Synthesis and characterization of \( n \)-octadecyl mercaptan-protected palladium nanoparticles

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Abstract

Long-chain \( n \)-octadecyl mercaptan (C\(_{18}H_{37}SH\))-passivated palladium nanoparticles are synthesized and characterized. The palladium nanoparticles are successfully capped by \( n \)-octadecyl mercaptan. These palladium nanoparticles have the same face-centered cubic crystalline structure as Pd in the bulk phase. The size of the capped palladium nanoparticles varies in the range of 1.3–5.5 nm for various reaction conditions. These results show that the long-chain \( n \)-octadecyl mercaptan-capped palladium nanoparticles are more stable than alkanethiolate-capped Pd nanoparticles with a shorter chain.

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1. Introduction

Nanostructured transitional metal particles are of great interest due to their quantitative and qualitative differences from their bulk materials and from the discrete atoms. Nanoparticles hold promise for use as innovative materials with new electronic, magnetic, optical and thermal properties [1–15]. They have also been applied to catalyst in, for example, hydrogenation of olefins and dienes [16], hydration of acrylonitrile to acrylamide [17], photogeneration of hydrogen from water [18] and reduction of carbon dioxide [19]. It has been noticed that catalytic activity and selectivity are strongly affected by particle size [20]. To investigate the physical and chemical properties of metal nanoparticles, especially for the size-dependent properties, precise control of the particle size and organization is necessary. Metal colloidal particles have been prepared by several methods such as sonochemical reduction [21], liquid phase reduction [22–26], decomposition of organometallic precursors [27,28] and electrochemical deposition [29]. However, preparation of small metal particles at relatively low temperature has been rarely reported. In this work, we synthesize long-chain \( n \)-octadecyl mercaptan-protected palladium nanoparticles using a liquid–liquid phase method at room temperature. We investigate the growth process of long-chain alkanethiolate-capped palladium nanoparticles while varying the molar ratio.
of Pd/thiol and the reaction time, and measure the structure and morphology of the Pd nanoparticles by XRD, FT-IR, XPS and TEM.

2. Experimental procedure

2.1. Materials

Palladium chloride (PdCl₂, 99%, Acros), n-octadecyl mercaptan (C₁₈H₃₇SH, Acros), tera-n-octylammonium bromide (TOAB, Tokyo Chemical) and Sodium borohydride (NaBH₄, Acros) are used as received.

2.2. Synthesis of particles

PdCl₂ (0.085 g) was dissolved in 20 ml of 0.5 M HCl under vigorous stirring. A total of 40 ml toluene with 1.1 g tetra-n-octylammonium bromide (TOABr) was then added into this solution, whereupon the bright orange-red Pd(II) transferred from the aqueous phase to the toluene phase. The Pd(II) in the organic phase was collected and the aqueous phase was discarded. To obtain the desired Pd=C₁₈H₃₇SH molar ratio, the calculated amount of aqueous phase C₁₈H₃₇SH was added into the toluene solution. The solution was stirred for 60 min and then 0.20 g NaBH₄ in 10 ml H₂O was quickly added into the solution. After a few seconds delay, the solution color changed rapidly from orange-red to dark-black, indicating the formation of palladium particles. Reactions were observed for palladium/n-octadecyl mercaptan molar ratios of 2:1, 3:1 and 4:1.

The solution was under vigorous stirring during the reaction time, which varied as specified below. The dark-black organic phase was separated from the aqueous phase and the solvent was then removed under reduced pressure with a rotary evaporator. After that, 200 ml of methanol was poured into the residual to precipitate the palladium nanoparticles. The black particles were collected by centrifugation and washed three times with methanol, to remove excessive thiols and reaction byproducts. The black precipitate was redispersed in 10 ml toluene solvent.

2.3. Measurement of structure and morphology

The structure of the nanoparticles was examined using Rigaku D/MAX 2400 X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The samples for XRD measurement were prepared by drying Pd nanoparticles under N₂. The TEM (JEOL, 200CX) was used to observe the size and morphology of the particles. The samples for TEM were prepared by depositing a drop of capped Pd nanoparticles onto a carbon-coated Cu grid, followed by natural evaporation of the solution. FT-IR spectra were obtained using a Calay 3000 FT spectrometer in the region of 4000–400 cm⁻¹. XPS was measured on the ESCA LAB5X-ray photoelectron spectrometer with the monochrometer Mg X-ray at 10 K.

3. Results and discussions

3.1. Formation of palladium nanoparticles

When a reduction reagent was added into a solution containing Pd salt and n-octadecyl mercaptan (C₁₈H₃₇SH), the color of the solution changed from orange-red to dark black in a few seconds. This indicates that metal Pd particles were formed. Chen et al. [20] reported that palladium particles were unstable and could be decomposed by stirring during a reaction time of 90 min. In our experiment, palladium particles synthesized with C₁₈H₃₇SH protection are very stable for a longer reaction time of 360 min, and no decomposition of palladium particles is observed. Why are the palladium particles synthesized in our experiment stable? This can be attributed to the formation of stable bonding between metal palladium and the longer chain n-octadecyl mercaptan. Chen et al. [20] used a shorter chain thiol (C₆H₁₃SH) to protect the surface of palladium. This thiol cap probably enables weaker Pd–S bonding interactions than does the mercaptan cap, so the thiol can easily break from the surface of the Pd nanoparticles during a longer reaction time.

In order to investigate this effect in detail, we made TEM measurements. The TEM images of palladium nanoparticles synthesized at different
reaction times are shown in Fig. 1, where it can be seen that the particle sizes are: $1.3 \pm 0.25$ nm ($\sigma = 1.5\%$) for 20 min, $2.1 \pm 0.41$ nm ($\sigma = 2.7\%$) for 120 min, and $5.5 \pm 0.85$ nm ($\sigma = 4.8\%$) for 360 min. Note that the core size increases with increasing reaction time. Furthermore, the core size dispersity increases similarly, from about $1.5\%$ for 20 min to $4.8\%$ for 360 min.

Thus, our growth process for Pd particles can be summarized as follows. (i) Pd ion was reduced rapidly to Pd$^0$ after the addition of a reducing reagent for a few seconds. (ii) Pd nanoparticles were stable and no decomposition of particles was observed during a longer reaction time. (iii) Core size and size dispersity increased with increasing reaction time.

3.2. Structural analysis

In order to compare the XRD spectra of ‘naked’ palladium nanoparticles to our mercaptan-capped particles, we prepared unprotected palladium particles using the same method of synthesis: 5 mmol of NaBH$_4$ solution was injected into 0.5 mmol of PdCl$_2$ aqueous solution without $n$-octadecyl mercaptan. The result is shown in Fig. 2d. The reflection peaks can be seen in an XRD pattern (Fig. 2d) at around 40.1°, 46.6°, 68.3°, 82.3° and 86.6°. These peaks correspond to the (111), (200), (220), (311) and (222) planes of an fcc lattice, respectively, indicating that an fcc crystalline structure was formed. The X-ray diffraction patterns of $n$-octadecyl mercaptan-capped Pd nanoparticles prepared at different molar Pd/$C_{18}H_{37}SH$ ratios are shown in Figs. 2a–c. In contrast to the XRD pattern of the naked palladium particles,
these peaks are broader. The diffraction peak at around 40° corresponds to the (1 1 1) plane of the fcc lattice, which indicates that the n-octadecyl mercaptan-capped Pd nanoparticles synthesized in the present study have the fcc crystalline structure.

In the XRD patterns, the diffraction angles shift toward lower values with a decrease in particle size, which means that the Pd–Pd interatomic distance expands with a decrease in particle size. The increase in the lattice constant is due to the structure change or smaller size [30,31]. In the XRD pattern, diffraction peaks broaden as the crystallite size decreases. The diffraction peaks gradually become sharper as the Pd/thiol ratio increases, revealing an increase of the Pd nanoparticles' size. No distinct peaks corresponding to PdO and PdB phases were detected.

3.3. Spectral properties study

In order to better understand the influence of the amount of n-octadecyl mercaptan for Pd nanoparticles, we used XPS to investigate the interaction between S atoms of n-octadecyl mercaptan and the Pd atoms during the formation of thiol-capped Pd nanoparticles. Fig. 3a shows the XPS spectra of the thiol-passivated Pd nanoparticles at a Pd/C18H37SH molar ratio of 2:1. For all samples, the XPS spectra show no oxygen, bromine, chlorine or boron. In Fig. 3b, the XPS spectrum of the Pd nanoparticles shows double peaks with the binding energies of 335.1 and 340.5 eV, corresponding to Pd3d5/2 and Pd3d3/2, respectively. These are the typical valence state peaks of Pd0 and are consistent with the standard spectra of metal Pd0.

The binding energy of Pd and S atoms did not change significantly at different Pd/C18H37SH molar ratios: 335.1 eV (Pd3d5/2) and 161.6 eV (S2p3/2) at 2:1, 335.2 eV (Pd3d5/2) and 161.7 eV (S2p3/2) at 3:1 and 335.3 eV (Pd3d5/2) and 161.4 eV (S2p3/2) at 4:1, respectively. This result indicates that the n-octadecyl mercaptan-capped Pd nanoparticles are stable at various Pd/C18H37SH molar ratios. However, the binding energy of Pd3d5/2 shifts to higher values as reaction time increases: 335.1 eV for 20 min, 335.5 eV for 120 min and 336.0 eV for 360 min. These results demonstrate that the long-chain n-octadecyl mercaptan can be adsorbed on the surface of Pd particles by the bonding between metal Pd and S atoms, which increases in stability as reaction time is extended.

The FT-IR spectra of the nanoparticles reveal more information about the local molecular environment of the thiolate ligands. Fig. 4 shows FT-IR spectra of the pure n-octadecyl mercaptan and n-octadecyl mercaptan-capped Pd nanoparticles. The comparison of these spectra reveals similar features in the wavenumbers range from 4000 to 400 cm⁻¹. This observation strongly suggests that n-octadecyl mercaptan is indeed an essential component of the composite. In the higher wavenumbers of Fig. 4, four peaks of octadecanethiol are found, which correspond to the C–H asymmetric, symmetric methylene stretching modes –
The asymmetric in-plane and symmetric stretching mode of the terminal methyl groups – $\nu_{as} (\text{CH}_3, \text{ip})$ $2955$ cm$^{-1}$ and $\nu_{s} (\text{CH}_3, \text{fr})$ $2871$ cm$^{-1}$. The maximum peaks shift slightly to lower wavenumbers in the nanoparticles spectrum, $\gamma_{as} (\text{CH}_2)$ shifts from $2921$ to $2917$ cm$^{-1}$ and $\gamma_{s} (\text{CH}_2)$ shifts from $2851$ to $2847$ cm$^{-1}$. In lower wavenumbers, at the same time, some differences in intensity are observed among the peaks. In Fig. 4, the three major peaks, from left to right, correspond to the in-plane bending mode of terminal methylene group $\rho (\text{CH}_2) = 720$ cm$^{-1}$, the bending mode of the methylene group $\omega (\text{CH}_2) = 1294$ cm$^{-1}$, and the non-in-plane wristing mode of the terminal methylene group $\tau (\text{CH}_2) = 1252$ cm$^{-1}$, respectively.

As we turn our attention to curve b of Fig. 4, some of curve as minor peaks disappear, which we believe to be due to the formation of the relatively closed-packed alkanethiol self-assembled monolayers (SAMs) on the nanocrystal surface and constrained motion of the molecules [32]. Obviously, the steric constraint affecting the transverse mode (for example, rocking mode, wagging mode) is stronger than that on the longitudinal mode (stretching mode). Therefore, the change of the peak intensity of the longitudinal mode is smaller than that of the transverse mode. These are the reasons that the in-plane rocking mode of the terminal methyl group and the non-in-plane rocking mode and wagging mode of the methylene group 'disappeared.'
3.4. TEM analysis

The passivated ligand, \(n\)-octadecyl mercaptan, apparently stabilizes the Pd nanoparticles by preventing them from aggregation. That effect was confirmed by the FT-IR measurement mentioned above. The thiol chain is expected to be adsorbed on the surface of the Pd particles by stable bonding between metal Pd and S atoms. Accordingly, the amount of thiol added to the solution is expected to affect the growth process for Pd nanoparticles. Therefore, we varied the amount of \(n\)-octadecyl mercaptan to investigate any effects on the size of Pd nanoparticles. Fig. 5 shows the TEM image of the capped palladium synthesized at various molar ratios of Pd/\(C_{18}H_{37}SH\) for 2 h. At Pd/\(C_{18}H_{37}SH\) = 2:1, the thiol-capped Pd nanoparticles has a mean diameter of 2.1±0.41 nm with a very narrow distribution (\(\sigma < 3\)). The mean diameter 2.6 ± 0.68 nm (\(\sigma < 5\)) was obtained at Pd/\(C_{18}H_{37}SH\) = 3:1. As Pd/\(C_{18}H_{37}SH\) molar ratios reach 4:1, we can see that the aggregation of Pd nanoparticles and the shape of nanoparticles becomes irregular. We deduce from these observations that the aggregation of palladium nanoparticles is due to the high Pd/\(C_{18}H_{37}S\) molar ratios. We observe that the thiol-capped Pd nanoparticles gradually grow larger with increasing Pd/\(C_{18}H_{37}SH\) molar ratio, resembling the formation of thiol-protected gold nanoparticles [33].

4. Conclusions

Monodispersed \(n\)-octadecyl mercaptan-capped palladium nanoparticles were synthesized by a liquid–liquid biphase method at room temperature. We observed that both size and dispersity of the synthesized particles gradually increase as either Pd/\(C_{18}H_{37}S\) molar ratios or reaction time increase. The XRD measurements indicate that the fcc phase of the Pd nanoparticles is realized. FT-IR results confirm that palladium nanoparticles have been capped by \(n\)-octadecyl mercaptan. XPS and TEM of the samples show the metallic state of the Pd\(^0\) and the capped palladium nanoparticles grow to sizes of 1.3–5.5 nm at various reaction conditions.

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References