

**Synthesis of Dispersing Palladium Nanoparticles
within Micelles: Phase Transfer by Regulation of
Preparation Time**

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Biomolecules has attracted attention as templates to construct advanced materials in size from meso- to macro-scale. These biomolecules include surfactant¹, DNA², thiol⁴⁻¹⁰, polymer³ and their derivatives. For the preparation of metal nanoparticle, the display of hydrophilic or hydrophobic property on particle surface is dependent on the characterization of these biomolecules. These surface properties often decide the potential applications of particles. Recently two research groups, Brust et al.⁴ and Murray et al.⁵ published many important results about monolayer-protected metal clusters (MPCs). These charge-neutral entities comprise entirely of an elemental metal core and a dense mantle of alkylthiol groups, normally straight-chain n-CH₃(CH₂)_mS, or some related side-chain structures, which have been referred to as self-assembled monolayer (SAM)⁴⁻¹⁰. Following their works, biphasic syntheses of CdS⁶, Au⁷, Ag⁸, Pt⁹ and Pd¹⁰ nanoclusters with thiols have been investigated. However, according to our survey, there is still not any method to selectively prepare hydrophilic and hydrophobic colloids within one simple template through a simple solution route. In this paper we report how to selectively prepare uniform hydrophilic and hydrophobic Pd nanoparticles templated with micelles through reflux of Pd salt (palladium acetate) and sodium alkyl sulfate solution by controlling the duration of reaction.

The formation of the hydrophilic (hy-Pd_{nm}) and hydrophobic Pd nanoparticles (hp-Pd_{nm}) in sodium dodecyl sulfate (SDS) or sodium tetradecyl sulfate (SC₁₄S) aqueous solution are illustrated in following descriptions. Initially, palladium acetate (Pd(OAc)₂) was gradually dissolved in a neutral aqueous SDS or SC₁₄S solution. The solution was then heated slowly in an oil bath and refluxed. After 1 hour, the absorbance of palladium complex capsulated in micelles was observed between 300 ~ 400 nm by UV-Vis spectroscopy. As the reaction time was prolonged, the intensity of the band decreased steadily. That band disappeared completely when the reflux time lasted for about 6 hours, which indicated all the palladium complexes were reduced to Pd(0). The newly formed SDS or SC₁₄S-capped Pd nanoparticles could only be dispersed in aqueous medium, as shown in Fig. 1A and Fig. 1C. However, if the reaction was continued to 12 hours, co-existence of the hydrophilic and hydrophobic particles could be observed. At this stage, most hp-Pd_{nm} tended to coat on the wall of the reaction flask and could be redispersed in CHCl₃. As for the particles still dispersed in the aqueous solution and could be precipitated by ultrahigh speed centrifuge and then be redispersed in H₂O or CHCl₃, indicating the transformation from hydrophilic to hydrophobic properties. At the end of reaction for about 15 hours, a black oil-phase containing Pd nanoparticles was formed above the colorless aqueous phase and hydrophilic particles almost disappeared. So two types of Pd powder,

either hydrophilic or hydrophobic can be formed by this strategy. If CHCl₃ is added into the flask, the hydrophobic particles can be extracted into the organic phase, as shown in Fig 1B and Fig. 1D. Consequently, the hydrophilic or hydrophobic Pd nanoparticles can be made depending on the length of reaction time.

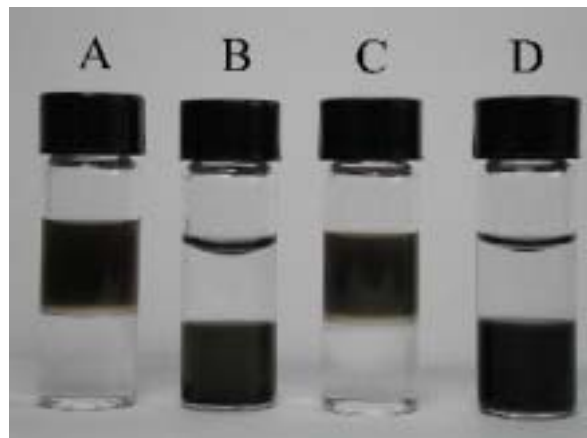


Figure 1. Hy-Pd_{nm} and hp-Pd_{nm}, which are prepared from SDS system (A, B) and SC₁₄S system (C, D) are suspended in H₂O (upper solution) and CHCl₃ (lower solution).

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