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Anomalous aggregation growth of palladium nanosphere with SPR band in visible range*

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The morphology and properties of nanostructures are significantly influenced by the chemical coordination during their growth procedure. Using small molecule N-vinyl pyrolidone as stabilizer, this paper introduces a new strategy for synthesis of palladium nanospheres, which has a novel surface plasmon resonance band in the visible range. An aggregation growth mode was observed in the growth process. More specifically, the growth rate increases with increasing concentration of stabilizer. The absorption in visible region suggests new optical applications for these Pd nanospheres, such as photocatalysis, photothermal heating and surface enhanced Raman scattering.

Keywords: palladium, nanosphere, aggregation growth, surface plasmon resonance
PACC: 3320L, 8110D, 8116

1. Introduction

Due to the extraordinary physical and chemical properties, palladium has attracted great attention as a popular material for catalysis, pollutant degradation, as well as hydrogen sensor/storage. For examples, the palladium-catalyzed Suzuki and Heck cross coupling reactions are versatile synthetic methods in organic chemistry.[1−3] The palladium nanostructure based hydrogen sensor shows a detection limit as low as 500 ppm.[4−6] To take full advantage of these properties, people have developed various methods, such as alcohol reduction,[7] hydrogen or carbon monoxide reduction,[8] liquid–liquid phase method[9] and thermal decomposition of palladium complexes,[10] to synthesize nanoscale palladium particles. In these methods, steric stabilizers like polymers, surfactants or ligands are deliberately chosen to obtain nanoparticles with desired morphology and properties according to their different coordinating ability.[11−17] Among these stabilizers, vinyl polymers with polar side group, such as poly (vinyl pyrrolidone) (PVP) and polyvinyl alcohol (PVA), have been successfully explored for the shape control synthesis of metal nanostructures with novel surface plasmon resonance (SPR) properties.[18−21] SPR is one of the most remarkable properties of metal nanostructures for its wide potential applications in sensing,[22] plamonics[23] and biochemistry.[24] For many metals other than Au, Ag and Cu, the intrinsic plasmon frequency lies in the ultraviolet region of the spectrum due to the strong coupling between plasmon transition and the interband excitation. Calculating by using Mie theory, we find that the SPR peak of Pd particles smaller than 10 nm is below 250 nm.[25] Fortunately, the optical properties of metal nanostructures are not only determined by the nature of metal, but also influenced by lots of parameters, such as morphology of particles, the capping molecule species, or the dielectric properties of the surrounding medium. More recently, Xia's group has successfully pushed the SPR band of single crystalline Pd nanostructures into visible region through tuning their size and shape.[26,27] However, stringent parameters are usually required in these preparations to obtain uniform products with high yield. Moreover, the collective effect on optical properties of Pd nanostructures remains relatively unexplored until now.

In this paper, we report a facile route for synthesizing polycrystalline palladium nanostructure with SPR band in visible region. The Pd nanospheres com-

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prising small subunits were synthesized using N-vinyl pyrrolidone (NVP) as the capping reagent. Compared to its polymer PVP with the same side group, NVP has enhanced coordination capacity, polarity and mobility due to the small size. Its size effect also induced an anomalous aggregation growth of Pd spheres: increasing the concentration of NVP, we found that the growth of Pd spheres was accelerated. The as-prepared Pd spheres were ∼100 nm in diameter and showed a broad absorption band in the visible range. The special optical absorption should be ascribed to the collective effect of SPR of aggregated small subunits, which were found about ∼ 14 nm by tunnelling electron microscope (TEM) investigation and x-ray diffraction (XRD) calculation.

2. Experimental section

2.1. Chemicals and materials

Anhydrous ethylene glycol (EG, 99%), palladium acetylacetonate (99%) were purchased from Acros Chemical. Acetone, N-vinyl pyrrolidone and anhydrous ethanol were obtained from Beijing Chemical Reagent Company. All the chemicals were used as received without any further purification.

2.2. Synthesis of palladium nanospheres

Under argon protection, 0.1 mmol $Pd(acac)_2$ (0.0305 g), 20 ml NVP solution in EG with various concentrations (0.02 mol/L, 0.1 mol/L, 0.25 mol/L, 1.0 mol/L) were mixed together. After keeping at 120°C for 30 min, the reaction mixture was heated to reflux for 4 h and allowed to cool to room temperature giving a black suspension. A set of samples were taken during the process for further characterization. The samples were precipitated by acetone and then washed by mixture of ethanol and cyclohexane (volume ratio of 1:5) several times to remove excess NVP and EG. The final product is dispersed in ethanol and kept for further characterization by TEM, XRD patterns and UV-vis spectroscopy.

2.3. Characterization of palladium nanospheres

Scanning electron microscopy (SEM) images were taken using a field-emission SEM (XL-SFEG, FEI Corp.) operated at an acceleration voltage of 5 kV or 10 kV. Powder XRD patterns were recorded from samples supported on a glass slide using Rigaku D/MAX 2400 x-ray diffractometer with Cu-Kα radiation (λ = 0.15405 nm). TEM images and selected area electron diffraction (SAED) patterns were taken using a JEOL 200CX microscope at 120 kV. UV-vis spectra were recorded using Cary 1E UV-vis spectrometer.

3. Results and discussion

Figure 1(a) shows the typical TEM image of palladium nanospheres synthesized using 0.1 mol/L NVP after reaction for 4 h. It can be seen that these nanospheres have a relatively uniform size of 100 nm. Further magnified TEM image, as shown in Fig.1(b), reveals that these nanospheres have rough surfaces and are composed of small particles. The inset is the SAED pattern of an individual Pd nanosphere, which also confirms the polycrystalline structure of the nanosphere. Figure 1(c) shows the XRD pattern of these large nanospheres. The peaks can be readily indexed to face-centred cubic palladium phase (JCPDS file No 46–1043). The size of particles calculated from the Scherrer formula is about 14 nm, which is in good agreement with the TEM characterization. In a control experiment we sonicated the sample for 4 h with a 300 W ultrasonicator and no disintegration of nanospheres was observed, which verifies that these nanospheres are not conglomeration of small particles during solvent evaporation. All of this suggest these nanospheres formed through aggregation growth of large numbers of crystalline subunits of only 14 nm or so. To further explore the growth procedure, SEM and UV-vis spectra were used to track the growth procedure. Figure 2 shows the UV-vis spectra of the as-prepared products sampled at different reaction times. The UV-vis spectrum of the initial reaction mixture is shown in Fig.2. The two peaks at 235 and 325 nm are attributed to the existence of NVP and $Pd(acac)_2$, respectively (Fig.3, Supporting information). The intensity of the peak at 325 nm is proportional to the concentration of $Pd(acac)_2$. After heating at 120°C for 30 min, that peak disappears, which denotes the complete decomposition of $Pd(acac)_2$. At the same time, one new peak around 275 nm reaches its maximum due to the byproduct formed in the decomposition process. When the mixture solution was continuously heated to reflux, the intensity of the two peaks

at 235 and 275 nm gradually reduces, indicating the increase of surface chemisorption of NVP molecules during aggregation growth and the evaporation of the byproduct simultaneously. The aggregation growth from small particles to large spheres was observed in the SEM characterization. The corresponding SEM images at different stages are shown in Fig.4. Particles with two distinct sizes are found and the volume ratio of small particles to large ones gradually decreases during the growth process (Figs.4(b) and 4(c)). The final product, as shown in Fig.4(d), is relatively monodisperse palladium spheres with coarse surfaces. These images clearly show the morphology evolution from small particles to nanospheres.

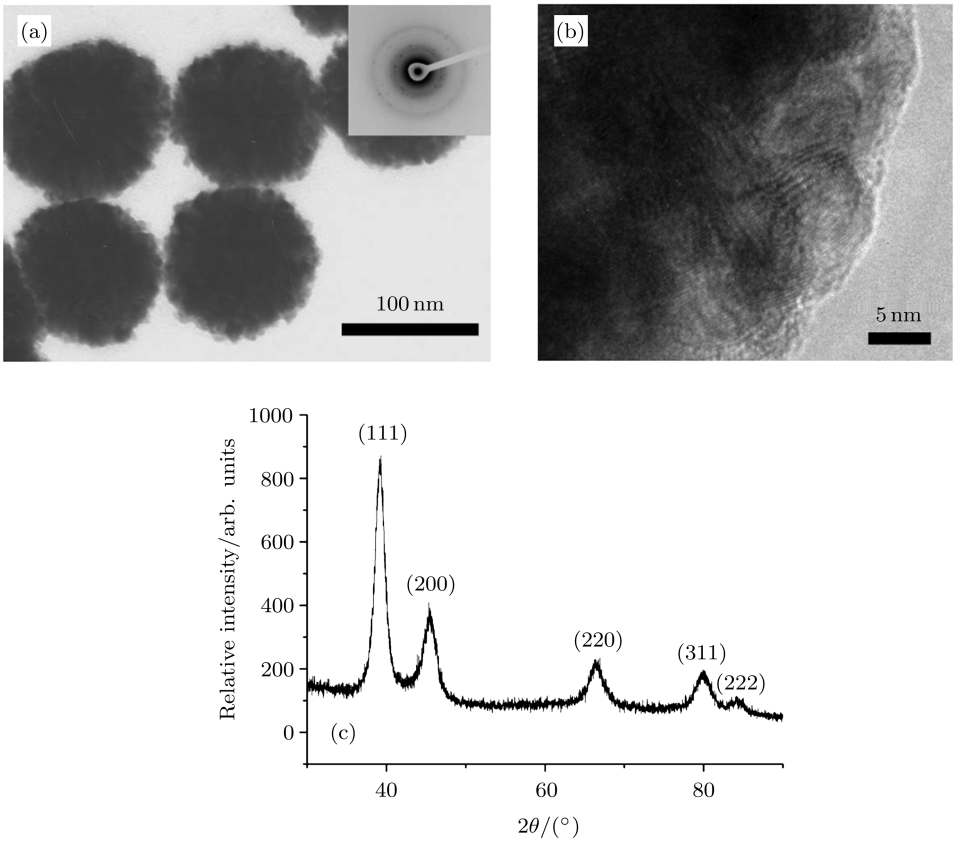


Fig.1. TEM images and XRD pattern of the Pd nanospheres synthesized with 0.1 mol/L NVP. The SAED pattern (inset) of individual nanosphere confirms its polycrystalline structure. Calculation from the XRD pattern reveals that the nanospheres are composed of 14 nm small subunits.

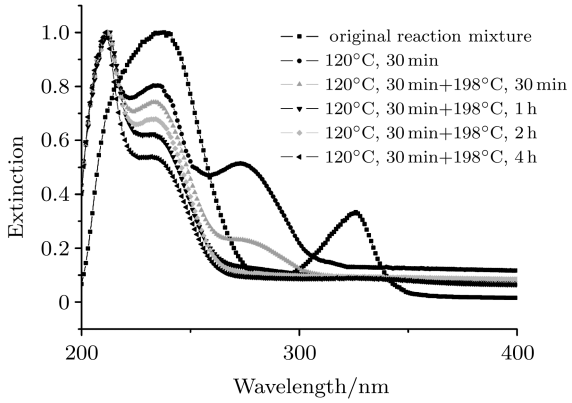


Fig.2. UV-vis extinction spectra recorded from the EG solution of as-prepared samples synthesized at different stages with 0.1 mol/L NVP.

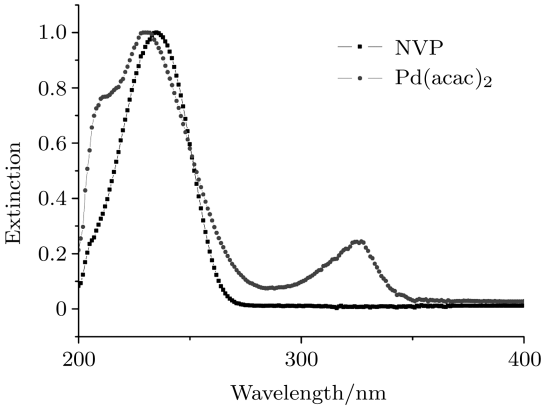


Fig.3. The UV-vis absorption spectra of NVP and $Pd(acac)_2$.

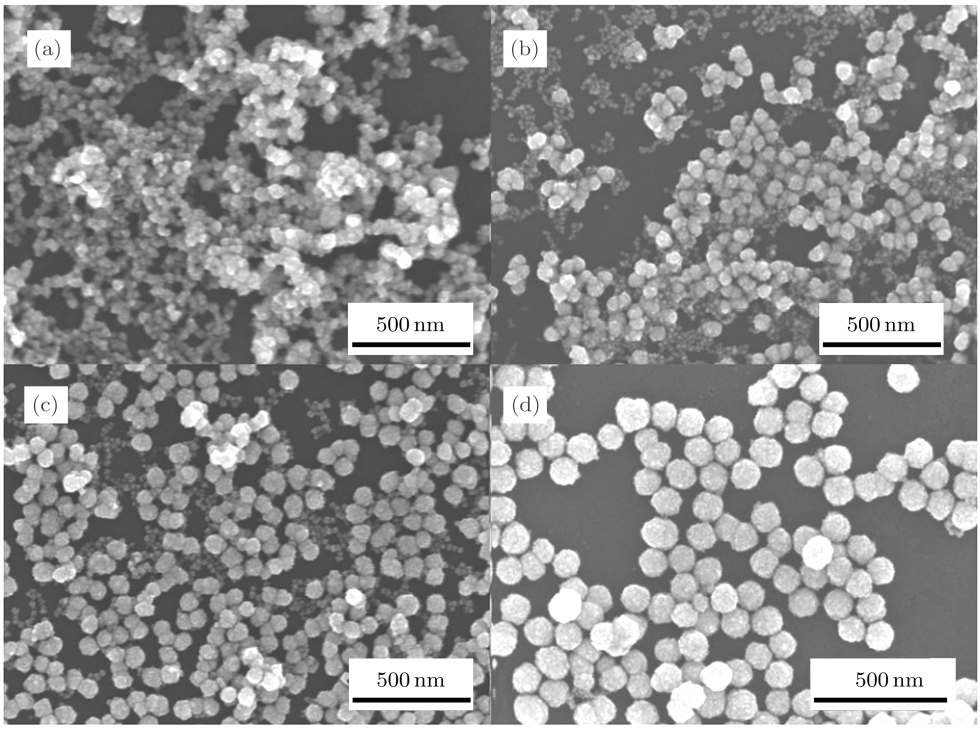


Fig.4. SEM images of Pd nanospheres at different reaction stages synthesized with 0.1 mol/L NVP. (a) 120°C, 30 min; (b) 120°C, 30 min + 198°C, 30 min; (c) 120°C, 30 min + 198°C, 2h; (d) 120°C, 30 min + 198°C, 4h.

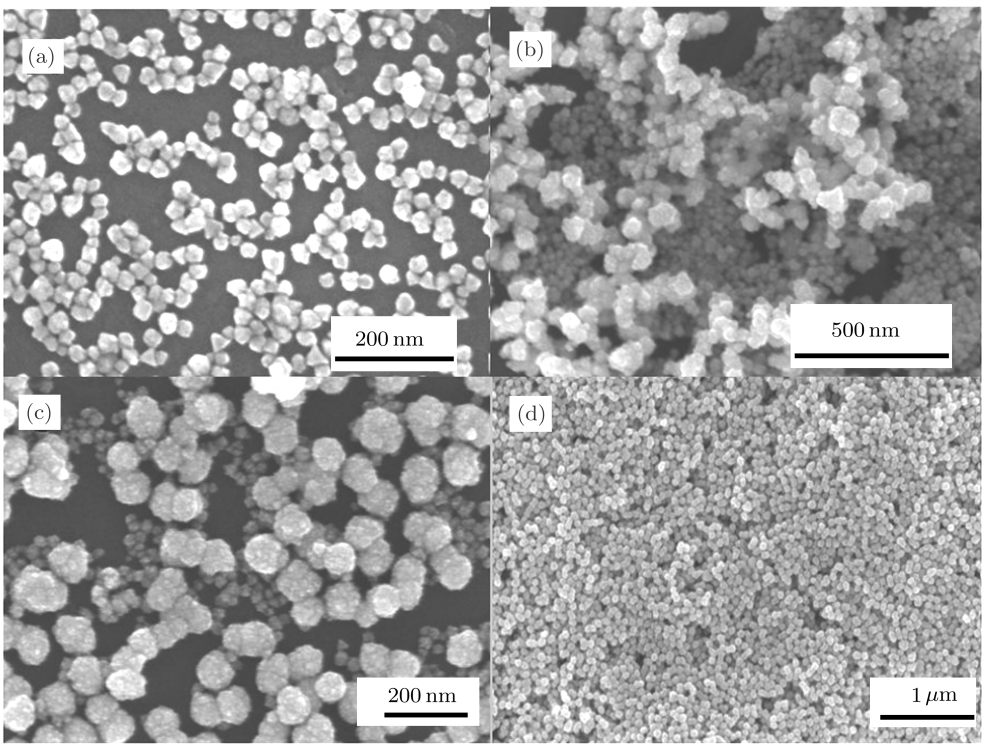


Fig.5. Typical SEM images of the intermediate products (120°C 30 min + 198°C 2h) synthesized with various amounts of NVP, showing the acceleration of aggregation growth with the increase of NVP concentration. The concentration of NVP is (a) 0.02 mol/L; (b) 0.1 mol/L; (c) 0.25 mol/L; (d) 1.0 mol/L.

An interesting phenomenon was observed in this aggregation growth procedure. The growth rate of the Pd nanospheres increases with the concentration of NVP molecule. Figure 5 shows typical SEM images of the intermediate products using different amount of NVP after refluxing for 2 h. When the concentration of NVP is low ($N_{\mathrm{NVP}} = 0.02$ mol/L), only well dispersed irregular palladium particles with diameters in the range of 10–20 nm are obtained (Fig.5(a)). While in a higher NVP concentration environment ($N_{\mathrm{NVP}} = 0.1$ mol/L, Fig.5(b) with the same reaction time, palladium particles with bimodal size distributions coexist in the products: some of them are still 10–20 nm in diameter, the others are large particles in the size range of $70 - 90$ nm. Continuing to increase the concentration of NVP to 0.25 mol/L, the volume ratio of small particles in the intermediate products decreases and there are mainly large particles in the products (Fig.5(c)). When the concentration of NVP reaches 1.0 mol/L, the 2h intermediate product is nanospheres with uniform size, which is almost the same as the 4h product synthesized in the presence of 0.1 mol/L NVP. So it can be concluded that the time needed for the aggregation growth of nanoparticles decreases with the increasing concentration of NVP. Though experimentally tuning the molar ratio of surfactant to precursor has been proved to be a versatile route for the shape and size control of nanoparticles, it is a rare phenomenon that tuning this ratio also influences the growth rate of nanostructures as in our case. That is the reason why we call it 'anomalous aggregation growth'. The cause of this phenomenon is still not clear. Yet it can be speculated that the growth mode is related to the interactions between NVP molecules for this growth mode has never been found when using its polymer PVP as surfactant (Fig. 6, supporting information). The NVP molecules may play a bifunctional role in this process: when small amount of NVP is introduced they serve as the stabilizer adsorbed on the particles while in large quantity the interaction of excess NVP molecules leads to the aggregation growth of these particles.

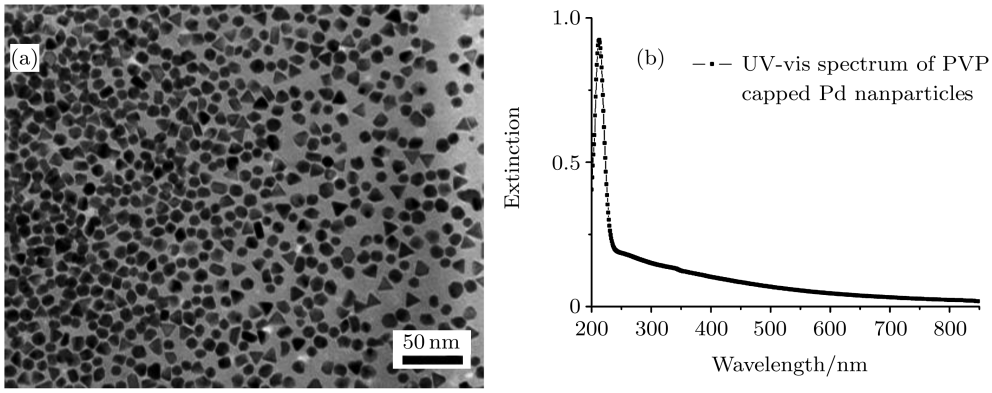


Fig.6. Typical TEM image and UV–vis spectra of Pd nanoparticles synthesized by replacing NVP with PVP.

UV-vis spectrum of the Pd nanospheres recorded from the same batch of sample in Fig.4(d) is shown in Fig.7. As seen from the curve, a broad absorption band exists, centred on 590 nm in the visible region apart from a sharp peak at 210 nm. As it is well known that single crystalline palladium particles in the range of 3–20 nm only have absorption in the ultraviolet region, the absorption band in visible region is attributed to the polycrystalline structure of these nanospheres. The surface plasmon band can be influenced by lots of parameters and the collective resonance property is believed to be quite different in comparison with that of small subunits.[28−30] The absorption band is remarkably wide due to the peculiar dielectric function of Pd.[26,27,30,31] Moreover, the strong interaction between NVP molecules and palladium particles also play an important role in the broadening of the resonant band. Theoretical calculation[32] and experimental measurements[33,34] suggest that the capping agent can broaden the SPR bands of metal nanoparticles for their strong chemisorption will cause charge localization at the surface of nanoparticles, whereas the inner core still presents metallic behaviour. This visible SPR band of the nanospheres could be helpful in the investigation of various optical phenomena, such as novel supported photocatalysis, photothermal heating and chemical optical sensors.

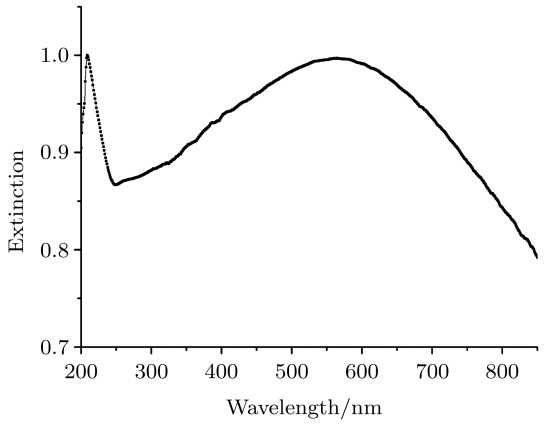


Fig.7. UV-vis spectrum of the Pd nanospheres recorded from the same batch of sample in Fig.4(d). Two extinction peaks are found in the spectrum: a sharp peak at 210 nm and a broad extinction band centred around 590 nm.

4. Conclusion

In summary, we synthesized Pd nanospheres using NVP, a small molecule with carbonyl group via a pyrolysis route. An anomalous aggregation growth mode is observed in their formation procedure. The obtained palladium spheres are composed of small subunits and show a novel SPR extinction band in the visible range due to its polycrystalline nature. Possessing this novel optical property and the well known catalytic ability simultaneously, these Pd nanospheres might have potential applications such as photocatalysis, photothermal heating.

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