

## CHAPTER 3

### FABRICATION TECHNOLOGIES OF CdSe/ZnS / Au

#### NANOPARTICLES AND NANODEVICES

##### 3.1 THE SYNTHESIS OF Citrate-Capped Au NANOPARTICLES

Au NPs with ~ 15 nm were prepared by citrate reduction of HAuCl<sub>4</sub> as described in literature [4]. The pale yellow HAuCl<sub>4</sub> solution (1 mM, 500 mL) was prepared and brought to reflux while stirring for 20 min. A solution of citric acid (38.8 mM, 50 mM) was then quickly injected into the flask. The color of the solution changed from pale yellow to deep red indicating the formation of Au NPs. After color changing, the solution was kept in reflux for additional 20 min and then standing in room temperature for another 30 min. Finally, the solution was filtered through 0.45 μm Nylon filter. The flow diagram of the Au NPs solution preparation is shown in Fig. 3.1. The close photograph of the Au NPs solution is shown in Fig. 3.2(a), (left). The TEM image of the approximately 15 nm diameter Au NPs is shown in Fig. 3.3(a) and the UV-visible absorbance spectrum of Au NPs solution is shown in Fig. 3.3(c).

##### 3.2 The SYNTHESIS OF MSA-Capped and AET-Capped CdSe/ZnS NANOPARTICLES

The emission efficiency, spectrum and time evolution of NPs are strongly affected by the surface. A better surface structure of NPs can provide higher stability, higher quantum yield and longer lifetime. Mostly the CdSe NPs lose a large portion of emission efficiency because of electron leakage resulting from the surface defect. Therefore, ZnS layer, a large band gap semiconductor, is

used to passivate the surface and improve the quantum yield of CdSe NPs. The band gap diagram and the surface structures of CdSe/ZnS NPs are shown in Fig. 3.4(a). Fig. 3.4(b) shows the PL intensity spectrum, which confirms the superior quantum yield property of CdSe/ZnS structure over the other two structures, CdSe and CdSe/CdS. The approximately 5 nm diameter fluorescent water-soluble (D, L-mercaptoposuccinic (MSA)-coated) and (2-aminoethane thiol (AET)-coated) CdSe/ZnS NPs were obtained from **Prof. Teng-Ming Chen's lab, National Chiao Tung University, Taiwan**. The surface of the MSA-coated CdSe/ZnS NPs had negative-charged carboxylate groups ( $-\text{COO}^-$ ), and the surface of the AET-coated CdSe/ZnS NPs had positive-charged amino groups ( $+\text{NH}_3^+$ ). In this section, we will to introduce the synthesis procedure of CdSe/ZnS NPs.

#### ***Synthesis of water-soluble MSA-capped CdSe/ZnS NPs***

Luminescent CdSe/ZnS NPs were synthesized according to the previously reported procedure [23-25]. MSA was selected as the surface-capping reagent to form water-soluble NPs. 30 mg of CdSe/ZnS NPs were dissolved in 10 ml of methanol and transferred to a reaction vessel. Then, a separate 50 ml methanolic solution of 1M MSA was added to the above-mentioned NP-containing solution and the pH was adjusted to 11 by adding tetramethylammonium hydroxide pentahydrate. The mixture was then heated at 60°C overnight with refluxing under  $\text{N}_2$ , and the sample was stored in the dark. The NPs were precipitated with anhydrous ether, centrifuged at 6000 rpm, and the supernatant was decanted to remove the organic solvent. Methanol was added to wash the precipitates four times. Finally, the precipitate was redissolved in a phosphate buffer solution, and stored in the dark.

#### ***Synthesis of water-soluble AET-capped CdSe/ZnS NPs***

In order to prepare positive charge on the NPs surface, the water stabilized amine terminating NPs ( $\text{NP-NH}_2$ ) was fictionalized. Adding methanol washed off the HDA stabilizing layer and rendered a cloudy suspension which was centrifuged and the pellet containing NPs were washed

with methanol 4 times to re-dissolve into chloroform. 1.0M 2-aminoethane thiol (AET) was added to the above solution and allowed to react for 2hr. When ZnS capped CdSe NPs were reacted with AET, the mercapto group in AET bind to the Zn atoms and render the NPs hydrophilic, in addition to facilitating further functionalization possibilities. After the reaction, excess AET was washed off with methanol/chloroform mixed solution and store into the D.I water.

The close photographs of the AET-CdSe/ZnS NPs solution is shown in Fig. 3.2(a), (right). Fig. 3.2(b) shows the close photographs of the mixture of 100  $\mu$ L Au NPs solution and 100  $\mu$ L AET-modified CdSe/ZnS NPs solution just after mixing (right), the mixture after standing 6 hrs (middle) in room temperature, and the mixture after standing 5 days in room temperature (left). As we can see, the color of mixture just after mixing was like that of Au NPs solution. However, after 6 hrs, it became dark purplish red. After 5 days, there was obvious precipitate at the bottom and the supernatant became pale yellow. The TEM image of the approximately 5 nm diameter CdSe/ZnS NPs is shown in Fig. 3.3(b) and the UV-visible/PL spectra of CdSe/ZnS NPs solution is shown in Fig. 3.3(d). The detailed modification processes of MSA-capped and AET-capped CdSe/ZnS NPs are shown in Fig. 3.5 and 3.6, respectively.

### **3.3 THE ASSEMBLY OF Au / AET-CdSe/ZnS AND MSA-CdSe/ZnS / AET-CdSe/ZnS ON SILICON OXIDE SUBSTRATE BY IONIC INTERACTION**

In the chapter 1, we have discussed the forces that direct the assembly of NPs is similar to those involving in the interaction between molecules, such as hydrogen bonds, Coulombic force, and Van der Waal force. In this work, we utilize the *Coulombic force system* control the assembly of NPs on the silicon substrate. In *Coulombic force system*, we take advantage of the positive or negative charges on the surfaces of NPs to induce repulsion or attraction forces between different NPs or between NPs and the substrate. The repulsion force will prevent NPs from random aggregation

before assembled on the substrate. On the other hand, the attraction force will assemble NPs on the substrate. By well controlling the two forces, we are able to construct the structure of photo-sensing nanodevice on the silicon oxide substrate effectively. The overall fabrication process of the photo-sensing nanodevice composed of CdSe/ZnS and/or Au NPs on the silicon chip by ionic interaction system is shown in Fig. 3.7.

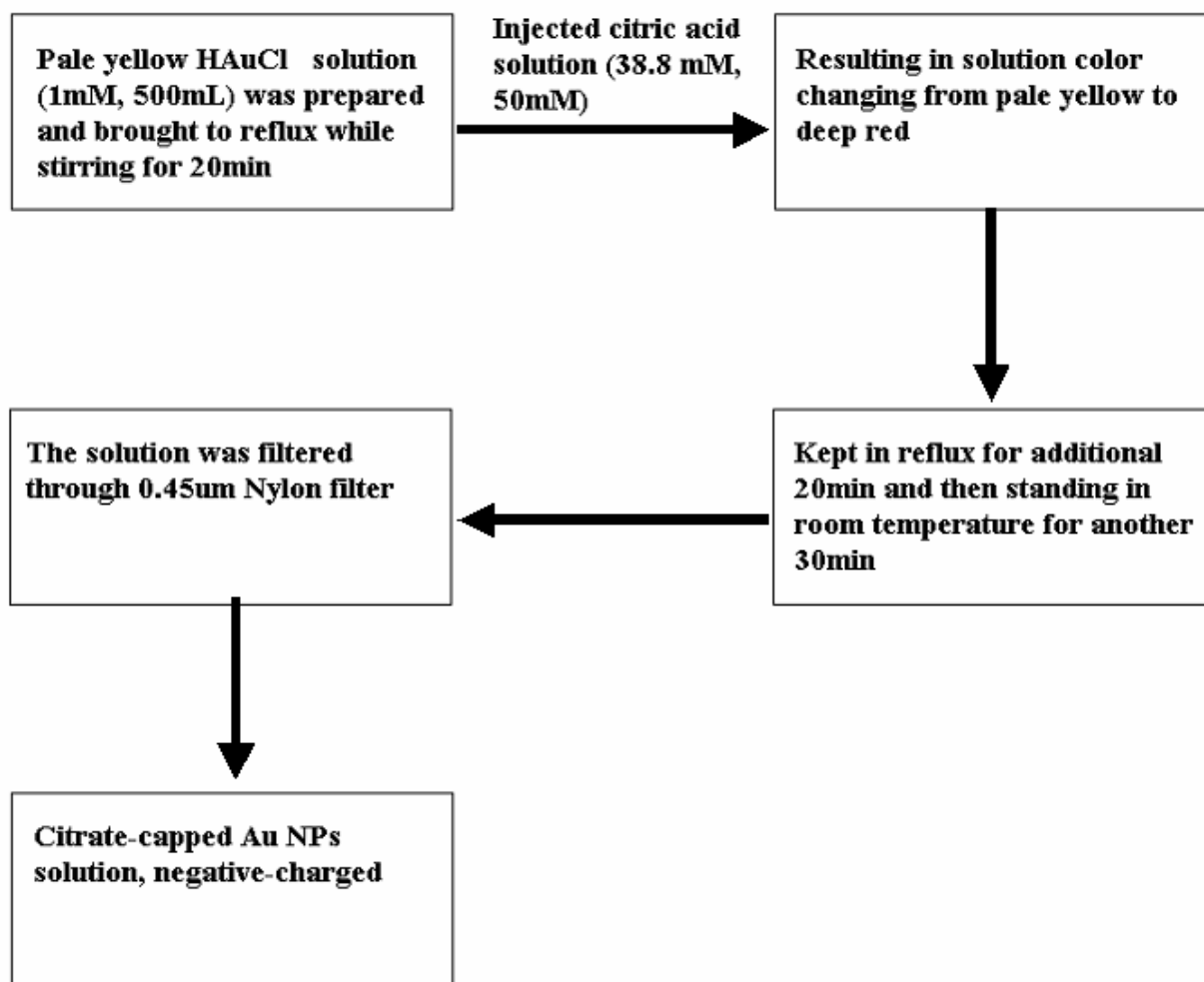
In this work, we used two kinds of silicon oxide substrate--- the SiO<sub>2</sub> (30 nm in thickness)/Si wafer fragments (~5 mm<sup>2</sup> in area) fabricated by National Nano Device Laboratories, Taiwan, and the silicon chip with electrodes structure fabricated by TSMC 0.35 μm 2P4M process. Generally, the process to construct the nanodevice structures of CdSe/ZnS and/or Au NPs is the same for the two kinds of silicon oxide substrate.

In order to modify the silicon oxide substrate with positive charges, the silicon oxide substrate was modified by N- [3-(trimethoxysilyl) propyl] ethylene diamine (TMSPED) to make the silicon oxide substrate provide amino groups (-NH<sub>3</sub><sup>+</sup>). Subsequently, Citrate-capped Au NPs (~15 nm) · MSA-capped and AET-capped CdSe/ZnS NPs (~5 nm) will be self-assembled layer-by-layer. First, the silicon oxide substrate was cleaned by acetone and methanol to remove organic matter. And then we used strongly N<sub>2</sub> flow to remove nonspecific particles attached on the surface. The silicon oxide was immersed in 10% TMSPED/methanol solution for 20 min [7]. Note that because TMSPED is very moisture sensitive, the methanol used here must be completely dried and all cleaned glasswares must also be dried in oven at 65°C for 30 min prior to use. After immersion, the silicon oxide substrate was cleaned by plenty of methanol to remove excess TMSPED staying on the surface, followed by dipping in 30 mM HCl for 3 seconds to protonate the amino groups. Finally, the silicon oxide substrate was cleaned by using plenty of D.I. water for several times and dried in vacuum.

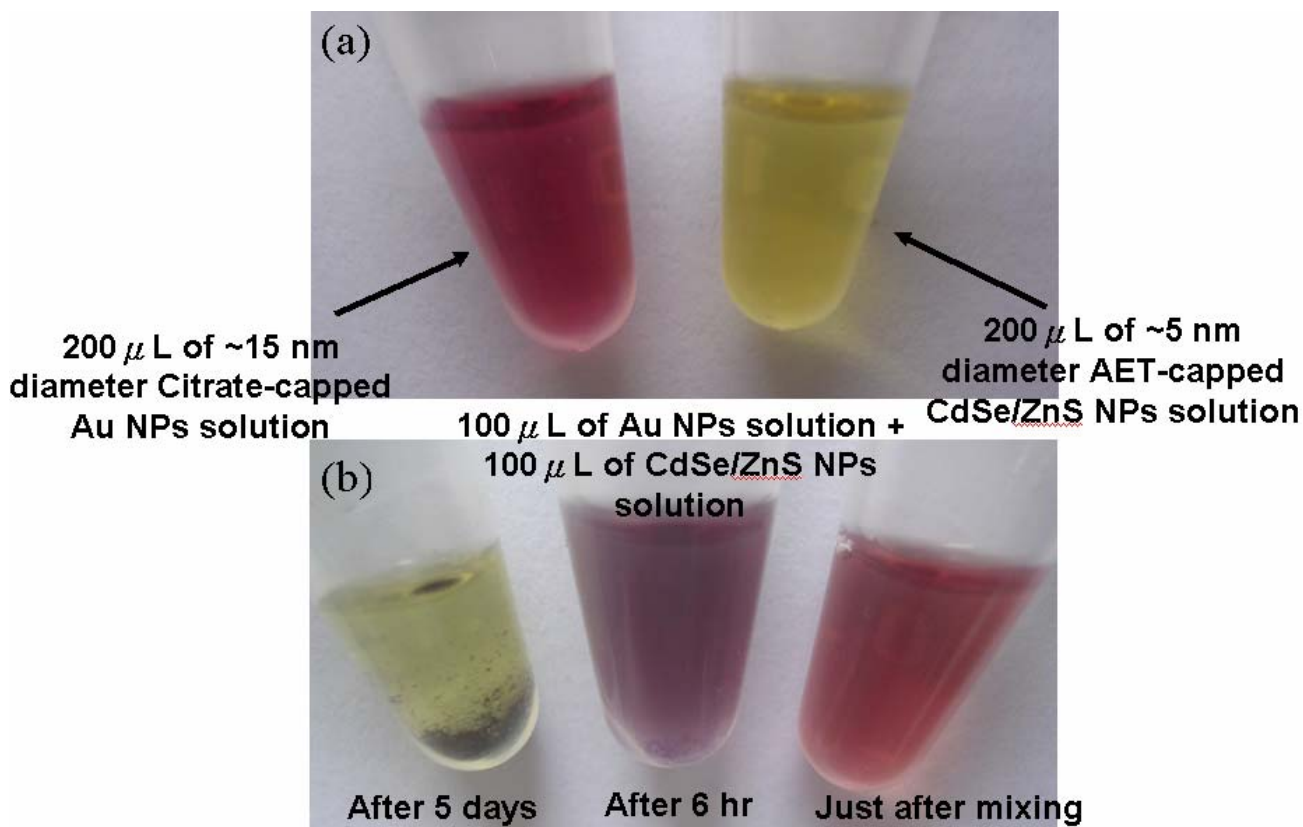
In order to construct photo-sensing nanodevice structures, the TMSPED-modified silicon oxide substrate was immersed in the Au NPs solution for 20 min to make negative-charged (-COO<sup>-</sup>) Au NPs or MSA-capped CdSe/ZnS NPs assembled on the positive-charged (-NH<sub>3</sub><sup>+</sup>) substrate by ionic interaction. After 20 min immersion, the silicon oxide was cleaned by D.I. water for several times to

remove free Au NPs or MSA-CdSe/ZnS NPs and then dried in vacuum. Subsequently, the silicon oxide substrate was immersed in AET-capped CdSe/ZnS NPs solution for 20 min to make positive-charged ( $-\text{NH}_3^+$ ) AET-CdSe/ZnS NPs assembled to negative-charged ( $-\text{COO}^-$ ) Au NPs or MSA-CdSe/ZnS NPs, followed by D.I. water cleaning and vacuum dry as described above. Theoretically, we can repeat this process for several times to form layers of closely packed CdSe/ZnS NPs and/or Au NPs nanostructures.

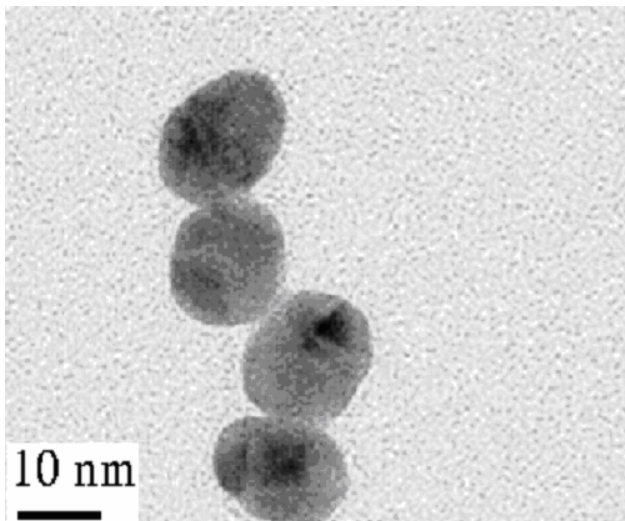




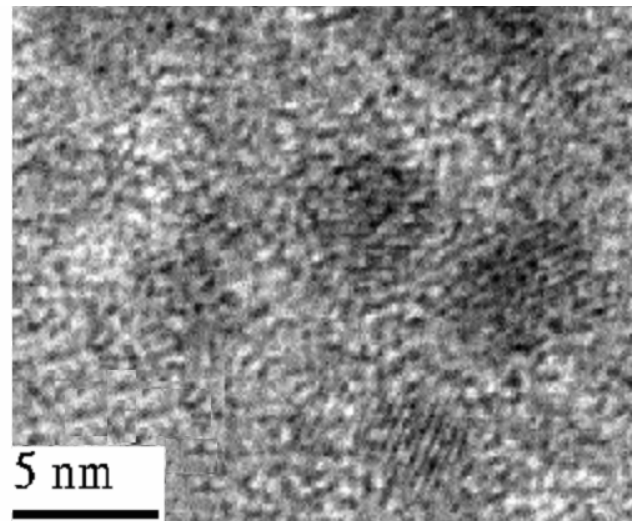
**Fig. 3.1** The flow diagram for preparing the Citrate-capped Au NPs solution.



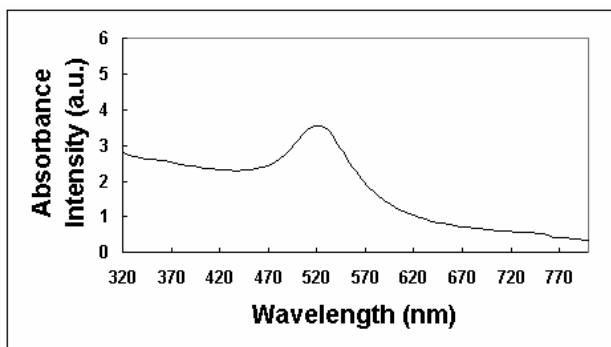
**Fig. 3.2** (a) The close photographs of 100  $\mu$ L of approximately 15 nm diameter Au NPs solution + 100  $\mu$ L DI water (left) and 100  $\mu$ L of approximately 5 nm diameter AET-CdSe/ZnS NPs solution + 100  $\mu$ L DI water (right). The Au NPs solution was in deep red while the AET-modified CdSe/ZnS NPs solution was in yellow. (b) The close photographs of the mixture of 100  $\mu$ L Au NPs solution and 100  $\mu$ L AET-modified CdSe/ZnS NPs solution just after mixing (right), the mixture after standing 6 hrs (middle) in room temperature, and the mixture after standing 5 days in room temperature (left). As we can see, the color of mixture just after mixing was like that of Au NPs solution. However, after 6 hrs, it became dark purplish red. After 5 days, there was obvious precipitate at the bottom and the supernatant became pale yellow.



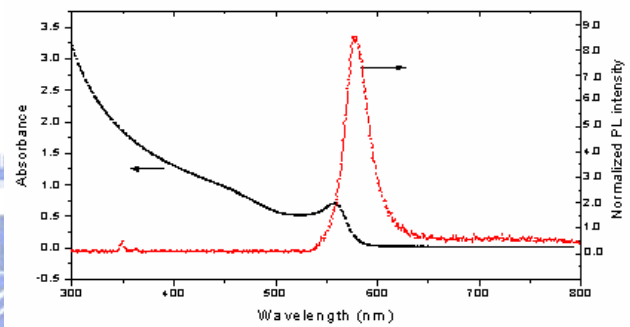
(a)



(b)



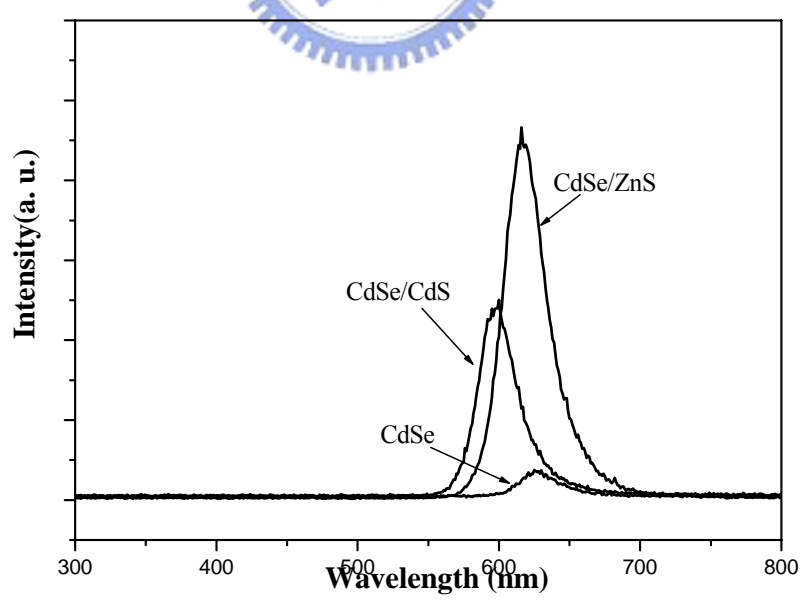
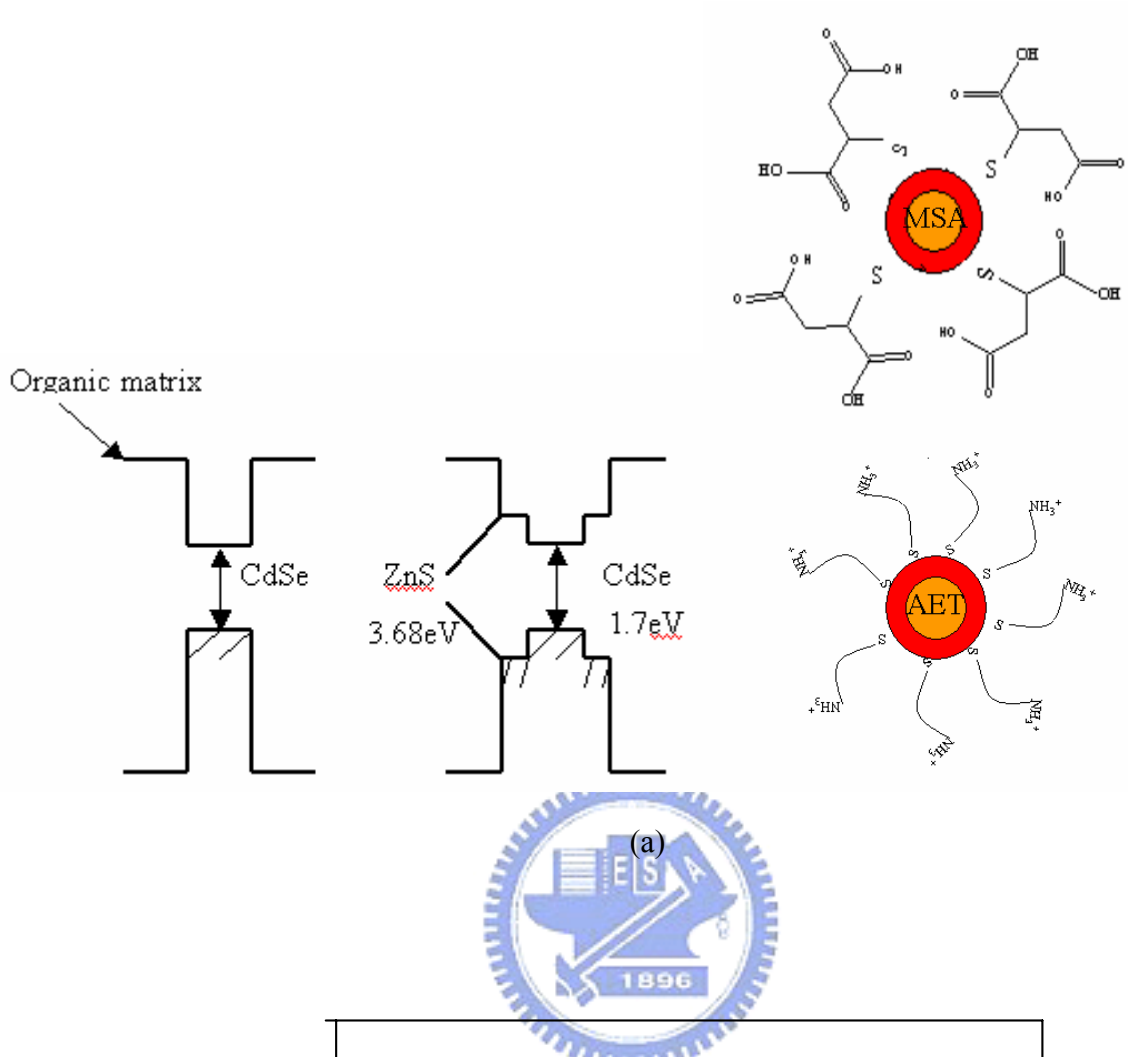
(c)



(d)

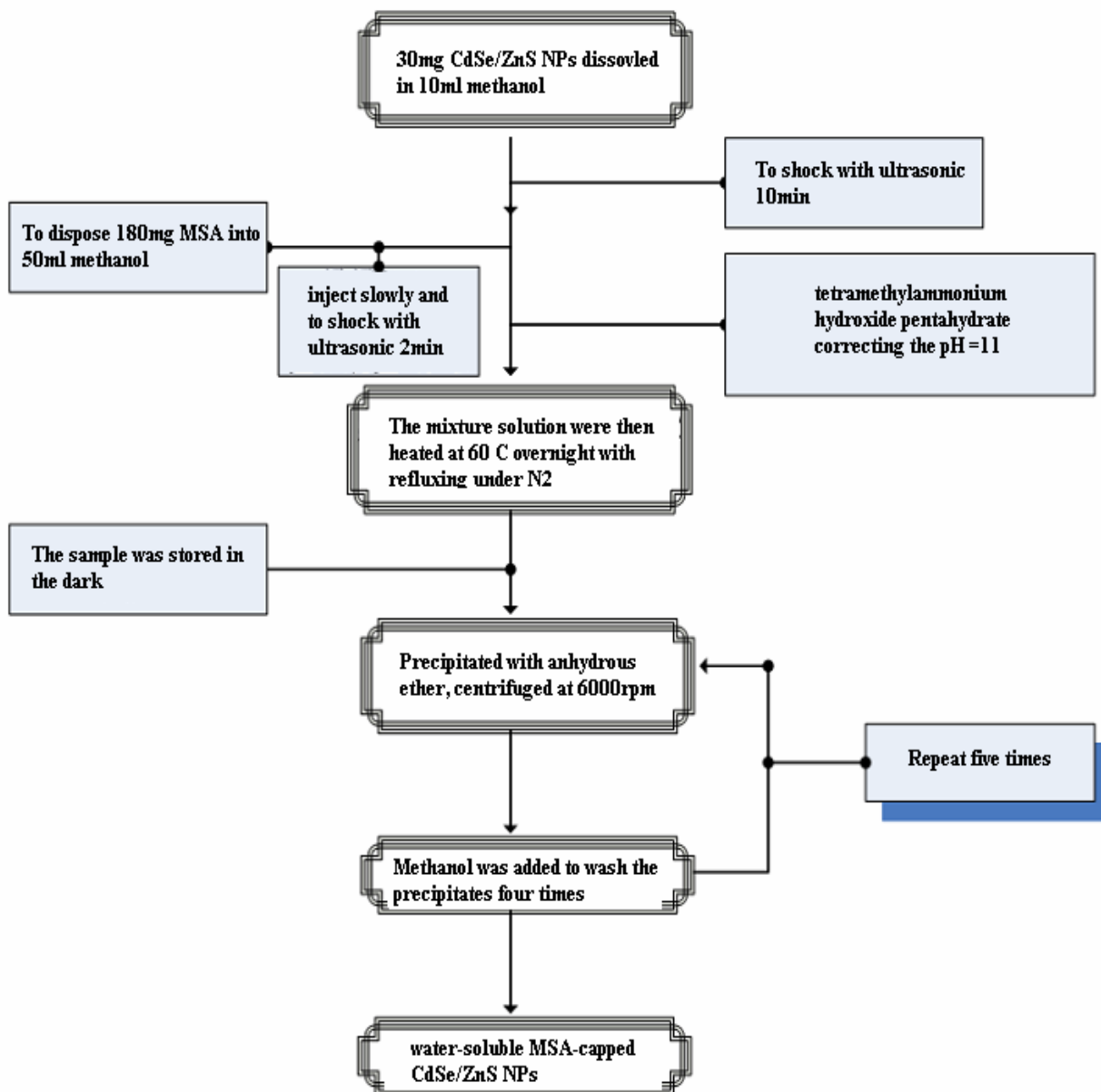
**Fig. 3.3.** (a) The TEM image of Citrate-capped approximately 15 nm diameter Au NPs. (b) The TEM image of MSA-capped or AET-capped approximately 5 nm diameter CdSe/ZnS NPs. (c) The UV-visible spectrum of Au NPs solution. (d) The UV-visible and PL intensity spectrum of MSA-CdSe/ZnS or AET-CdSe/ZnS NPs solution.



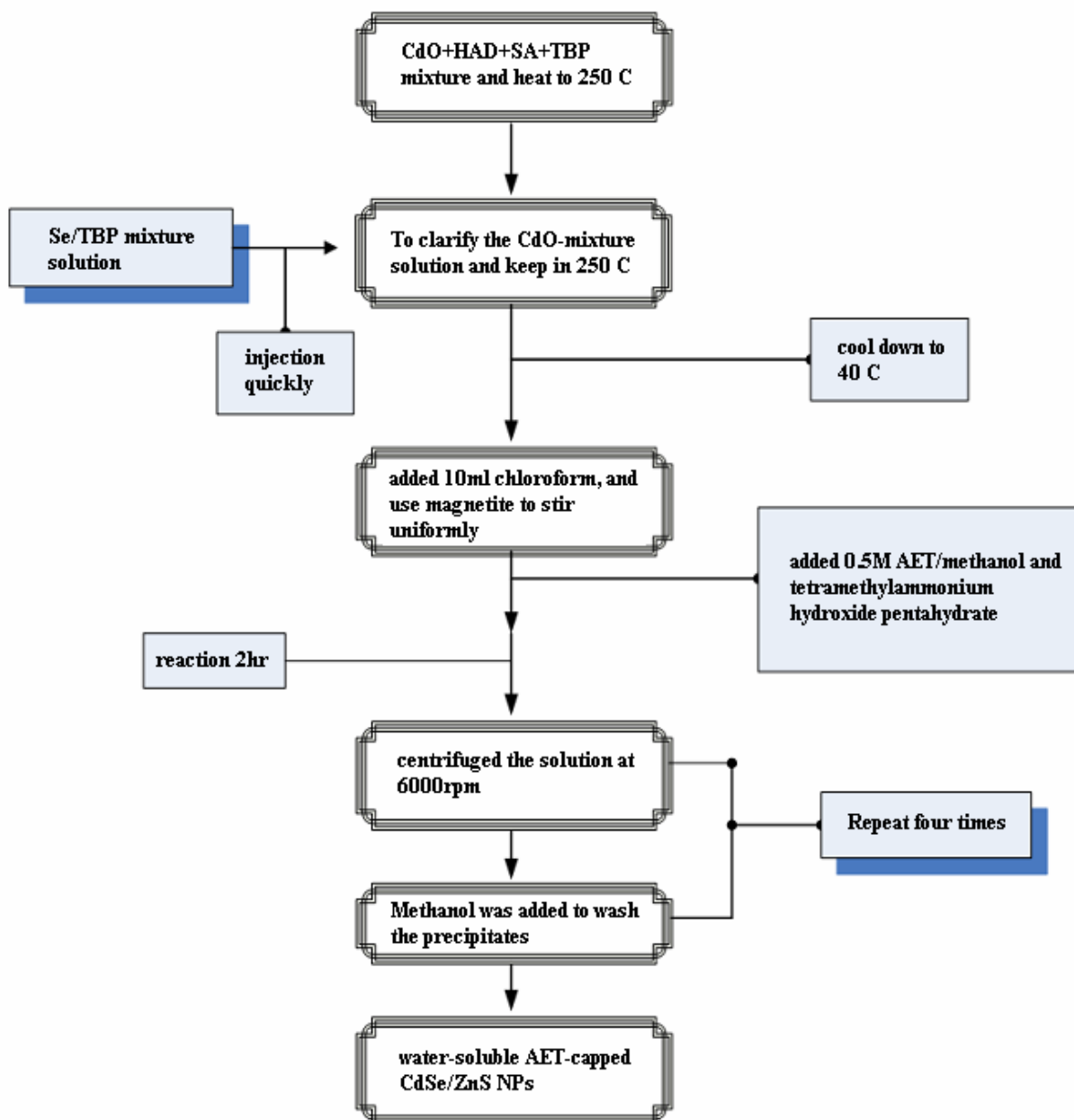


(b)

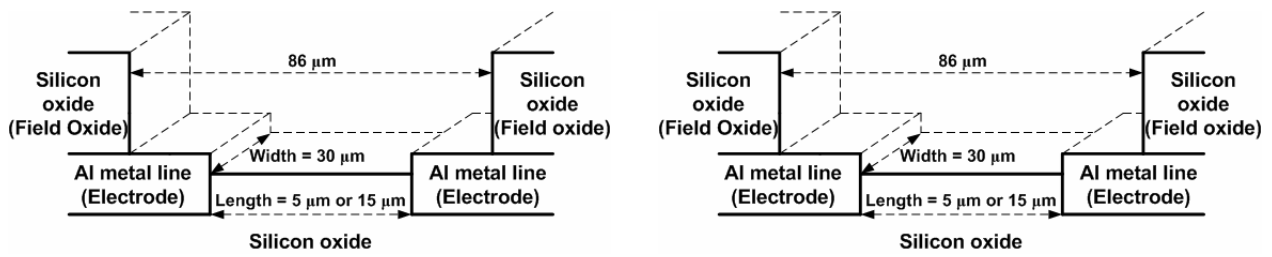
**Fig. 3.4** (a) The band gap and surface structure diagram of CdSe/ZnS NP. (b) The PL intensity spectrum of different kind of surface capping method of CdSe NP.



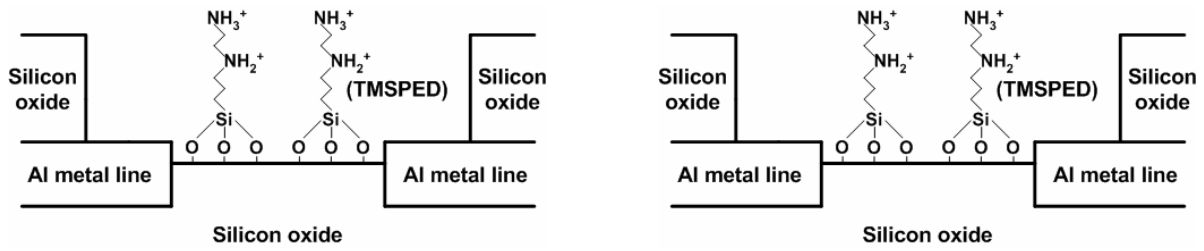
**Fig. 3.5** The flow diagram for preparing the MSA-capped CdSe/ZnS NPs solution.



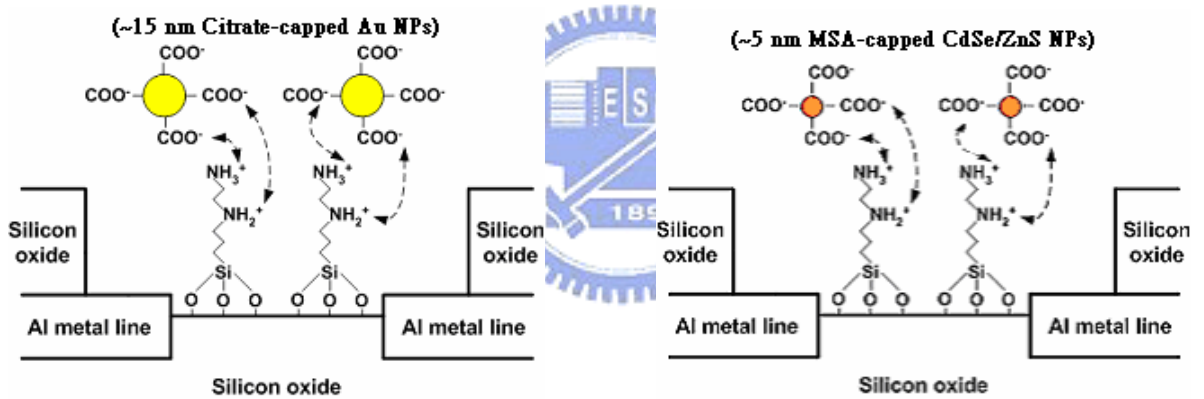
**Fig. 3.6** The flow diagram for preparing the AET-capped CdSe/ZnS NPs solution.



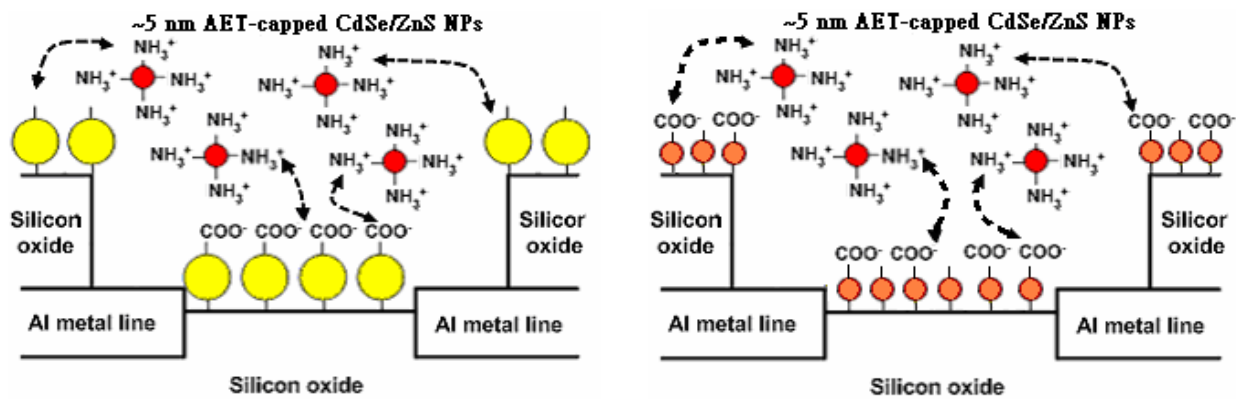
(a)



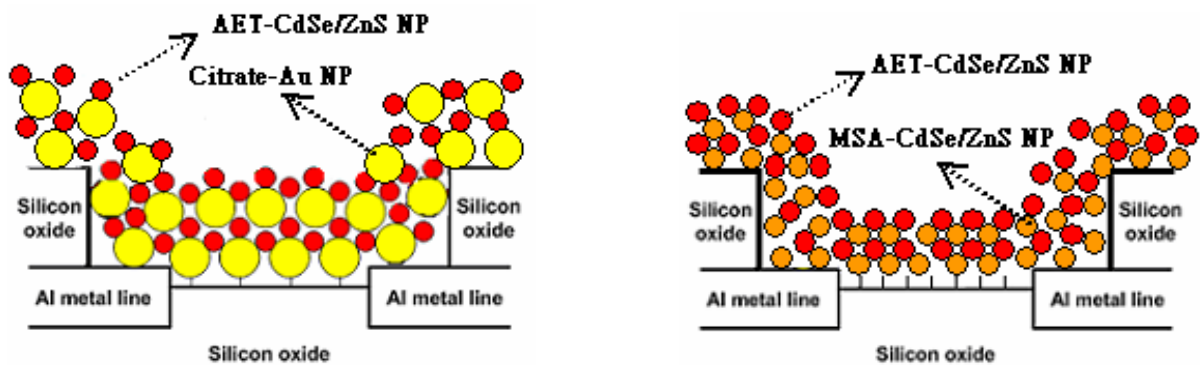
(b)



(c)



(d)



(e)

**Fig. 3.7** The overall fabrication process of the photo-sensing nanodevice by Coulombic force system on the silicon chip substrate is shown above. (a) The cross-section figure of the surface of the silicon chip designed for photo-sensing nanodevice fabrication, (b) The modification of TMSPED on the silicon oxide surface and the protonation of amino ( $-\text{NH}_3^+$ ) groups, (c) The assembly of  $\sim 15$  nm diameter Au NPs or  $\sim 5$  nm diameter MSA-CdSe/ZnS NPs on silicon oxide substrate by ionic interaction, (d) The assembly of  $\sim 5$  nm diameter AET-CdSe/ZnS NPs on the silicon oxide substrate by ionic interaction, and (e) The formation of the photo-sensing nanodevice structures after repeated assembly process. (Not to scale)

