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# Synthesis of nearly monodispersive gold nanoparticles by a sodium diphenylamine sulfonate reduction process

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Au nanoparticles have been prepared by the reaction of $HAuCl_4$ and sodium diphenylamine sulfonate in the presence/absence of poly(vinylpyrrolidone)(PVP) at room temperature. The nanoparticles were characterized by Transmission electron microscopy (TEM), UV-Vis absorption spectrum. The research showed that the molar ratio of PVP/ $HAuCl_4$ has effect on the size and the morphology of Au nanoparticles. © *2006 Springer Science + Business Media, Inc.*

## 1. Introduction

Many characteristics of nanoscale noble metal materials are size-and shape-dependent, including their optical, electronic, and catalytic properties [1–4]. Therefore the applications of noble metal nanomaterials are strongly dependent on the size and shape of them. Varieties methods have been exploited to control the size, the shape and the distribution of the nanoparticles, such as, two-phase liquid–liquid [5], micelle [6], surfactant-directed and seed-mediated growth method [7], porous alumia templates [8], electrochemical [9], ultraviolet irradiation [10], laser-induced ablation [11], and so on. Moreover, organized two-dimensional and three-dimensional array of colloidal Au and other noble metal nanoparticles and special morphological nanostructure consisted of the nanoparticles have attracted considerable attention recently [12–14]. Except for a few methods involving in using bulk gold metal [11, 14], most make use of the reaction between $Au^{3+}$ and reductant in the presence of varieties of protecting agents, such as citrate ions [15], polymers [16, 17], dendrimers [18], organic ligands [19] and so on, to generate Au nanoparticles. Though many reductants, such as $NaBH_4$ [5], sodium citrate [1, 15, 20], ascorbic acid [7, 16], white phosphorus [1], ethanol or polyols [21], DMF [22] and so on, have been exploited to produce Au nanoparticles, exploiting new reductants and protecting agents for founding the novel synthetic methods of noble metal nanoparticles are still considerably attracted. For example, Potassium bitartrate and oleylamine have been used in syntheses of noble metals nanoparticles recently [23, 24], most recently, we have successfully synthesized silver nanowires on a large-scale using sodium diphenylamine sulfonate as a reductant in the absence of seeds, heating, surfactants, and inorganic templates [25]. Herein, we report a novel and simple wet chemical reduction method for producing Au nanoparticles at room temperature, using $HAuCl_4$ as the gold source and sodium diphenylamine sulfonate as the reductant [26] in the presence/absence of poly (vinyl pyrrolidone) (PVP) as the capping agent. To the best of our knowledge, this is the first report on the producing gold nanoparticles using sodium diphenylamine sulfonate as a reductant.

## 2. Experimetal

### 2.1. Chemicals

High purity $HAuCl_4$ was provide by Changzhou Rare and Noble metal Factory (China). Sodium diphenylamine sul-

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fonate (sodium diphenylaminesulfonic acid), poly(vinyl pyrrolidone) (PVP) (average molecular weights ($M_w$) of 40 000) and polyvinylalcohol(PVA) (average molecular weights ($M_w$) of 80 000) were obtained from Shanghai Chemical Reagent Company. All agents were of analytical grade. The water used was two-distilled water.

## 2.2. Materials preparation

A 100 ml aqueous solution of sodium diphenylamine sulfonate (0.5 mmol or 0.15 mmol) and PVP (average molecular weights ($M_w$) of 40 000) at a selected amount (0, 0.1, 1, 2 mmol) was stirred for 30 min at room temperature. The above solution was then added dropwise to 5 ml aqueous solution of $HAuCl_4$ containing 0.045 mmol or 0.135 mmol, and stirred for 24 h. The resulting Au colloids solution was obtained. Au nanoparticles can be obtained by centrifugal separation.

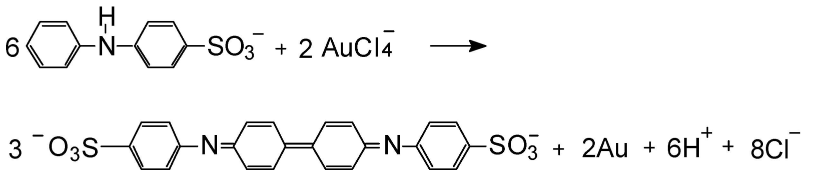
## 2.3. Characterization

Transimission electron microscopy (TEM) and selected area electron diffraction (SAED) images of the products were taken with a JEOL JEM-200CX transimission electron microscope, using an accelerating voltage of 200 kV. Samples for TEM and SAED were prepared by placing a drop of the colloidal dispersion of Au nanoparticles onto a carbon-coated grid and dried at room temperature. The disappearance of $[AuCl_4]^-$ ions and the formation of Au nanoparticles were monitored by UV-Vis spectra recorded on a Shimadzu UV-3100 photospectrometer.

## 3. Results and discussion

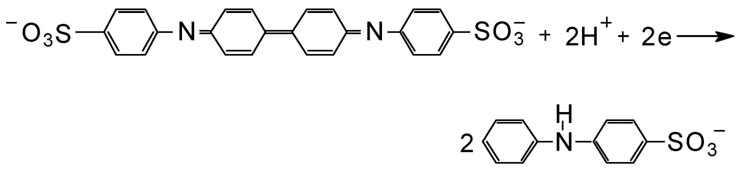
### 3.1. Formation of Au nanoparticles

The redox reaction for synthesizing gold nanoparticles can be formulated as follows:



(1)

The above reaction is comprised of two half reactions, as shown in the following:



$E^0 = 0.83V$ (2)

$$AuCl_4^- + 3e \longrightarrow Au + 4Cl^- \qquad E^0 = 0.994\ V \qquad (3)$$

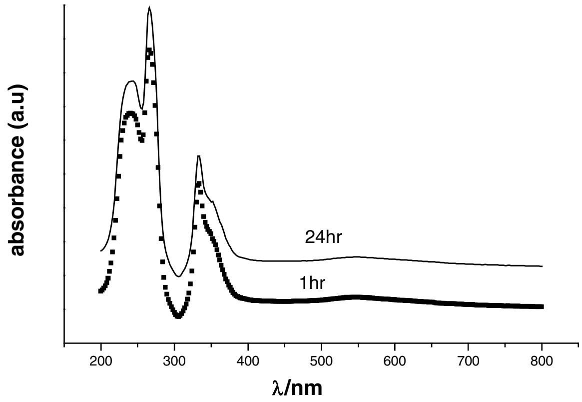


*Figure 1* UV-vis spectral change during the formation of Au nanoparticles. (Sodium diphenylamine sulfonate = 0.5 mmol, PVP = 2 mmol, and $HAuCl_4$ = 0.045 mmol).

The standard Gibbs free energy change $\Delta_r G_m^0$ of the redox reaction **1** was calculated to be $-94.56\ kJ \cdot mol^{-1}$ based on the standard reduction potential $E^0$ values, which implied a very strong tendency for the reaction **1** to progress toward the right (the products).

For examining the formation process of Au nanoparticles, we selected the reaction conditions as follows: the amount of sodium diphenylaminesulfonic acid, PVP and $HAuCl_4$ is 0.5 mmol, 2 mmol and 0.045 mmol respectively (the ratio of $PVP/HAuCl_4 = 44$), as a representative example. The mixed solution of PVP and sodium diphenylamine sulfonate is colorless. After adding the solution of $HAuCl_4$, the color of the solution turns blue violet soon, which is right color of the corresponding redox product N, N′-diphenylbenzidinedisufonate [26]. As the reaction proceeds following to the equation **1**, the ligand-metal charge-transfer characteristic bands (LMCT) of $[AuCl_4]^-$ at 218 nm and 310 nm disappear nearly after reaction

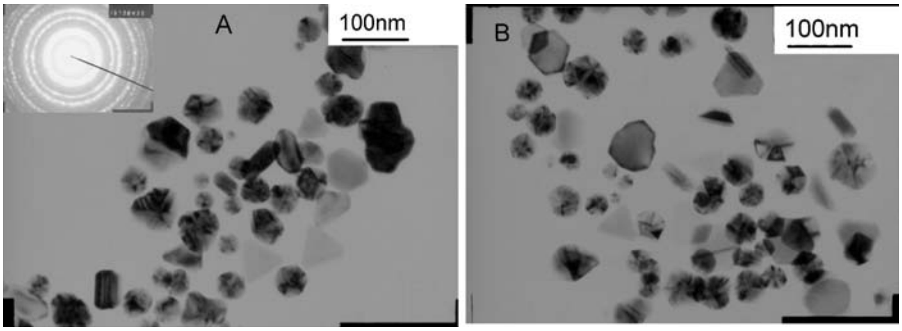


*Figure 2* The TEM images of Au nanoparticles. The reaction times are (a) 24 hr, (inset, ED pattern) (b) 48 hr. (Sodium diphenylamine sulfonate = 0.5 mmol, PVP = 2 mmol, and $HAuCl_4$ = 0.045 mmol).

for 1 h, and a abroad peak appears at about 530 nm, which is the characteristic absorption band of Au nanoparticles.Two new absorption bands at about 265 and 334 nm should be attributed to the characteristic absorption peaks of the redox product N,N′-diphenylbenzidinedisufonate (Fig. 1). The UV-Vis spectrum of the solution obtained after reaction for 24 h is almost same as that of the solution after reaction for 1 h, indicating that $[AuCl_4]^-$ ions are completely reduced (Fig. 1). The TEM images show that the average size of the Au nanoparticles formed after 24 h is almost the same as that formed after 48 h (Fig. 2). The corresponding electron diffraction (ED) pattern reveals that the Au nanoparticles are polycrystals. The diffraction rings correspond to four crystal planes of (111), (200), (220), and (311) of the cubic phase structure Au respectively, which is in accord with the data of the JCPDS4-0784 file.

### 3.2. Size control of Au nanoparticles by amount of sodium diphenylamine sulfonate

Fig. 3a is a typical TEM image of Au nanoparticals obtained via the reaction of $HAuCl_4$ (0.045 mmol) and sodium diphenylamine sulfonate (0.5 mmol) for 24 h in the absence of PVP, which indicates the average size of Au nanoparticles with $10.1 \pm 1.38$ nm and the Au nanoparticles with a narrower size distribution (standard deviation = 1.38) and nearly monodispersion. By keeping the amount of $HAuCl_4$ at 0.045 mmol, and decreasing the amount of sodium diphenylamine sulfonate from 0.5 mmol to 0.15 mmol, we found that the average size of Au nanoparticles increased to $22.2 \pm 3.52$ nm (Fig. 3b), the result was relevant to the reduction rate of $[AuCl_4]^-$. As the amount/concentration of reducing agent sodium diphenylamine sulfonate increasing, the reduction rate of $[AuCl_4]^-$ also increased, and the pro-

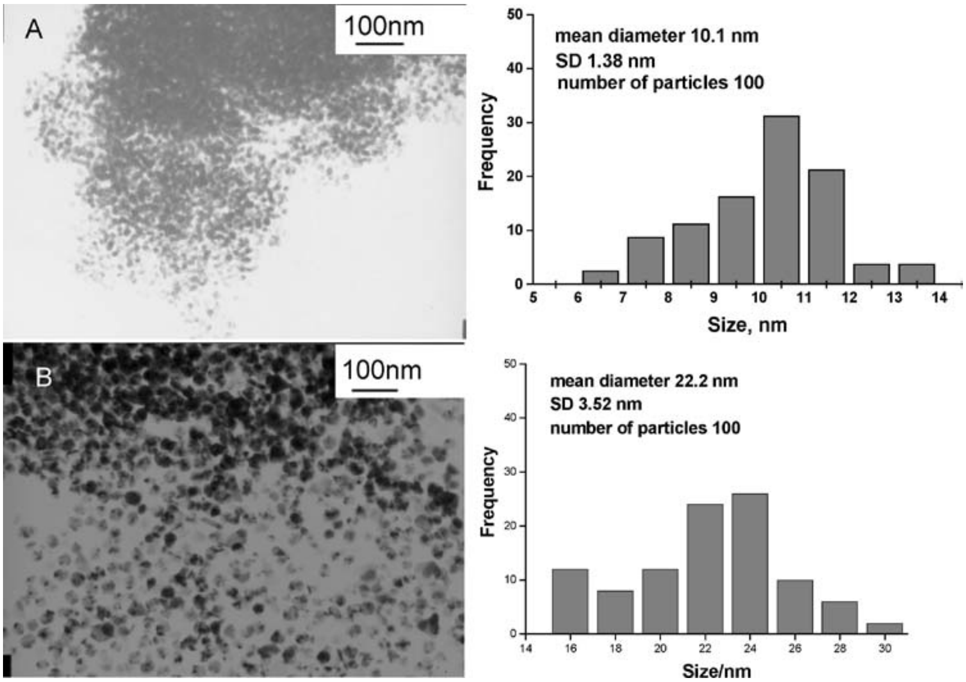


*Figure 3* The TEM images of Au nanoparticles obtained using different reductant concentration and the corresponding histogram (SD = standard deviation). (a) $HAuCl_4$ = 0.045 mmol, Sodium diphenylamine sulfonate = 0.5 mmol, (b) $HAuCl_4$ = 0.045 mmol, Sodium diphenylamine sulfonate = 0.15 mmol. Reaction times are 24 hr.

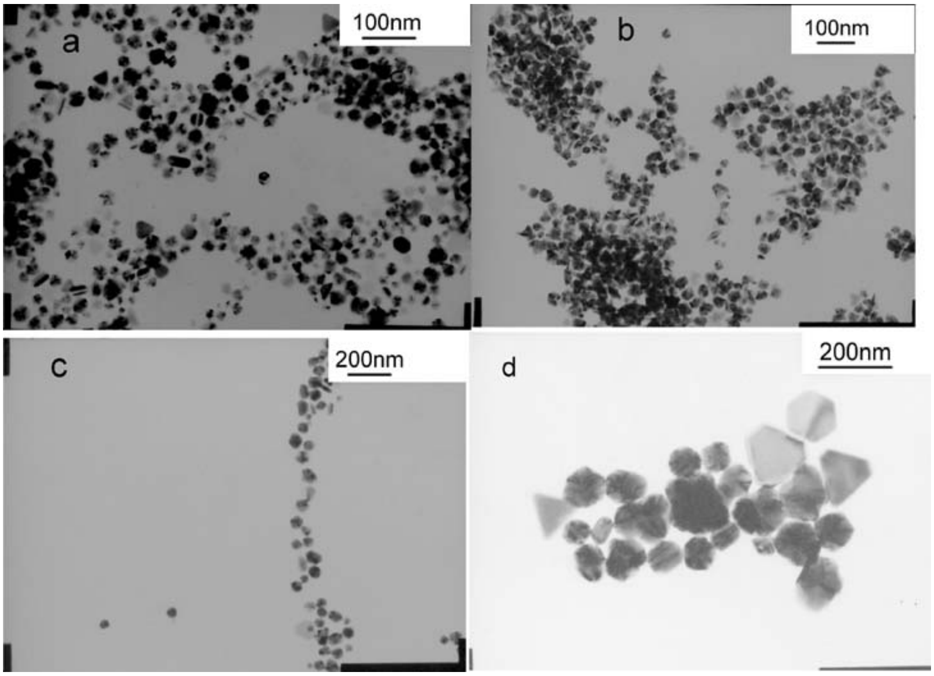


*Figure 4* The TEM images of Au nanoparticles obtained using different PVP/$HAuCl_4$ ratio. $HAuCl_4 = 0.045$ mmol, Sodium diphenylamine sulfonate = 0.5 mmol, (a) PVP = 0.1 mmol, PVP/$HAuCl_4 = 2.2$ (b) PVP = 1 mmol, PVP/$HAuCl_4 = 22$ (c) PVP = 2 mmol, PVP/$HAuCl_4 = 44$ (d) PVP = 4 mmol, PVP/$HAuCl_4 = 88$.

duced more Au nuclei in a shorter period and suppressed the growth of Au nanoparticles, resulting in smaller Au nanoparticles with narrower distribution forming. Such phenomenon is the same as that reported by Miyake *et al.* [27]. The Au colloids solution can be stable for about one week, indicating reductant sodium diphenylamine sulfonate unreacted and the redox product N,N′-diphenylbenzidinedisufonate still act as protecting agent and can prevent the Au nanoparticles from aggregating via the coordination interaction between the N and O atoms of N,N′-diphenylbenzidinedisufonate or sodium diphenylamine sulfonate and the surface Au atoms of the Au nanoparticles [25].

### 3.3. Influence of variation of the amount of PVP on size and morphology of Au nanoparticles

In all these experiments, we used a constant $HAuCl_4$ amount of 0.045 mmol and sodium diphenylamine sulfonate amount of 0.5 mmol. For this study, we chose four molar ratios PVP/$HAuCl_4$ (2.2, 22, 44, 88) and the reduction was performed at room temperature for 24 h. According to the TEM images shown in Fig. 5, the average size of Au nanoparticles measured increase from $25.3 \pm 3.21$ to $28.2 \pm 5.26$, $40.5 \pm 5.31$, $65.6 \pm 10.12$ nm with the molar ratio of PVP/$HAuCl_4$ increasing from 2.2 to 22, 44, 88 respectively. The result is different from that reported by Liz-Marzán *et al.* [22] and Miyake *et al.* [27], where the mean size of metal nanoparticles tends to decrease with an increase in the concentration ratios of the protective agent to $[AuCl_4]^-$ or $[PtCl_4]^-$. We speculated that the difference of the results might be related to the different reducing agents used. They used DMF or ethanol as both reducing agent and solvent, and PVP as a protective agent. In our case, PVP, as a protective agent also, mixed with the reductant first prior to the reaction. It is favourable for the reductant dispersing in PVP solutions in water and interacting with PVP via the intermolecular force or hydrogen bond. As the amount/concentration of PVP increases, the PVP molecules around the reductants increase, which may hamper the reaction between the reductants and $[AuCl_4]^-$ and lead to the reduction rate of $[AuCl_4]^-$ decreasing, and to producing less Au nuclei in a shorter period, which favors growth of Au nanoparticles, and the larger Au nanoparticles forming finally. Meanwhile, we also examined the influence of other protective agent polyvinylalcohol(PVA) on the size and morphology of Au nanoparticles. When 3 wt.-% PVA was used instead of PVP, the nanoparticles aggregated together were obtained (Fig. 5). The difference of PVA and PVP in structure may lead to the result.

### 3.4. Influence of variation of the amount of $HAuCl_4$ on size and morphology of Au nanoparticles

Keeping the amount of PVP and sodium diphenylamine sulfonate at 1 mmol and 0.5 mmol respectively, and increasing the amount of $HAuCl_4$ from 0.045 mmol to 0.135 mmol, the larger irregular particles consisted of smaller Au nanoparticles were obtained (Fig. 6), while dispersive Au nanoparticles were obtained in the former case (Fig. 4b). As the amount of $HAuCl_4$ increases, the number of Au nanoparticles formed in the solution increases, the molar ratio of $HAuCl_4$/PVP also increase,

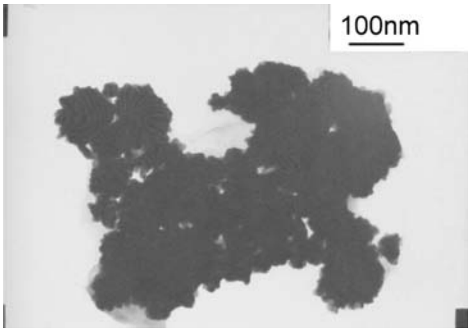


*Figure 5* The TEM image of Au nanoparticles obtained using protective agent PVA. $HAuCl_4 = 0.045$ mmol, Sodium diphenylamine sulfonate = 0.5 mmol, PVA = 3 wt%, reaction time is 24 hr.

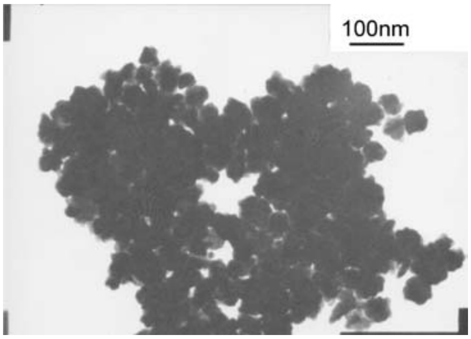


*Figure 6* The TEM image of Au nanoparticles at following reaction conditions: $HAuCl_4 = 0.135$ mmol, Sodium diphenylamine sulfonate = 0.5 mmol, PVP = 1 mmol, reaction time is 24 hr.

leading to smaller nanoparticles aggregating into larger particles.

## 4. Conclusion

In this work, we successfully synthesized Au nanoparticles using sodium diphenylamine sulfonate as a novel reducing agent of gold salts in the absence/present of PVP. The smaller and narrower distributed Au nanoparticles were obtained when using the higher concentration of reducing agent and in the absence of PVP. The molar ratio of $PVP/HAuCl_4$ has effect on the size and the morphology of Au nanoparticles. The average diameter of Au nanoparticles increases with the molar ratio of $PVP/HAuCl_4$ increasing. It is a novel and simple wet chemical reduction method for synthesizing Au nanoparticles, and it may be applied in preparing Pd and Pt nanoparticles.

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