

Preparation of Nickel Nanoparticles in the Presence of Sodium Dodecyl Sulfate - Polyvinylpyrrolidone Clusters

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Abstract

Polyvinylpyrrolidone (PVP) and sodium dodecyl sulfate (SDS) can form clusters (bound-micelles) in aqueous solution. In our study, we found nickel ions interact with SDS-PVP clusters as a supermolecule interaction. The existence of this interaction indicated the template function of the SDS-PVP clusters. In the presence of SDS-PVP clusters, nickel nanoparticles were obtained by reduction of nickel chloride with NaBH₄. The prepared particles were characterized by transmission electron microscope (TEM) and FT-IR. The results show that the dispersion and average size of spherical nickel nanoparticles can be controlled by mediating SDS-PVP clusters; additionally, PVP molecules adsorbed onto the particles. The template function of SDS-PVP clusters was studied via surface tension, ultra-filtration, UV Spectroscopy, etc. From the experiment results, we deduce that PVP and SDS were both accounted for the role of template. First, nickel ions associated onto the headgroups of SDS by electrostatic interaction when the nickel nanoparticles formed by reduction, then PVP adsorbed onto the particles' surface to prevent the agglomeration of nickel particles and stabilize the nanoparticles.

Keywords: Polyvinylpyrrolidone; Sodium Dodecyl Sulfate; Soft template; Nickel nanoparticle

1. Introduction

The preparation of nickel nanoparticles has attracted extensive attention during the past decades, for they have unusual properties and potential applications in catalytic, electronic and magnetic materials (Harada, 1977). Till now, nickel nanoparticles are most commonly prepared by electro-deposition, radiolytic reduction, microemulsion, alcohol reduction, wet chemical reduction in aqueous solution, and so on (Cao, 2003). Among them, chemical reduction of metal ions from the solutions became one of the main preparation methods due to the desired properties of metal powders and the economical aspects of the process. In this method, macromolecule can be added into the solution to prevent the growth and oxidation of nanoparticles (Hegde, 1997) and also surfactant can be added to lower interfacial tension and prevent agglomeration (Kameo, 2001).

Macromolecule and surfactant can form soft matter clusters in aqueous solution spontaneously. Such clusters have self-assemble behavior and supermolecule interaction existed between the clusters and metal ions (Lehn, 1995), so surfactant-macromolecule clusters can be used as the template to prepare metal nanoparticles. Up to now, there were some studies about preparation of metal salts in the presence of soft matter clusters (Torigoe, 1995; Leontidis, 1999; Cheng, 2003; Ma, 2003), but the using of it to prepare

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nickel nanoparticles has not been reported.

In this paper, we prepared nickel nanoparticles in the presence of SDS-PVP clusters by reduction of nickel chloride with NaBH_4 in aqueous solution. Transmission electron microscope (TEM) was used to characterize the size and morphology of the resultant nanoparticles. The template function of SDS-PVP clusters on particles' size and dispersion was investigated via surface tension, ultra-filtration, UV absorption Spectroscopy, etc.

2. Experimental

2.1. Materials

Sodium dodecyl sulfate (SDS, Across Organics, 99%, was used as received), Polyvinylpyrrolidone (PVPK-30, ISP Co.), NaBH_4 (Shanghai Chemistry Reagents Co. of China Medical Corp. 96%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Shanghai Chemistry Reagents Co. of China Medical Corp.), all the materials used were of analytical grade and doubly de-ionized distilled water was used throughout.

2.2. γ -lgc curves of NiCl_2 -SDS-PVP System

Surface tension (γ) of NiCl_2 -SDS-PVP solution were measured by drop volume method at $(40.0 \pm 0.5)^\circ\text{C}$ (Zhao, 1991). The drop volume measurements were repeated at least 4 times. Two critical concentrations of the solution (c_1 and c_2 in Figure 2) were obtained from γ -lgc curves. When $c_1 < c_{\text{SDS}} < c_2$, SDS adsorbs onto the PVP chains and form SDS-PVP clusters (Fang, 2004; Dong, 2004).

2.3. Ultra-filtration of the NiCl_2 -SDS-PVP Solution

The SDS-PVP solution containing nickel chloride were prepared and stirred in the thermostat. Starting the ultra-filtration process when the mixture reached 40°C , the mixture was recycled for 30 min, the final filtrate was collected thereafter.

2.4. UV Spectroscopy

Model TU-1901 UV Spectroscopy was used to determine the amount of nickel ions in filtrate and mother solution, and the associate ratio of nickel ions with SDS-PVP clusters was calculated according to the formula below:

$$\beta = [c_{\text{Ni}^{2+}} - (c_{\text{Ni}^{2+}})_{\text{uf}}] / (c_{\text{SDS}} - c_1) \quad (1)$$

Here, β is defined as the associate ratio of nickel ions with SDS-PVP clusters, $c_{\text{Ni}^{2+}}$ is concentration of nickel ions in the mother solution, $(c_{\text{Ni}^{2+}})_{\text{uf}}$ is the concentration of nickel ions in filtrate, c_{SDS} is the concentration of SDS in mother solution, and c_1 is the first critical concentration of surfactant determined by γ -lgc curves.

2.5. Preparation and Characterization

A series of NiCl_2 -SDS-PVP solutions were prepared and left in water-bath at $(40 \pm 0.5)^\circ\text{C}$ for 2 hours. Then adding dropwisely a certain amount of NaBH_4 solution under stirring, a

black product was obtained. The nanoparticles were collected by centrifugation (10,000 r/min), washed with distilled water and ethanol for three times, respectively, and then lyophilized. The size and morphology of the particles were characterized by a Hitachi Model H-7000 transmission electron microscopy (TEM). MB-104 FT-IR spectrometer was used to study the surface adsorption of nanoparticles.

3. Results and Discussion

3.1. TEM image of nickel nanoparticles

NaBH_4 is a strong reducer and only stable in alkaline solution. In the solution, NaBH_4 would decompose slowly and release hydrogen at room temperature. During the preparation of nickel nanoparticles, stirring can accelerate the decompose speed, maintaining $n_{\text{NaBH}_4}/n_{\text{Ni}^{2+}} = 10$ to make sure the plenitude of NaBH_4 . To control the process of reaction, a certain amount of NaBH_4 solution was added dropwisely under stirring. After several drops, black products formed, it indicated the nucleation of nickel particles, then the addition can be speeded up. During the reaction course, continuous stirring (400 r/min) was needed to prevent the formation of large particles. Nickel nanoparticle surface has high activity, and can be oxidized while exposed to the air. In this experiment, no visible oxidation was observed in the absence of nitrogen, it may be due to the SDS-PVP's protection to the particles.

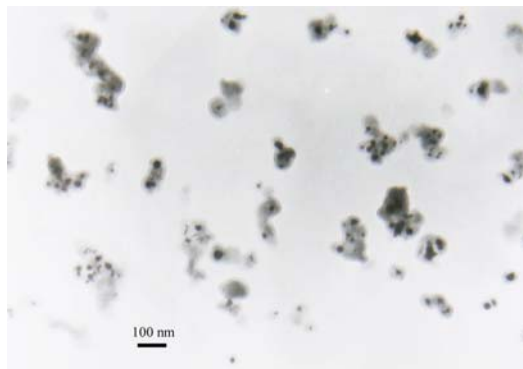


Figure 1. TEM image of nickel nanoparticles prepared at $\rho_{\text{pvp}} = 7 \text{ g}\cdot\text{L}^{-1}$, $c_{\text{Ni}^{2+}} = 15 \text{ mmol}\cdot\text{L}^{-1}$, $c_{\text{SDS}} = 3.4 \text{ mmol}\cdot\text{L}^{-1}$.

Figure 1 is the TEM image of prepared nanoparticles at one of the experiment conditions. It shows that the sizes of the particles were in the range of nano-scale and the particles were spherical. In the mean time, Figure1 showed there were many gray materials in the surrounding of black particles, which implies soft matter such as PVP, SDS or SDS-PVP clusters adsorbed onto the particles, further investigation was made by FT-IR test.

3.2. γ -lgc curves of NiCl_2 -SDS and NiCl_2 -SDS-PVP systems

γ -lgc curve of SDS-PVP system had two critical concentrations (Fang, 2004), the first critical concentration c_1 and the second critical concentration c_2 . When $c_{\text{SDS}} > c_1$, SDS adsorbed onto the PVP chains and formed SDS-PVP clusters, this made surface tension decrease slowly. When $c_{\text{SDS}} > c_2$, SDS formed free micelles and γ -lgc curve overlapped with that in the absence of PVP.

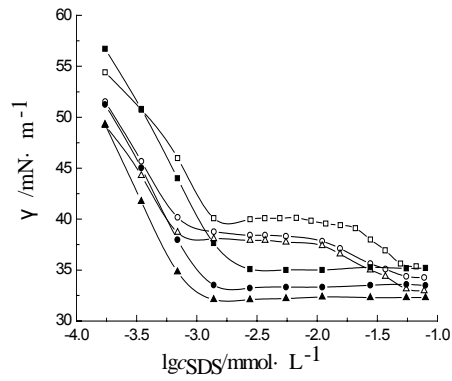


Figure 2. γ -lgc curves of NiCl₂-SDS and NiCl₂-SDS-PVP systems

$\rho_{\text{PVP}} = 7 \text{ g}\cdot\text{L}^{-1}$, ■ NiCl₂ (2 mmol·L⁻¹)-SDS; ● NiCl₂ (15 mmol·L⁻¹)-SDS; ▲ NiCl₂ (30 mmol·L⁻¹)-SDS; □ NiCl₂ (2 mmol·L⁻¹)-SDS-PVP; ○ NiCl₂ (15 mmol·L⁻¹)-SDS-PVP; △ NiCl₂ (30 mmol·L⁻¹)-SDS-PVP

The interaction between SDS-PVP and metal ions can be studied with surface tension experiment. Figure 2 shows that γ -lgc curves of SDS-PVP system containing nickel ions also have two critical concentrations, and c_1 decrease with the increasing of nickel ions, which means that nickel ions accelerate SDS binding to PVP chains at lower concentration of SDS, thus more SDS adsorb onto PVP chains and result in the decrease of surface tension. The experiment result indicated nickel ions has interaction with SDS-PVP system, and can strengthen this interaction. Existence of this interaction was the foundation of the template function of SDS-PVP cluster when it was used to prepare nanoparticles.

As for the preparation of nickel particles, the agglomeration of particles changed with the change of c_{SDS} . When $c_{\text{SDS}} < c_1$, there were many visible black particles appeared in the solution. When $c_1 < c_{\text{SDS}} < c_2$, the particles dispersed very well in the solution and formed black liquid, no visible particles existed as showed in Figure 1.

3.3. Nickel ions associated with SDS-PVP clusters

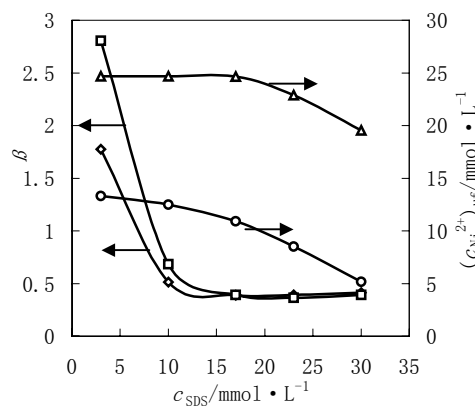


Figure 3. Amount of nickel ions associated with SDS-PVP clusters

$\rho_{\text{PVP}} = 7 \text{ g}\cdot\text{L}^{-1}$, ◇. $c_{\text{Ni}^{2+}} = 17.24 \text{ mmol}\cdot\text{L}^{-1}$, □. $c_{\text{Ni}^{2+}} = 31.03 \text{ mmol}\cdot\text{L}^{-1}$, ○. $c_{\text{Ni}^{2+}} = 17.24 \text{ mmol}\cdot\text{L}^{-1}$, △. $c_{\text{Ni}^{2+}} = 31.03 \text{ mmol}\cdot\text{L}^{-1}$

Through ultra-filtration, SDS-PVP clusters and SDS monomer can be separated. The

amount of nickel ions in filtrate and mother solution was estimated by UV Spectroscopy, respectively. The results were showed in Figure 3.

Figure 3 shows the amount of nickel ions in filtrate is less than that in the mother solution. It proved nickel ions can associate with SDS-PVP clusters and so the concentration of nickel ions in filtrate decreased. When $c_{\text{SDS}} > c_1$, the amount of nickel ions associated with clusters increased with the increasing of c_{SDS} , so the concentration of nickel ions in filtrate decreased with the addition of SDS. With the increasing of c_{SDS} and the invariability of $c_{\text{Ni}^{2+}}$ in the mother solution, the amount of nickel ions associated with each SDS-PVP cluster decreased, so β decreased. When the concentration of Ni^{2+} was higher, the amount of nickel ions associated with SDS-PVP clusters increased and β became higher. The above results implied that nickel ions associated with SDS headgroups through electrostatic interaction (Nassar, 1997; Huang, 2005), and thus associated with SDS-PVP clusters.

3.4. FT-IR of the prepared particles

PVP has carbonyl group characteristic absorption at 1660cm^{-1} , carbon-nitrogen absorption at 1290cm^{-1} (Cui, 2001). SDS has characteristic absorption at 1222cm^{-1} (S=O). The FT-IR experiment implied that PVP adsorbed onto the particles, but no SDS characteristic absorption (S=O) was found in the IR proof, which, might be induced by the loss of SDS during the wash, or it implied that the SDS molecules had weaker interaction with the particles compare to PVP. PVP has N and O atom in its five-atom loop; they can associate with the nickel atom on the surface of the crystal. While the long chains of PVP stretch out around, through this steric hindrance effect can PVP depress the collision between nickel crystals and thus prevent the growing up of particles effectively. In the meantime, the surface energy of nickel particles decreased and became consistent in all the direction for the adsorption of PVP, so the new reduced nickel atoms will grow evenly onto the surface of nickel crystals and yield spherical particles. The carbonyl group absorption at 1658cm^{-1} became wider, it might be due to the nanoparticles. Nanoparticle has large surface area, so the surface atom coordination is low and this made the wider IR absorption (Cao, 2003).

4. Conclusions

Surface tension measurement of NiCl_2 -SDS-PVP illustrated that supermolecule interaction exists between SDS-PVP clusters and nickel ions. Ultra-filtration and UV Spectroscopy proof indicated that nickel ions associated with the clusters, so SDS-PVP clusters can be used as the template in the formation of nickel nanoparticles. TEM showed the nanoparticles were spherical and soft matter adsorbed onto the surface of particles. FT-IR showed that PVP adsorbed onto the particles and had stronger interaction with the particles compare to SDS.

Acknowledgment

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