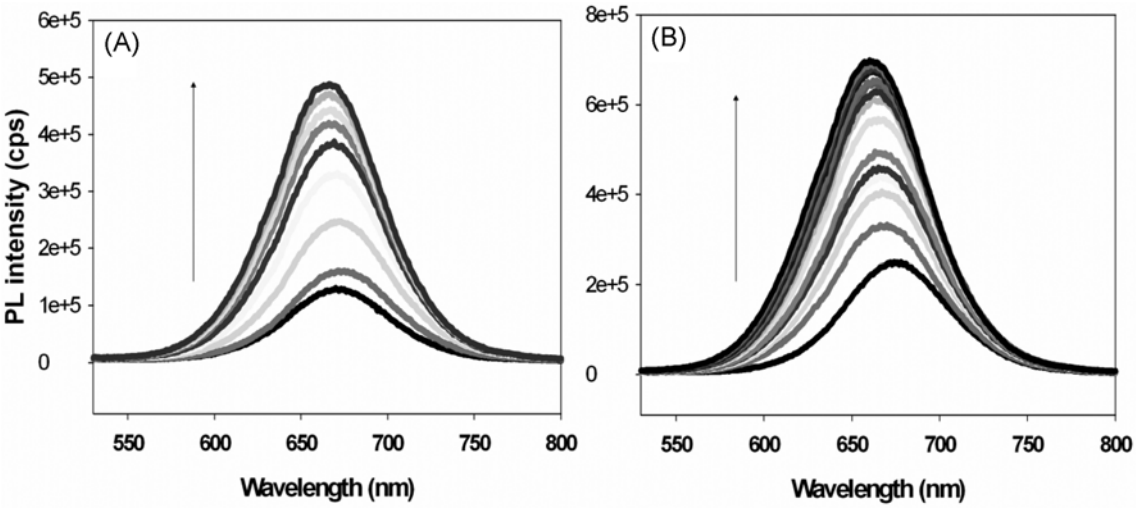

Fig. 3. PL enhancement of the bioconjugated superstructures for 2 hrs, Au NP-B-SA-CdTe NW in different pH, (A) 7.4 and (B) pH 11.1.

ment ratio did not depend on the pH in the range of pH 6-12. Note that the pH ranges showing remarkable PL enhancements correspond to that of stable non-covalent linkage of biomaterials, i.e., SA-B. This indicates that secure bioconjugation would be more crucial than respective nanomaterials in the superstructure constructions in order to collect designated optical properties [20-24]. Furthermore, the interaction of plasmon and exciton can be considered in this experiment due to two noticeable optical phenomena, such as PL enhancement and its continuous blue-shift. The PL enhancement was previously explained in detail with theoretical calculations elsewhere [12]. In brief, to explain this effect in view of quantitative investigation, this enhancement resulted from collective interactions between plasmons of Au NPs and excitons of CdTe NWs. The PL enhancements of the Au NP bioconjugated CdTe NW were implicative of SERS resulting from the electromagnetic enhancement of the incident light fields due to polarization of metal NPs [25-29]. Incident light illumination can excite plasmons of the metal NPs in the solution. Plasmon excitations resulted in strong electromagnetic fields in the vicinity of Au NPs, which caused the strong enhancement effect by the collective response of an ensemble of interacting Au-NPs. In addition, one can observe a blue shift of the peak wavelength of each spectrum up to 30 nm. The blue shift can be

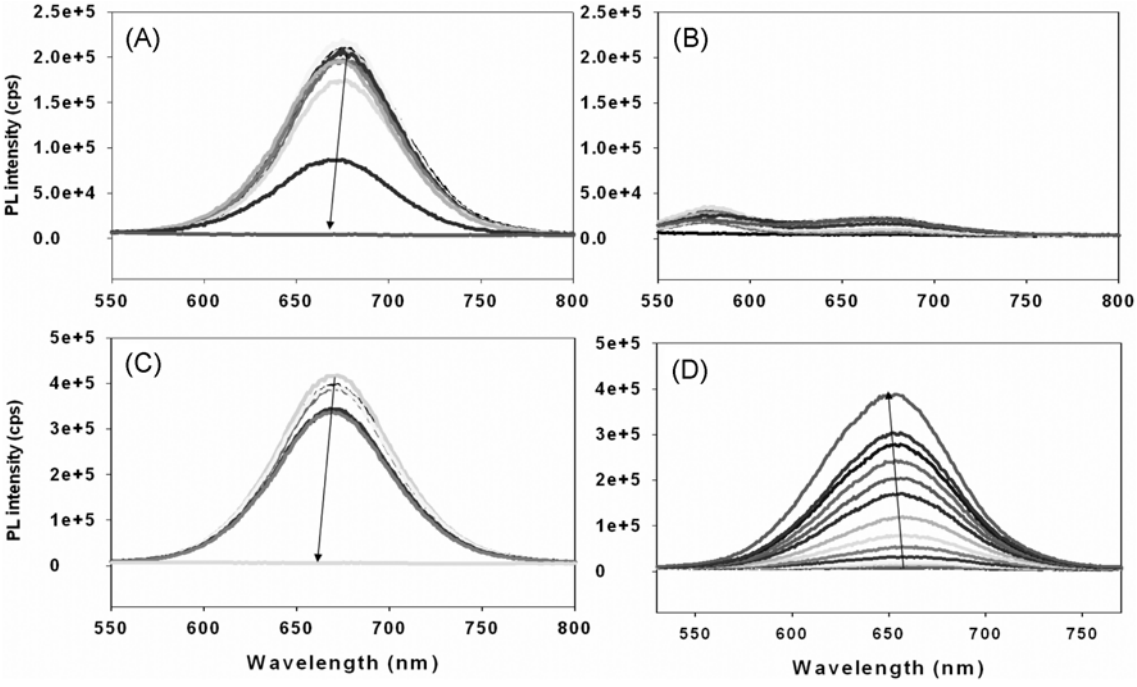

Fig. 4. PL change depending on pH: NW-SA only (A) pH 9 to 4 (B) pH recovered to 9 for 90 min; Au NPs conjugated CdTe NWs (C) pH 9 to 4, and (D) recovered to pH 9 for 150 min. At pH 4, there were 10 min of retention time to increase the pH of solution by dropping of 1M NaOH solution.

explained as that excitons inside the NW can diffuse in the presence of a non-uniform potential from the variance in the NW diameter where the energy band gap of NW is defined by its diameter. The originally generated exciton by external irradiated light source will emit a photon at lower energy after diffusion, and it will eventually become preferentially located in the regions of smaller exciton energy. However, when the resonance of plasmon-exciton between NPs and NWs inhibits the movement of excitons inside the NW, excitons may have a chance to be inducing the PL emission at high energy because of diffusion, presenting the blue shift of PL spectra [9].

Fig. 4 shows the PL intensity change of the bioconjugated NP-NW nanohybrids depending on pH in aqueous solution. The starting solution was pH 9 and the pH value was changed by the addition of 1 M HCl solution and 1M NaOH solution with gentle stirring before spectroscopic measurements. Fig. 4(A) and (B) show the PL in various pH for unconjugated NW-SA. The PL of the superstructure was totally disappeared at pH 4. After 10 min at pH 4, the solution was returned to pH 9 with the addition of 1 M NaOH solution. Continuous measurement for 90 min of the CdTe NW-SA solution does not show any reversible effect of PL without Au NP-B The PL of the Au NP bioconjugated CdTe NW solution is also essentially quenched as pH is lowered from 9 to 4 (Fig. 4(C)). After pH 7, the PL is rapidly quenched until it is difficult to measure spectroscopically. However, when the pH of solution is returned from 4 to 9, the PL of the superstructure returns to about the same as the original intensity of PL at the measurement of 150 min. The PL dependence on pH in both experiments is very similar to the pH dependence of CdTe NWs in Fig. 2. The result of the PL restoration of the Au NP bioconjugated NW (Fig. 4(D)), compared with the CdTe NW-SA without Au NPs (Fig. 4(A) and (B)), suggests that the conjugated Au NPs assist to recover the PL of NW after quenching in low pH. The CdTe NWs that are surrounded by Au NPs have lesser chances to be directly affected by acidic solution in localized microfluidic areas from the disturbance of conjugated Au NPs, which are fuzzy dispersed layers on the surface of NWs. The Au NP bioconjugated NW solution is less likely to precipitate because the functional groups in both NW-SA and NP-B are locked together by the ligand-receptor reactions and become more stable colloids in solution to avoid aggregation. Furthermore, although these geometrical and electrical parameters are profitable to decrease the permanent damage, i.e., total quenching of the NW PL in low pH solution, the additional factor to rebound the PL intensity is the enhancement properties by the collective resonant interaction of plasmons and excitons in the Au NP-CdTe NW bioconjugates from the two experiments [30]. The assisted electromagnetic field of Au NPs manipulates the optical properties of NWs to amplify exciton energies for luminescence in the solutions with different pH.

CONCLUSIONS

This paper discussed pH dependence of CdTe NW luminescence intensity, showing that the PL intensity of CdTe NWs decreased at low pH, contrary to the PL change of CdTe NPs. The aggregation of NWs may be a more dominant factor than the chemical modifications of NP surfaces by the interaction of cadmium ions and thiolic stabilizers in acidic pH because the surface/volume ratio was markedly decreased in NWs. The intensity change of the PL was observed in CdTe NWs and the bioconjugated CdTe NW superstructure with Au NPs in different pH solutions. The PL of CdTe NW without Au NPs conjugation was extensively decreased and quenched at low pH solution and was not recovered when pH of the solution was returned to 9. The quenching can be explained by the instability of stabilizers on the NW surface in low pH, inducing aggregation and precipitation. However, the nanohybrids with Au NPs showed remarkable PL restitution after quenching in pH 4 when returned to pH 9. The conjugated Au NPs became a shell to avoid the rapid change of pH in nano/microfluidic areas, and their polarized plasmons around NWs interacted collectively with the excitons of NWs, resulting in the enhancement of NW PL, and eventually recovered similar intensity to the original NW PL.

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