

Highly Efficient Functionalization of Gold Nanoparticles: Strong Coupling Applications.

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ABSTRACT

Fine metal nanoparticles have unique properties different from those of the corresponding bulk material. Properties of these nanoparticles are preserved if the general tendency to aggregation can be overcome, as when a suitable stabilization can be developed. Generally, the stabilization of colloids is performed by surface modification process which brings new properties to the particles. This can be done either to enhance double layer interaction or to adsorb macromolecules that can form a physical barrier against other approaching particles.

Keywords: metal nanoparticles, functionalization, layer-by-layer self-assembled, polyelectrolytes, organic dyes, ligand exchange.

1 INTRODUCTION

Nanoparticles and nanostructured metal possess a strong well-defined surface plasmon resonance (SPR) which gives them a number of unique optical properties. They have been widely used for many applications such as catalysis [1-2], medicine [3-5] electronic [6-7], and optics [8-10]. The optical properties of silver and gold nanoparticles are tunable throughout the visible and near-infrared region of the spectrum as a function of nanoparticles size, shape, aggregation state, and local environment. This can be explained by the fact that metallic nanoparticles can absorb and scatter electromagnetic radiation with wavelength greater than the particle size. The intrinsic properties of metal nanoparticles are largely influenced by several parameters such as its size, shape, composition, refractive index of the surrounding medium, and structure. For example, the dependence between the refractive index of the surrounding medium can be used to obtain quantitative information on the environment from the optical absorption spectrum of the metals nanoparticles.

The coupling of organic molecules and metallic nanostructures brings new opportunities to develop highly

efficient photonic devices that combine the best features of those two specific materials. Indeed, the interactions between the electronic transitions of organic components and the plasmon modes of noble metal nanoparticles are responsible for emerging mixed states thus creating new optical and electronic properties. As one increasingly important class of nano-structures, the immobilizations of dye molecules onto nanoparticles have interesting properties for chemical, biological and optical applications.

Manipulating the SPR is considered to be a key issue leading to the development of technologies in the areas of photonics, optoelectronics and plasmonics. Additionally, molecules adsorbed to the surface of gold and silver nanoparticles undergo enhanced surface-enhanced Raman scattering (SERS) [11-12] effects, due to the coupling of the plasmon band of the irradiated metal (i.e. the collective oscillation of the conduction band electrons upon absorption in the visible for the particular metals, due to their dielectric constant) with the molecules electronic states.

There are many examples that exploit nanoparticles interfacial properties such as ligands exchange reaction, layer by layer assembly, and DNA linked assembly. The layer by layer (LBL) technique is generally used for surface functionalization. It uses sequential adsorption of oppositely charged materials from solution onto various charged supports. The process started by adsorbing a charged polymer onto an oppositely charged surface, thereby reversing the surface charge. Further layer can be added by the alternate deposition of oppositely charged polyelectrolytes. This method was introduced by Iler [13] in the mid 1960s by adsorbing particles onto solid substrates. In 1990s, Decher and al [14-15] extend Iler's work to a combination of linear polycations and polyanions. The LBL method has attracted increasing attention for preparing layered thin film with tailored properties on the nanometer scale. One of the key advantages of the LBL method is that it is simple experimentally and because water is the main solvent used, the technique is considerably more environmentally friendly than techniques that use organic solvents.

Here we present the modification of gold nanoparticles by organic molecules. In the first time we describe a surface modification procedure involving ligand exchange of citrate stabilized gold nanoparticles with TDBC and layer-by layer polyelectrolytes assembly around gold nanoparticles. The surface modification of the gold nanoparticles has been proven by means of UV-Visible and Infrared spectroscopy.

2 EXPERIMENTAL SECTION

2.1 J-aggregates stabilized gold nanoparticles: strong coupling.

Molecular organic compounds such as J-aggregates (JA) support excitonic states which are electrically neutral electrons/holes pairs created by the absorption of photons. JA exhibits characteristic optical absorption called J-band which is red shifted from the monomer band, ultra-short radiative lifetime and nonlinear optical susceptibility. These properties are interesting for applications in imaging materials, optoelectronic devices and dye-sensitive solar cells [16-18].

We have developed a facile route to prepare monodisperses Au@TDBC NPs allowing the direct and efficient coating of pretreated citrate-stabilized gold NPs with TDBC, without supplementary adding of salts and bases during the coating and at room temperature. Citrate-stabilized gold nanoparticles are obtained by the Fren's method [19]. The size of particles is tune to optimize the strong coupling between the electronic transitions of organic components and the plasmon modes of gold NPs.

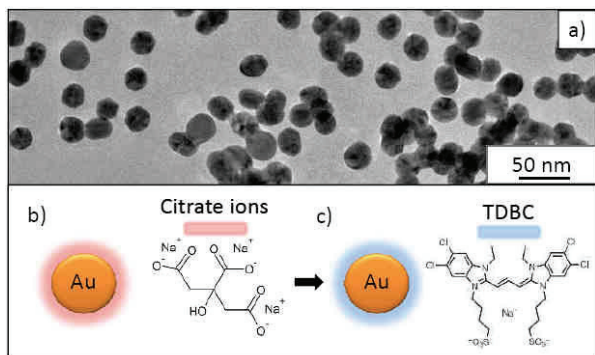


Figure 1: a) TEM images of Nps of different sizes coated with TDBC molecules, b) Citrate ions molecule, c) TDBC molecules.

The coating was realized by a ligand exchange reaction between citrate and TDBC, during the mixing of the NPs colloidal solution and the TDBC solution. Since the citrate is linked to the gold NPs surface by the oxygen atom, it can be easily replaced by the TDBC molecules which adsorption on the gold nanoparticles will be done by the nitrogen atom. Through ligand exchange reaction, the dye molecules are adsorbed uniformly on the NPs. The adsorbed dyes exhibit both monomer and J-aggregates absorption

bands. Strong coupling have been studied by using NPs with different size i.e. with different resonances energies (figure 2).

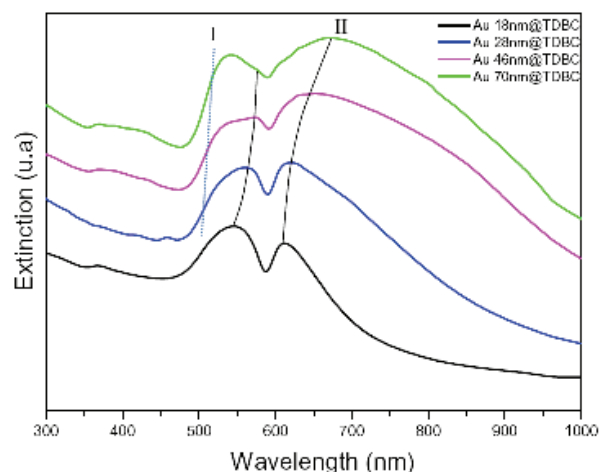


Figure 2: Extinction spectra of Au Nps with different sized coated with TDBC.

Four interesting parts can be distinguished on those spectra. The first denoted by the dotted line I correspond to the bare Au NPs adsorption. It is clearly shows that some particles are not coated with TDBC. This remark confirms the observations made by microscopy. The second part noted II localized at 586nm is directly related to the absorption wavelength of TDBC. Two mixed states of resonance are created.

As we can see in the extinction spectra, few particles are coated with TDBC and some are aggregated. This clearly indicates that the coating is not perfect but do not avoid the strong coupling to occur. At the contrary to previous studies, we do not manage to improve this coating by adding salts (NaCl, KCl) that is known to promote adsorption of dye molecules. The reason is that the additive salts amounts in the TDBC solution can modify the stability and the citrate ions adsorption on gold NPs.

2.2 Polyelectrolytes coated gold nanoparticles

In this work we used polyethylenimine (PEI) as cationic polyelectrolyte and poly (styrene sulfonate) sodium (PSS) as anionic polyelectrolytes. The 20nm diameter CTAB-stabilized gold nanoparticles used here are obtained prepared using the Gole et al method [20]. We have built thin films around gold nanoparticles by sequential adsorption of polyanions and polycations in aqueous medium.

Gold nanoparticles were mixed with a solution containing cationic polyelectrolytes, and a layer of polycation is adsorbed. Since the adsorption is carried out at a relatively high concentration of polyelectrolyte, a number of ionic groups remain exposed to the interface with the

solution, and thus the surface charge is effectively reversed. After rinsing with deionized water, the particles were mixed with a solution containing the anionic polyelectrolyte.

The following experimental conditions were found, 10mL of the as prepared gold nanoparticles were mixed with absolute ethanol at the proportion 5:1 (nanoparticles: ethanol) and washed with water by centrifugation three times to remove the excess of CTAB. The solution is then redispersed in 5mL of Milli-Q water. For the polyelectrolytes deposition, 3mL of the colloid solution are added to 3mL of the aqueous polyelectrolyte solution of the desired concentration. The resulting solution was then left undisturbed. After 24 hours, the solution is then centrifugated three times during 20min at 13000g to eliminate the excess of polyelectrolytes. The supernatant is removed and the pellet is redispersed in milli-Q water for UV-visible and IR spectrum and TEM record.

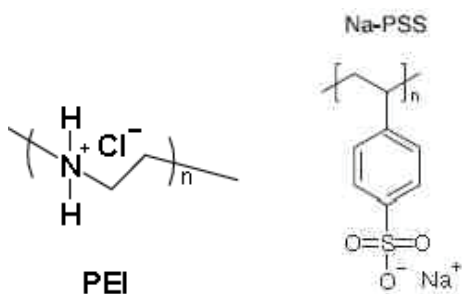


Figure 3: Polyelectrolytes structural formula.

2.3 results and discussion

For the PEI (seen figure 3) which has coexisting primary, secondary and tertiary amine groups, bonding to the gold nanoparticles occurs through the amine functionalities. It has been reported that amine binds to gold nanoparticles through the amines functionality via weak covalent bond [21-23]. The absorption spectrum is red-shifted and broadened (figure 4), this is mainly due to the change in the refractive index (since the refractive index of PEI is 1.65, water 1.33) as a result of the absorption of PEI onto the gold nanoparticles. These suggest that CTAB is displaced from the surface of the gold nanoparticles upon the PEI adsorption. Despite the CTAB-stabilized gold nanoparticles, it can be adsorbed/desorbed from the gold nanoparticles surface.

For the Au@PEI@PSS, the environment of the particle changes again. Although the refractive index of the surrounding medium is decreasing (1.395 for PSS), we observe a red shift of the optical band of the Au@PEI@PSS (green and blue curves) with respect to that of Au@PEI (red curve). This red shift can be explained by increasing of the polyelectrolyte layers thickness.

Concerning the Au@PEI@PSS@PEI system, the blue shift observed in the case is attributed to the change of the refractive index of the surrounding medium.

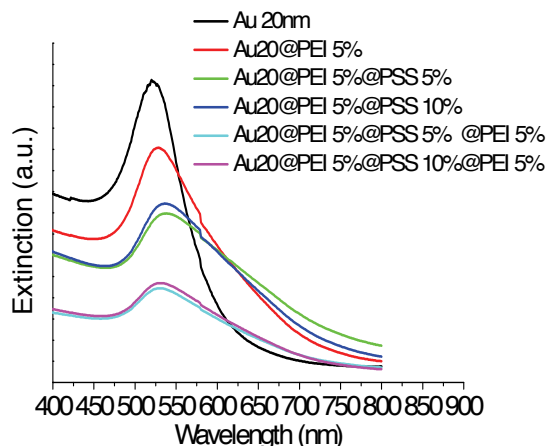


Figure 4: UV-Visible absorption spectra change with PEI and PSS functionalized gold nanoparticles.

The functionalization of gold nanoparticles by PEI (Au@PEI) was also determined by FTIR (figure 5). The main characteristic band of PEI is determined by measuring the amine absorption band. Figure 5 shows the FT-IR spectra of solutions of PEI and PEI-stabilized gold nanoparticles. In these spectra, we can distinguish the N-H stretching band at 3300 cm^{-1} , N-H deformation band of secondary amine at 1620 cm^{-1} and C-N stretching band at 1050 cm^{-1} . We also have the C-H stretching band (2930 cm^{-1} and 2860 cm^{-1}) and C-H deformation band (1500 cm^{-1}) of aliphatic $-\text{CH}_2-$.

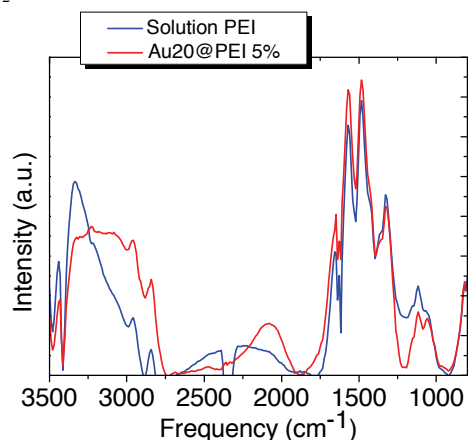


Figure 5: FTIR spectra of PEI solution and PEI functionalized gold nanoparticles.

Comparing these two spectra, we observed that in the case of Au@PEI, the absorbance peak at 3300 cm^{-1} corresponding to the N-H stretching is broadened. This is due to interactions between the amine group and the gold nanoparticles. The vibrations of the molecules between 800 and 1700 cm^{-1} corresponding to the C-C, CH_2 and the C-N bonds are unchanged, this means that these groups do not participate in the bond Au NPs-PEI.

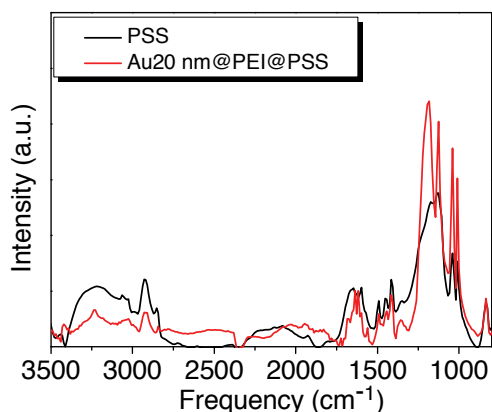


Figure 6: FTIR spectra of PSS solution and Au@PEI@PSS.

For the FT-IR characterization, the main characteristic band of PSS is determined by the absorption bands between 1000cm^{-1} and 1300cm^{-1} corresponding to the SO_3^- group. The SO_3^- group antisymmetric and symmetric vibrational adsorption peaks can be assigned to the peaks at 1195 and 1039cm^{-1} respectively. Peaks at 1128 and 1011cm^{-1} are attributed to the in-plane skeleton vibration of benzene ring and in-plane bending vibration of benzene ring. The spectral changes observed in the Au@PEI@PSS spectrum, clearly demonstrate the interaction between the PEI and the PSS.

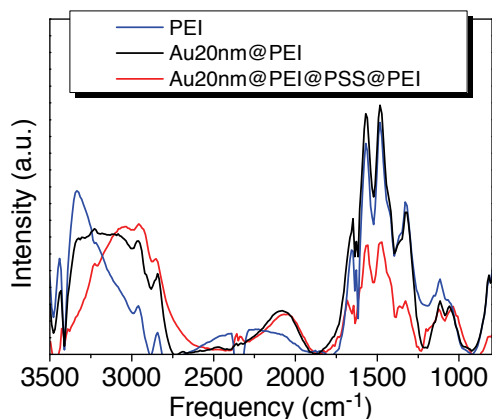


Figure 7: FTIR spectra of PEI solution, Au@PEI and Au@PEI@PSS@PEI.

The above results show that we can make a deposit layer by layer polyelectrolytes on gold nanoparticles. We also note that the absorption spectrum obtained after deposition depends on the nature of the polyelectrolytes since they don't have the same refractive index. Since the refractive index of the surrounding medium is increased. For both Au@PEI and Au@PEI@PSS@PEI, (5% and 10%) there is a red-shift of 5nm in the resonance band. In this case, the shift observed in the optical band of gold nanoparticles is due to the increase of the average refractive index of the surrounding medium of the nanoparticles i.e. to

the coating of nanoparticles by a layer of PEI. This value corresponds to the expected value obtained by theoretical data.

These results show us that gold nanoparticles surface can be easily modified by different molecules such as organic dyes and polyelectrolytes. Adsorption of these molecules onto gold nanoparticles surface is principally due to the presence of atoms having high affinity with gold.

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