

Synthesis of silver nanoparticles and the optical properties*

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Silver nanoparticles (NPs) of 5–15 nm are synthesized with the reduction of silver nitrate (AgNO_3) by formaldehyde (HCHO) and using polyethylenimine (PEI) as a stabilizer. Transmission electron microscopy (TEM) analysis shows the size of the Ag NPs increases with the increase of HCHO contents. The absorption and emission peaks of the original colloids are red shifted with increasing the size of Ag NPs. The absorption and emission peaks are at 344 nm, 349 nm, 357 nm, 362 nm, 364 nm and 444 nm, 458 nm, 519 nm, 534 nm, 550 nm, respectively. The fluorescence intensities of the silver colloids increase with increasing the NPs size (or the contents of HCHO). With the diluted fold increasing, the fluorescence intensity of the diluted silver colloids increases firstly then decreases. Compared with that of the original silver colloids, the emission peaks are blue shifted. For the diluted silver colloids, when the fluorescence intensity is maximum, the emission peaks are all near 444 nm. The 16-fold diluted silver colloid gets to the maximum emission intensity when the mole ratio of AgNO_3 and HCHO is 1:6.

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Nanoparticles (NPs) have special physical and chemical activities for their high surface to volume ratios^[1], so NPs have potential applications in many areas, such as electronics^[2], bio-sensing^[3], optical logic devices^[4] and spectroscopy^[5]. Silver NPs have been widely used because of their lower cost, easy preparation, better optical properties and better adhesion to glass substrates^[6]. Under ultraviolet (UV) or visible (VIS) light exciting, silver NP clusters can emit bright blue fluorescence^[7], and can be used for fluorescence enhancement^[8]. Up to now, many synthetic routes have been reported for the preparation of silver NPs with different sizes and shapes, including chemical reduction^[7-11], thermal growth^[12-14], photo-induced methods^[15-18] and so on. Chemical reduction method is the most popular approach to synthesize Ag NPs. Recently, several research results showed that polyethylenimine (PEI) can be used to slowly reduce AgNO_3 by sonicating^[14] or heating^[19] for 1–3 h, and at the same time, PEI is also as a stabilizer. Ref.[7] reported a method to quickly synthesize colloidal solutions of silver NPs by adding a reducing agent of formaldehyde (HCHO) into the solution of PEI and AgNO_3 . The relationship between NP size and the ratio of PEI and AgNO_3 was probed. It is well known that HCHO is a strong reducer, and it can effectively affect the particle

sizes and luminescence properties. In this paper, silver NPs are synthesized by HCHO to reduce AgNO_3 , and PEI is as a stabilizer. By changing the concentrations of HCHO, we find that the colors, fluorescence intensities and peak positions of the Ag NPs are highly sensitive to the concentration of HCHO. The diluted silver colloids show some new optical properties.

For particle preparation, HCHO solution (AR, 37.0%–40.0%) and AgNO_3 (AR, content 99.8%) were purchased from Sinopharm Chemical Reagent Co. Ltd (SCRC), China. PEI solution (50.0% w/v in water, molecular weight 750000) was purchased from Fluka, Germany.

1.7 ml PEI was diluted into 100 ml deionized water by ultrasonic dispersion for 5 min. Then 0.2012 g AgNO_3 was dissolved in 100 ml aqueous solution of PEI, and homogenized by ultrasonic dispersion for 10 min at room temperature. PEI is a very weak reducer, so within a short time and at room temperature, it is difficult to reduce AgNO_3 to Ag. The solution is colorless. The above solution was divided into five equal parts. Finally, 0.04 ml, 0.08 ml, 0.12 ml, 0.16 ml and 0.2 ml HCHO were separately added into solutions, and the final solutions were named as Ag0, Ag1, Ag2, Ag3 and Ag4. For the five solutions above, the mole ratios between

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AgNO_3 and HCHO are 1:2, 1:4, 1:6, 1:8 and 1:10, respectively.

In the preparation, after HCHO was added into solutions for several minutes, the colors of solutions quickly changed from colorless into light green (Ag0), light yellow (Ag1), yellow (Ag2), brown yellow (Ag3) and brown red (Ag4), respectively. We can see that the colors changed with the concentration of HCHO. The higher concentration of HCHO is, the darker the colloids, and the larger size of the NPs. It indicates AgNO_3 was quickly reduced by HCHO. Here PEI is almost as a stabilizer.

In order to observe microstructures of Ag NPs, transmission electron microscopy (TEM) (H-7650, Japan) analyses of Ag NPs for Ag0, Ag2 and Ag4 were conducted after 2 h storage and then dried in an oven at 60 °C for 6 min, which are shown in Fig.1. The substrates of TEM are Cu/PVF/C grids. From Fig.1, we can see that the Ag NPs are almost spheres. The sizes of the Ag NPs are in the range from 5 nm to 15 nm, and can increase with the contents of HCHO.

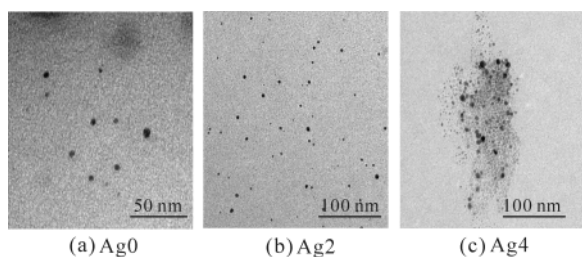


Fig.1 TEM images of Ag0, Ag2 and Ag4 after 2 h storage and dried in an oven at 60 °C for 6 min

Absorption spectra were recorded with a UV-VIS spectrophotometer (Cary 50). Photoluminescence (PL) spectra were measured at room temperature by a spectrophotometer (Fluomax-4, Horiba Jobin Yvon, Japan) with a 150 W xenon lamp as source.

Fig.2 shows the UV-VIS absorption spectra of the silver colloids. An absorption spectrum of the deionized water was

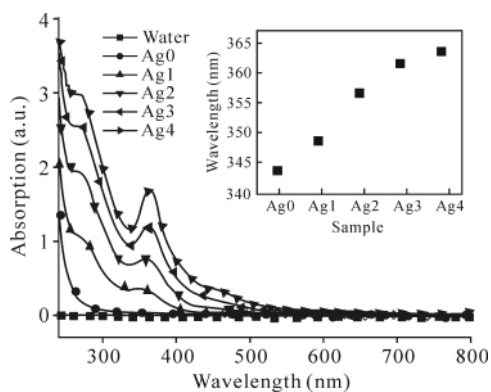


Fig.2 UV-VIS absorption spectra of Ag colloids with different contents of HCHO after storage for several minutes (Absorption peaks are shown in the inset.)

also shown as a reference. For the five silver colloids, the adsorption peaks are at 344 nm, 349 nm, 357 nm, 362 nm and 364 nm, respectively. The adsorption peaks are red shifted from 344 nm to 364 nm with increasing the contents of HCHO, which also indicates the absorption peaks of silver colloids have red shifts with the size of the Ag NPs increasing. This result correlates with that in Ref.[7]. The above experiments show HCHO plays a very important role in size control of NPs in synthetic process.

The NPs may aggregate in the colloids, which can cause a red shift of the fluorescence peak relative to that of the original colloid, and the fluorescence intensity changes. For these reasons, we measure the fluorescence spectra of the original and diluted colloids. For the fluorescence spectra, the above absorption peaks are chosen as excitation wavelengths. The slits of excitation and emission are 2 nm and 3 nm, respectively.

Fig.3 shows the emission spectra of the original and diluted colloids. The emission peaks of original and diluted colloids are illustrated in Tab.1. We can find that: (1) For the five original silver colloids, the order of the fluorescence intensities is $\text{Ag0} > \text{Ag1} > \text{Ag2} > \text{Ag3} > \text{Ag4}$. And the emission peaks are at 444 nm, 458 nm, 519 nm, 534 nm and 550 nm, respectively. With increasing contents of HCHO or the size of the NPs, the emission peaks have red shifts from 444 nm to 550 nm. For the numbers of silver atoms in the five colloids are the same, above results show the smaller the NPs size, the more NPs in the colloids and the higher fluorescence yield. (2) Except for Ag0, the emission peaks of the diluted colloids have blue shifts relative to that of the original colloids. The blue shift rates decrease with dilution folds increasing. The reason is that the aggregation of NPs is decreased by dilution, and the small NPs have higher fluorescence yield. But as the dilution folds increase to a higher fold, the small NPs in the unit colloid will decrease, which leads to the fluorescence intensity decreasing. And the aggregated force is not strong. After diluting, the sizes of the Ag NPs become small. (3) For the original and diluted colloids, when the intensities are maximum, the emission peaks are all near 444 nm, which also indicates the aggregation of the silver NPs in the colloids decreases after dilution. (4) Except for Ag0, the fluorescence intensities of the colloids present an increasing then decreasing trend with the dilution folds increasing. From Fig.4, for Ag1, Ag2, Ag3 and Ag4, when the intensities are maximum, the dilution folds are 8, 16, 16 and 32, respectively. For these diluted colloids, the 16-fold diluted Ag2 has the maximum intensity. The content of HCHO is 0.12 ml. That is, when the mole ratio of AgNO_3 and HCHO is 1:6, the 16-fold diluted colloid has the maximum emission intensity as shown in Fig.4.

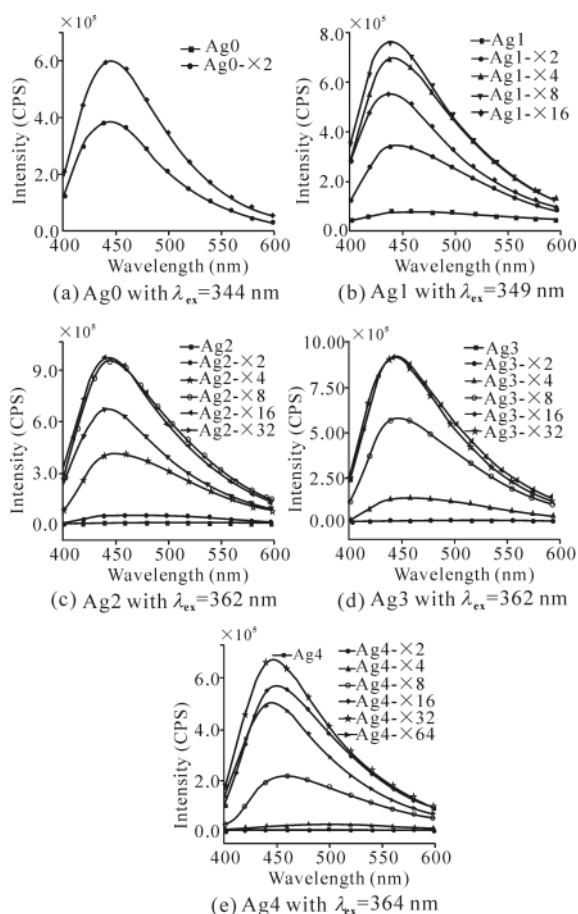


Fig.3 Emission spectra of the original and diluted silver colloids, where $Ag_i \times j$ ($i=0, 1, 2, 3$ and 4 ; $j=2, 4, 8, 16, 32$ and 64) indicates Ag_i is diluted by j folds

Tab.1 Emission peaks of original and diluted colloids

Sample	Position of emission peak (nm)						
	Original colloids	Diluted colloids					
		× 2	× 4	× 8	× 16	× 32	× 64
Ag0	444	444	-	-	-	-	-
Ag1	458	446	442	444	436	-	-
Ag2	519	474	447	443	443	442	-
Ag3	534	509	456	447	445	443	-
Ag4	550	538	491	458	452	444	444

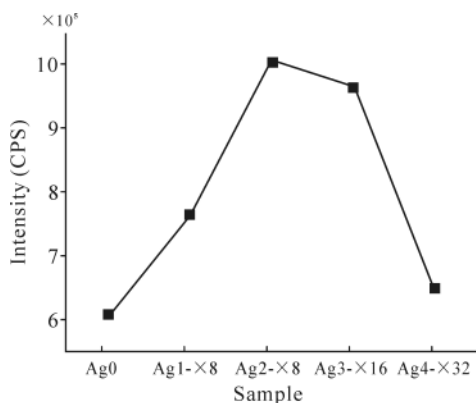


Fig.4 Maximum fluorescence intensities for the five Ag colloids

Silver NPs of 5–15 nm are synthesized with HCHO reducing $AgNO_3$ and PEI as a stabilizer. TEM analysis shows the sizes of the Ag NPs are increased with the contents of HCHO increasing. The emission peaks of the original silver colloids have red shifts from 444 nm to 550 nm with increasing the sizes of NPs. Except for Ag0, the emission peaks of the diluted silver colloids have blue shifts relative to that of the original silver colloids. For Ag1, Ag2, Ag3 and Ag4, when the intensities are maximum, the dilution folds are 8, 16, 16 and 32, respectively. The 16-fold diluted Ag2 has the maximum intensity in all the samples. The maximum intensity emission peaks of the diluted silver colloids are all near 444 nm, and the mole ratio of $AgNO_3$ and HCHO is 1:6. This result is promising for fluorescence enhancing or resonant Raman enhancing with silver NPs.

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