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Fluorescent Property of Gold Nanoparticles with Different Surface Structures†

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Fluorescence spectra of naked gold nanoparticles, triphenylphosphine stabled gold nanoparticles, and 3-mercaptopropionic acid substituted gold nanoparticles were studied. It was found that fluorescence intensities of gold nanoparticles were highly sensitive to surface molecules. The fluorescence quenching effect of these gold nanoparticles on CdSe nanoparticles was also investigated. This quenching effect was related to the overlap degree between the absorption spectra of gold nanoparticles and the emission spectrum of CdSe nanoparticles, and was surface-dependent as well.

Key words: Gold nanoparticle, CdSe nanopraticle, Fluorescence, Surface structure

I. INTRODUCTION

Gold nanoparticles (GNPs) can be widely used in catalysis, chemical sensor, biomarker, molecular recognition, nanoelectrode and so on [1-4]. Surface plasmon resonance (SPR) scattering and absorption of GNPs have been extensively investigated. There are a few reports about the fluorescent properties of GNPs. Cui *et al.* observed light emission at about 415 nm for gold particles with diameters of 2.6-6.0 nm dispersed in a solution containing bis(2,4,6-trichlorophenyl)oxalate and hydrogen peroxide [5]. Zhu and his coworkers have reported that colloidal gold nanoparticles of 20-30 nm in diameter synthesized via electrochemical method had two fluorescence emission peaks at 377 and 459 nm respectively [6]. Wilcoxon *et al.* found that nanosized gold clusters could show visible light emission, and relatively intense photoluminescence happened only when the size of the metal nanocluster was sufficiently small (<5 nm) [7]. It is known that surface molecules can alter the optical properties of GNPs, such as SPR spectra [8,9], but there is no in-depth investigation on fluorescent properties of GNPs with different surface structures. Further surface functionalization of GNPs contribute to the extensive application in many fields. For example, various biosensor and biotechnological applications require the attachment of a ligand to the particle surface to provide the selective and specific binding of a target analyte. The size control of the noble metal nanoparticles can be achieved by adding specific molecules, which physically or chemically interact with the surfaces of the forming particles to limit their growth [10]. GNPs with various surface molecules could be obtained by surface ligand exchange [11-13]. As a surface ligand, triphenylphosphine can be easily replaced by many functional groups, which supply a convenient method to modify the surface of gold nanoparticles, and then for further surface functionalization [14]. Fluorescent properties of surface functionalized GNPs are of importance to understand the interaction and mechanism during various applications.

Fluorescence quenching is a common method for chemical and biological analysis. It can be used to detect the content of various substances, and get information about the interaction between fluorescent molecules and quenchers. In the past year, CdSe semiconductor nanoparticles (NPs) have gained the most attention due to their unique optical properties. Such as high emission quantum yield, sharp emission spectra and high chemical and photostability [15-19]. Recently CdSe NPs are increasingly used as fluorophore in bioanalytics, imaging applications, and LED type and photovoltaic devices [20]. Fluorescence quenching of CdSe NPs by GNPs was reports due to fluorescence resonance energy transfer (FRET), which can be utilized as a basis for ultrasensitive analytical techniques in biology and medicine [21,22], but there is little research about the effect of the surface molecules on GNPs to such FRET process.

In research reported in this work, the fluorescent properties of three kinds of GNPs with different surface molecules (i.e. naked GNPs, triphenylphosphine stabled GNPs) and 3-mercaptopropionic acid substituted GNPs, and the fluorescence quenching of CdSe nanoparticles caused by these three GNPs were investigated.

II. EXPERIMENTS

In our experiments, all chemicals were analytical agents. Chloroauric acid ($HAuCl_4 \cdot 4H_2O$), K_2CO_3,

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and $NaBH_4$ were all purchased from Sinopharm Group Chemical Reagent Co. Ltd (China). Triphenylphosphine (TPP) was obtained from Jiangsu Huakang Chemical Reagent Co. Ltd (China). Dichloromethane was bought from Nanjing Reagent Co. Ltd (China). 3-mercaptopropionic acid (MEA) is the product of Merck Co. in Germany.

The fluorescence spectrum was surveyed on a PerkinElmer LS-55 spectrophotometer. The UV-Vis spectrum was measured on a SHIMADZU UV-3150 spectrophotometer. The images of transmission electron microscopy (TEM) were obtained by a JEM-200CX microscope, where TEM samples were prepared by placing a drop of gold products aqueous dispersion on carbon-coated copper grid.

Naked GNPs (about 5 nm in diameter) were prepared through the redox reaction of $HAuCl_4{\cdot}4H_2O$ and $NaBH_4$ according to the literature procedures [23-26], using water as the solvent. To synthesize TPP stabled GNPs (about 5 nm in diameter), TPP dissolved in anhydrous ethanol was added during the redox reaction, the volume ratio of water (18.23 MΩ) and ethanol was kept as 1:1 [27,28]. After synthesis, TPP stabled GNPs were transferred into dichloromethane, then the solvent was volatilizated to obtain GNPs powder. After washing with anhydrous ethanol this powder could be re-dissolved in water. The procedure to prepare 3-mercaptopropionic acid (MEA) modified GNPs was as follows: MEA was dissolved in anhydrous ethanol, then mixed with TPP stabled GNPs dissolved in dichloromethane. Two kinds of MEA modified GNPs, i.e. MEA-1 GNPs and MEA-100 GNPs were obtained when the solvent was volatilizated after 12 h reaction. The molar ratio of MEA and GNPs during synthesis was kept as 1:1 and 100:1 respectively for MEA-1 GNPs and MEA-100 GNPs. The sample was dried, and then dissolved in distilled water again. All the resulted samples were stored at 4 °C.

III. RESULTS AND DISCUSSION

A. Characterization of GNPs

UV-Vis spectra of the samples are shown in Fig.1, and it can be seen that the maximum absorption wavelength of four samples are 512, 521, 523, and 539 nm respectively. An obvious red shift has happened following the order of naked GNPs, TPP stabled GNPs, MEA-1 GNPs, and MEA-100 GNPs.

The absorption spectrum of GNPs is related closely to the particle size and surface structure. In this work, all the samples possess the same diameter about 5 nm, but different surface molecules. The surface of naked GNPs was occupied by Cl^-, while in TPP stabled GNPs, TPP was associated onto the surface of GNPs through Au−P coordinating bonds. If GNPs were treated as electrical dipoles, all the coordinating

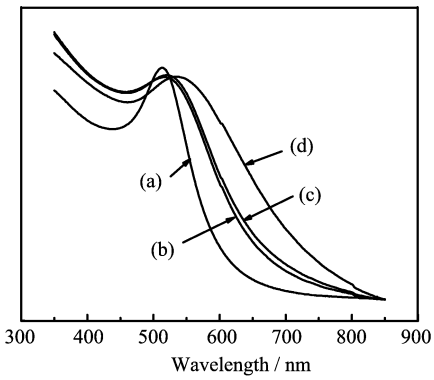

FIG. 1 Absorption spectra of GNPs with different surface structures. (a), (b), (c), and (d) correspond to naked GNPs, TPP stabled GNPs, MEA-1 GNPs, and MEA-100 GNPs respectively.

ligands could be assigned as a layer of static negative charges added on the surface of GNPs, which would affect the movement of free electrons heavily, and led to a decrease in the vibration frequency of plasma, and shift the plasma absorption to longer wavelength [29]. Hence the maximum absorption wavelength of TPP stabled GNPs was shifted comparing to that of naked GNPs (512 nm→521 nm).

Hutchison and his coworkers pointed out that TPP stabled GNPs could be replaced completely by compounds containing SH, and GNPs with different surface functional molecules were prepared easily in this way [30]. When added minor amounts of MEA were added into the solution of TPP stabled GNPs, the absorption spectrum of sample (MEA-1 GNPs) deviated from 521 nm to 523 nm due to the surface replacement of TPP by MEA. Because the bonding interaction of Au−S was stronger than that of Au−P, and Au−S bonding has larger effect on plasma absorption of GNPs, therefore the absorption spectra moved to the longer wavelength after TPP was replaced by MEA. When the molar ratio of MEA and GNPs increased (sample MEA-100 GNPs), red shift became much larger (521 nm→539 nm).

Figure 2 demonstrates the replacement process of surface molecules during the synthesis. The surface of naked GNPs was covered with $AuCl_2^-$. When TPP was added, part of Cl^- are replaced by TPP molecules, and further replaced by MEA after addition of MEA.

The morphologies of the resulting samples were examined by TEM. As shown in Fig.3, all of them were in spherical-like shapes with an average diameter of about 5 nm, and naked GNPs dispersed more uniformly than TPP stabled GNPs and MEA substituted GNPs.

B. The fluorescent properties of GNPs with different surface structures

Figure 4 is the fluorescence emission spectra for naked GNPs, TPP stabled GNPs, and 3-mercaptopropionic

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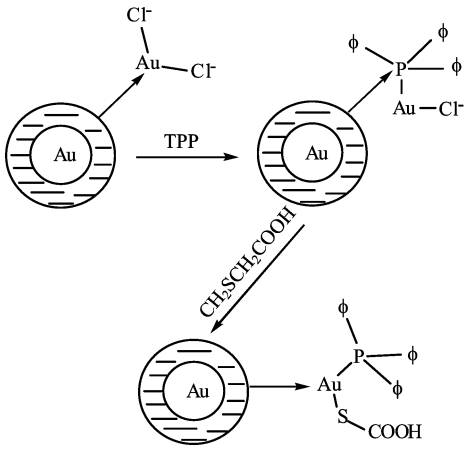

FIG. 2 Structure sketch of GNPs during preparation, Φ stands for benzene group.

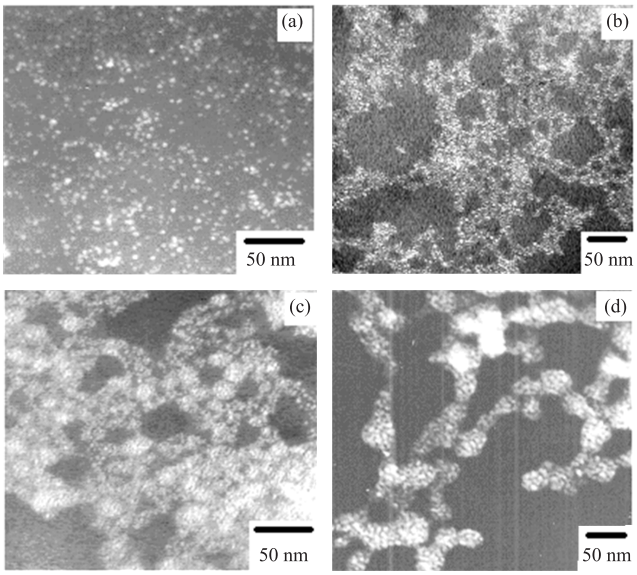

FIG. 3 TEM images of GNPs with different surface structure, (a), (b), (c), and (d) correspond to naked GNPS, TPP stabled GNPs, MEA-1 GNPs, and MEA-100 GNPs respectively.

acid substituted GNPs (MEA-1 GNPs and MEA-100 GNPs) recorded in the same concentration with excitation wavelength in 300 nm. It can be seen that all four samples have fluorescence emission at the wavelength of 330 and 440 nm. The fluorescence intensity of the naked sample is relatively fainter than the other three. When the surface of GNPs was changed, the fluorescence emission peaks were not shifted accordingly, while the fluorescence intensity was obviously increased. For example, the fluorescence intensity of MEA-100 GNPs was 600 times stronger than that of the naked GNPs.

It is commonly known that the fluorescence of GNPs is arisen from transition of d→sp bands, and the half width of emission peak is more than 50 nm. In our experiments, the fluorescence intensity of the four GNPs

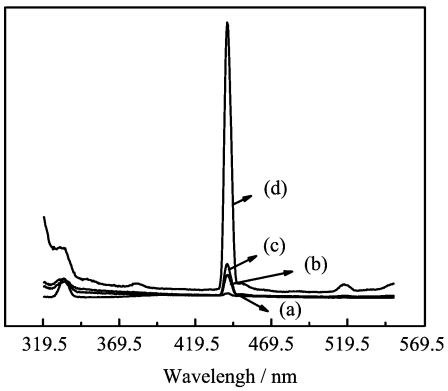

FIG. 4 The fluorescence emission spectra of GNPs with different surface structure, (a), (b), (c) and (d) correspond to naked GNPs, TPP stabled GNPs, MEA-1 GNPs, and MEA-100 GNPs respectively.

samples exhibited intense surface-dependent. But all the half width of emission peaks were narrow (<10 nm), which is the characteristics of molecular fluorescence. With this consideration, it may be concluded that the fluorescence of four samples did not derive from the transition of d→sp bands of Au crystal. Instead, the compounds formed by Au(I) atoms with coordinating ligands on the surface of nanoparticles were the origins of observed fluorescence.

The fluorescence of Au(I) compounds is widely studied at present. It is known that the Au-Au interaction (aurophilic attraction) is an essential factor for the fluorescence emission [31-34]. Several Au(I) compounds with S-containing ligands show Au(I)-Au(I) interaction and have obvious emission at about 454 nm [9]. Generally, solid fluorescence of Au(I) compound is stronger than that of samples in solution, because Au(I)-Au(I) bands may break in solution, and leads the fluorescence disappear [35-40].

Pan *et al.* reported some fluorescent Au(I) complexes with phosphorous and/or thio ligands, and pointed out that the fluorescence was due to the metal-metal to ligand charge transfer (MMLCT) in excited state [41]. MMLCT is clearly related to Au(I)-Au(I) interaction, which was affected by Au(I)-L bonding. Different bonding characteristics between the Au and S or P atoms result in the different transition properties [9,42,43]. Because Au(I)-L (L=Cl^-, P, and S) bonding is enhanced according to the order of Cl^-→P→S, the MMLCT was the largest in Au-S compounds, and the fluorescence intensity in Fig.4 increased from naked GNPs, TPP stabled GNPs to MEA modified GNPs.

C. The fluorescence quenching of CdSe NPs caused by GNPs

In this experiment, a series of naked GNPs, TPP stabled GNPs, and MEA-100 GNPs solutions with different concentration were prepared by diluting an ini-

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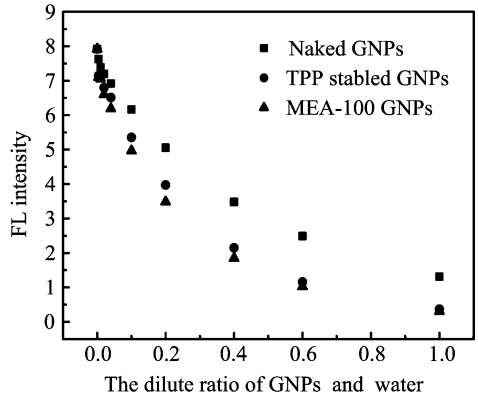

FIG. 5 The relation of CdSe fluorescence intensity with dilute ratio of GNPs solution. Emission spectra of all the samples were obtained with excitation at 392 nm and emission maximum at 535 nm.

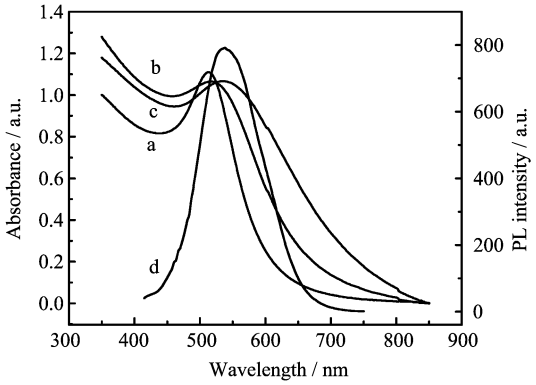

FIG. 6 Absorption spectra of GNPs and fluorescence emission spectrum of CdSe NPs, (a), (b), (c), and (d) correspond to the spectra of naked GNPs, TPP stabled GNPs, MEA-100 GNPs, and CdSe NPs respectively.

tial solution. In all cases, the original concentration was 0.17 μmol/L. The dilute volume ratios of GNPs solution with distilled water were 1:250, 1:100, 1:50, 1:25, 1:10, 1:5, 1:2.5, 3:5, and 1:1 respectively. The as-prepared GNPs solutions were mixed with CdSe solution, and fluorescence spectra before and after mixing were determined.

It can be seen from Fig.5 that those samples all can quench the fluorescence of CdSe NPs. With the increasing of the concentration of GNPs, the fluorescence intensity of CdSe NPs decreased correspondingly. However, the quenching efficiency of TPP stabled GNPs and MEA-100 GNPs was obviously higher than that of naked GNPs.

The fluorescence can be quenched through several ways, such as energy transfer, charge transfer, and collision. In the resonance energy transfer, the efficiency depends on the overlap degree of the emission spectra of donor and the absorption spectra of acceptor; the more the overlap, the higher the efficiency [44].

Figure 6 shows the absorption spectra of GNPs and the emission spectrum of CdSe NPs, and it can be seen that the absorption spectra of all three kinds GNPs have the overlaps with the emission spectrum of CdSe NPs, which provides probability of energy transfer from CdSe NPs at excited state to GNPs, and hence the quenching of the fluorescence. It also can be found from Fig.6 that the overlap degree gradually increases in the order of naked GNPs, TPP stabled GNPs, and MEA-100 GNPs, which is in agreement with their quenching efficiency.

Fluorescence quenching indicates that there is interaction between GNPs and CdSe NPs. Assuming that GNPs and CdSe NPs can form a comboination in 1:1 proportion in the process of energy transfer, this process can be shown as the following equations:

$$\mathrm{CdSe} \xrightarrow{h\nu} \mathrm{CdSe}^* \tag{1}$$

$$\mathrm{CdSe}^* + \mathrm{Au} \xrightarrow{k} [\mathrm{CdSe/Au}] \tag{2}$$

$$\mathrm{CdSe}^* \longrightarrow h\nu + \mathrm{CdSe}^* \tag{3}$$

Eq.(2) and (3) show the de-excitation process of excitated CdSe NPs. k is apparent association constant, it can be used to evaluate the power of interaction between CdSe NPs and GNPs. Without the presence of GNPs, the fluorescence intensity of CdSe is I_0. After adding GNPs to CdSe solution, the fluorescent intensity is I. The apparent association constant k can be obtained from experimental data based on the Stern-Volmer equation [44,45]:

$$I_0/I = 1 + k\,[\mathrm{Au}] \tag{4}$$

where [Au] stands for the concentration of GNPs.

The apparent association constant k of three kinds of GNPs Naked GNPs, TPP stabled GNPs, and MEA-100 GNPs with CdSe NPs was 3.05×10^8, 6.38×10^8, and 7.86×10^8 mol/L, respectively. The value of k increases according to the order of naked GNPs, TPP stabled GNPs, and MEA-100 GNPs. The apparent association constant all reaches 10^8 mol/L, which means that there exists intensive interaction among these GNPs and CdSe NPs. But this interaction could be altered by changing GNPs surface structures as shown here, and induce different fluorescence quenching efficiency of CdSe NPs.

IV. CONCLUSION

The fluorescence characteristics of GNPs with different surface structures were investigated in this work. It was found that the observed fluorescence of these GNPs may originate from the aurophilic interaction of the surface Au(I) atoms, and the fluorescence intensity was very sensitive to surface molecules. The fluorescence quenching effect of these three kinds of GNPs on

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CdSe NPs was also studied, and it was found that the efficiency, which depended on the overlap degree of the absorption spectra of GNPs and the emission spectrum of CdSe NPs, gradually increased in the sequence of naked GNPs, TPP stabled GNPs, and MEA-100 GNPs. The apparent association constant of GNPs with CdSe NPs in mixed solution reached 10^8 mol/L, which proved that there existed intensive interaction between GNPs and CdSe NPs. This interaction was strongly affected by the surface structures of GNPs, and finally produced different fluorescence quenching efficiency.

V. ACKNOWLEDGMENTS

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