Shape-Selective Synthesis of Gold Nanoparticles with Controlled Sizes, Shapes, and Plasmon Resonances**

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The attachment of water molecules to poly(vinylpyrrolidone) (PVP) is used in conjunction with the region-selective distribution of PVP and water in a water/PVP/η-pentanol system to confine reactions along the surface of PVP, thus achieving the highly shape-selective synthesis of anisotropic Au nanostructures with controlled sizes and remarkable shapes such as regular octahedrons, triangles, rods, dumbbells, belts, and hexagons. The IR absorption spectra of the Au nanoparticles confirm that the nanoparticles are formed around PVP, and corroborate the adsorption of PVP on Au. The size, shape, and plasmon resonance of the Au nanoparticles can be readily tuned by modifying the adsorption behavior and/or the reducing ability of PVP by adjusting the relative amounts of PVP and water, directly adding gold seeds, or changing the stirring conditions in the reaction mixture. The obtained highly pure anisotropic Au nanostructures and the synthesis method demonstrated here enable us to study distinct nanostructures to search for novel physicochemical properties and technological applications. Our method is also successfully extended to prepare highly pure silica spheres, tubes, and needles with controlled aspect ratios.

1. Introduction

The physicochemical and optoelectronic properties of nanometer-sized metallic objects are not only size dependent but also shape dependent. Controlling the shape of metallic nanostructures has been a subject of intensive research in recent years because it provides an effective route for tuning the electronic, magnetic, optical, optoelectronic, and catalytic properties of the metal. Many shape-selective synthesis strategies have been developed to prepare anisotropic metal nanoparticles with a variety of shapes including cubes, prisms, plates, tadpoles, tripods, pyramids, decahedra, rods, wires, belts, and dendrites. In these synthetic approaches, poly(vinylpyrrolidone) (PVP) has been frequently used as a crucial reagent to kinetically control the growth rates of various facets of the metal crystal for the formation of anisotropic metal nanostructures. Owing to its excellent adsorption abilities, PVP has been used as the capping or stabilizing reagent. For example, under the protection of PVP capping layers, anisotropic Au nanostructures such as tetrahedrons, cubes, octahedrons, decahedra, icosahedrons and plates as well as Ag nanostructures such as prisms and plates have been successfully synthesized. Triangular and hexagonal nanoplates of Pd have also been reported.

Currently, PVP is most commonly used to direct anisotropic metal growth by selectively adsorbing on specific metal crystallographic planes. Under the direction of PVP, the highly shape-selective synthesis of Ag nanostructures such as cubes, nanowires, nanobelts, nanowires and bipyramids as well as Au nanostructures such as nanocages and nanoprismoids has been successfully realized. Furthermore, the directed synthesis and assembly of rafts of Ag nanowires has been achieved. The formation of Ag nanobelts or nanowires has also been ascribed to the possible assembly of small Ag nanoparticles initiated by the selective disruption of passivating PVP layers.

Owing to its long chain structure, PVP has also been used as a soft template to directly synthesize and assemble anisotropic metal nanoparticles. For instance, novel chain-like and dendritic Ag nanostructures with fractal features have been prepared by a simple solvothermal method using PVP both as an adsorption agent and an architectural soft template. Recently, PVP has been used as a reductant because of its weak reducing ability. By simultaneously using PVP as the reductant and stabilizer, Ag nanoparticles and gold plates and dendrites have been successfully prepared. Recently, it has been determined that the reducing ability of PVP arises from the hydroxyl end groups that are present in the polymer because of the use of water as the polymerization solvent. Indeed, the presence of water dramatically enhances the reducing ability of PVP. For instance, PVP in aqueous solution has a relatively strong reducing ability and is able to reduce AgNO₃ at 60 °C or even at room temperature. In contrast, when anhydrous ethylene glycol is used as the reaction solvent instead of water, AgNO₃ is reduced by ethylene glycol at a relatively high reaction temperature (160 °C). In this case, PVP acts just as the stabilizer or capping reagent rather than as a reductant.
previous reports clearly suggest that the ability of PVP to kinetically control metal growth varies with the reaction circumstances such as the solvents used (ethylene glycol, pyridine, and water), reductants (such as ethylene glycol, sodium citrate, NaBH₄, PVP, and ascorbic acid), and the temperature, thus yielding different product morphologies. Therefore, exploring new reaction conditions or approaches for using PVP to kinetically control the growth of anisotropic metal nanostructures may lead to the development of novel methods for the synthesis of anisotropic metal nanoparticles with well-defined shapes.

In this contribution, a novel two-phase system—water/PVP/npentanol (WPN)—has been successfully exploited to realize the highly shape-selective synthesis of anisotropic Au nanoparticles with controlled sizes and remarkable shapes such as regular octahedrons, triangles, rods, dumbbells, belts, and hexagons. The design of this novel WPN system has been spurred by the following motivations. First, as discussed above, water can greatly enhance the reducing ability of PVP and facilitate the reduction of metal ions. Thus modifying the amount of water in the WPN system can provide easy control over the reducing ability of PVP or the reaction speed, thus improving the ability of PVP to kinetically control the growth of Au. Secondly, water can be bound by PVP in aqueous solutions of high-concentration PVP, wherein water does not act as a solvent in the usual sense. Indeed, it is customary to refer to such water as “bound” water. We have been able to achieve the highly shape-selective synthesis of Au nanostructures by controlling the nucleation and growth of Au along PVP by using water “bound” to the polymer. In the WPN system, PVP locally concentrates in water since it needs to entirely remain in the aqueous phase of the water/npentanol system. Therefore, locally high concentrations of PVP are achieved in the aqueous phase, and water “bound” to PVP is obtained. In addition, as a surfactant, it is likely that PVP keeps the WPN system stable by binding water, since it is unable to form microemulsions or micelles in this system. Thirdly, the region-selective distribution of PVP and water in the WPN system provides additional opportunities to kinetically control the growth of Au, thus yielding novel or designed Au nanostructures.

To confirm the region-selective distribution of PVP and water in our WPN system, the surface tensions of the WPN and PVP/npentanol systems have been investigated. As shown in Figure 1, with increasing amounts of PVP, the surface tension of the PVP/npentanol system decreases slowly and almost linearly, whereas the surface tension of the WPN system decreases non linearly at a relative rapid rate. In other words, PVP in the WPN system has a stronger effect in reducing the surface tension as compared to PVP in the PVP/npentanol system. These observations strongly suggest that the distribution of PVP in the WPN system is very different from that in the PVP/npentanol system (a uniform PVP solution). In other words, the distribution of PVP in the WPN system is region-selective and not uniform.

2. Results and Discussion

2.1. Growth of Regular Octahedrons with Controlled Sizes and Plasmon Resonances

Regular Au octahedrons have been obtained by sequentially adding aqueous C₆H₅O₇Na₃·2 H₂O and ethanol solutions of HAuCl₄·H₂O to a npentanol solution of PVP with 30 and 5 min of stirring, respectively, followed by heating the mixture at 95 °C for 24 h. Figure 2 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of typical regularly shaped octahedral Au samples with different average edge lengths. As shown in Table 1 and Figures 2a and 3a, by using 0.6 g of PVP and 1.0 mL of aqueous C₆H₅O₇Na₃·2 H₂O, regular Au octahedra have been obtained with 90% purity. The edge lengths of the regular octahedrons...
range from 25 to 44 nm, with an average edge length of 33 nm. By using appropriate amounts of PVP, water, and C₆H₅O₇Na₃·2H₂O, the average edge length of the regular octahedra can be tuned to 130 nm. As shown in Figures 2 and 3, for edge lengths of 33, 47, 81, and 130 nm, the purity of the regular Au octahedra are 90, 86, 77, and 74 %, respectively, and the size distributions range from 25–44, 37–60, 60–96, and 99–156 nm, respectively.

High-resolution TEM (HRTEM) has been performed on an individual regular octahedron from the sample shown in Figure 2b to further investigate the crystallographic structure of the regular octahedra. Figure 4a shows a HRTEM image and the corresponding selected area electron diffraction (SAED) pattern obtained from a single regular octahedron with the electron beam perpendicular to one of the triangular facets. The fringes are separated by 0.25 nm, which can be ascribed to the (1/3){422} reflection that is generally forbidden in a typical face-centered cubic (fcc) single-crystal structure. This forbidden reflection has been frequently observed in thin plates of Ag or Au or films bound by atomically flat surfaces.[2h,i,k,3a] The six-fold rotational symmetry revealed by the diffraction spots and the fringe spacing indicate that all the triangular faces of the regular octahedron are surrounded by [111] planes. Figure 4b shows a HRTEM image and the corresponding SAED pattern obtained from a regular octahedron standing on the support film with the electron beam perpendicular to the square facet. The observed spacing of 0.20 nm between adjacent lattice planes corresponds to the distance between two [200] crystal planes. The diffraction spots in the SAED pattern can be indexed to the [020] and [200] planes, suggesting that the square facet is surrounded by [100] planes, which is consistent with the HRTEM image. These findings confirm the previous proposed model for Pt octahedrons and show that the regular octahedra produced here are single crystalline in nature.[16]

Table 1. Au nanoparticles prepared under different experimental conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PVP [g]</th>
<th>Au suspension [mL]</th>
<th>Citrate [mL, %]</th>
<th>Stirring [%]</th>
<th>Ratio</th>
<th>Average edge length [nm]</th>
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<tbody>
<tr>
<td>Octahedron 1</td>
<td>0.6</td>
<td>0</td>
<td>1.7, 0.5</td>
<td>No</td>
<td>90</td>
<td>33</td>
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<tr>
<td>Octahedron 2</td>
<td>2.4</td>
<td>0</td>
<td>1.3, 0.5</td>
<td>No</td>
<td>86</td>
<td>47</td>
</tr>
<tr>
<td>Octahedron 3</td>
<td>2.4</td>
<td>0</td>
<td>1.7, 0.5</td>
<td>No</td>
<td>77</td>
<td>81</td>
</tr>
<tr>
<td>Octahedron 4</td>
<td>3.0</td>
<td>0</td>
<td>3.0, 0.5</td>
<td>No</td>
<td>74</td>
<td>130</td>
</tr>
<tr>
<td>Triangles</td>
<td>3.0</td>
<td>0</td>
<td>2.2, 0.5</td>
<td>No</td>
<td>75</td>
<td>120</td>
</tr>
<tr>
<td>Polyhedrons</td>
<td>3.0</td>
<td>0</td>
<td>1.7, 0.5</td>
<td>No</td>
<td>85</td>
<td>90</td>
</tr>
<tr>
<td>Dumbbells</td>
<td>3.0</td>
<td>0</td>
<td>1.7, 0.5</td>
<td>Yes</td>
<td>59</td>
<td>29 × 65</td>
</tr>
<tr>
<td>Rods</td>
<td>1.5</td>
<td>0</td>
<td>1.7, 0.5</td>
<td>No</td>
<td>81</td>
<td>30 × 72, 33 × 53</td>
</tr>
<tr>
<td>Belts</td>
<td>4.5</td>
<td>3.9</td>
<td>0</td>
<td>No</td>
<td>88</td>
<td>130 × 21</td>
</tr>
<tr>
<td>Hexagons</td>
<td>3.0</td>
<td>0.8 concentrated</td>
<td>1.2, 0.8</td>
<td>No</td>
<td>45</td>
<td>200</td>
</tr>
</tbody>
</table>

Figure 3. Histograms showing 1) the abundance of different shapes and 2) the size distribution of regular octahedra for the samples shown in a) Fig. 2a, b) Fig. 2b, c) Fig. 2c, and d) Fig. 2d. The histograms shown in (a), (b), (c), and (d) have been obtained by counting 610, 280, 430, and 290 particles, respectively.

Figure 4. a) HRTEM image obtained near the top end of a triangular facet of a regular octahedron (right inset). A low-resolution TEM image of this sample is shown in Fig. 2b. b) HRTEM image of the square facet of an erect regular octahedron (right inset). A low-resolution image of this sample is shown in Fig. 2b. The left insets of (a) and (b) show the corresponding selected area electron diffraction patterns.
The overall purity of the regular Au octahedra is reflected in their absorption spectra because the optical properties of metal nanoparticles are highly dependent on the particle shape. As shown in Figure 5, all the regular octahedral Au samples exhibit characteristic surface plasmon resonance (SPR) peaks. These bands are similar to the theoretically predicted absorption bands for regular Ag octahedra, which further indicates the high purity of these samples. As the average edge length increases from 33 to 130 nm, the SPR peak broadens and red-shifts from 538 to 693 nm. The broadening of the SPR peak is attributed primarily to the broader size distribution and increasing presence of impurities (such as triangles and decahedra) with increase of the edge length.

2.2. Growth of Anisotropic Au Nanoparticles with Other Shapes: Triangles, Polyhedral Spheres, Rods, Dumbbells, Belts, and Hexagons

Upon reducing the volume of the aqueous C₆H₅O₇Na₃·2H₂O solution from 3.0 to 2.1 mL and then to 1.7 mL while keeping the amount of PVP constant (3.0 g), the primary products change in shape from regular octahedra to triangles and then to polyhedrons, respectively (Table 1, Figs. 2d and 6). As shown by the different side-view images of the triangular particles in Figure 6a, each triangular particle has two regular trapezium planes diverging from a common line (symmetrical boundary) on each side, and can be obtained from a triangular bipyramid by cutting the two tips. In other words, the triangular Au particles produced here are actually octahedral and not conventional triangular nanoprisms with six planes. The unique structure of the sides reduces the real average edge length of the triangular planes in these particles to 120 nm. The corresponding SAED patterns (Fig. 6a, inset) of the triangular Au particles have been obtained by aligning the electron beam perpendicular to the triangular facets of an individual particle. The six-fold rotational symmetry seen in the diffraction spots implies that the triangular faces are surrounded by [111] planes. The strong spots can be indexed to allowed [220] reflections, whereas the inner weak spots can be assigned to the formally forbidden (1/3)[422] reflection. The triangular Au plates are similar to previously reported Au microplates with symmetrical boundaries. It has been suggested that the boundaries arise from twinned crystalline structures originating from the stacking faults.

As the amount of PVP is decreased to 1.5 g and the volume of aqueous C₆H₅O₇Na₃·2H₂O is reduced to 1.7 mL, the obtained product is dominated by rod-like particles (Fig. 7a and b). The Au nanorod samples consist primarily of two kinds of rods: the first type of nanorods have one tip and an average aspect ratio of 1.6, whereas nanorods of the other type have two tips and exhibit an average aspect ratio of 2.4. The aspect ratio is defined as the ratio of the rod length to the maximum rod diameter. The product shape not only varies with the amount of PVP, water, and C₆H₅O₇Na₃·2H₂O, but is also sensitive to the stirring conditions. When the reaction solution for the synthesis of polyhedral spheres is stirred during the entire reaction process, the product is dominated by dumbbell-like nanoparticles.

Figure 5. Absorption spectra of ethanol solutions of the regular octahedral Au samples shown in a) Fig. 2a, b) Fig. 2b, c) Fig. 2c, and d) Fig. 2d.

Figure 6. SEM images of a) triangular and b) polyhedral Au samples. The insets of (a) and (b) show the corresponding SAED pattern and a high-magnification SEM image of a polyhedron, respectively.

Figure 7. SEM and TEM/HRTEM images for a,b) rod-like and c,d) dumbbell-like Au samples.
To further investigate the crystallographic structure of the dumbbell-like particles, HRTEM images of the junction of a single dumbbell have been acquired. As shown in Figure 7d, similar to body of the dumbbell, the junction also exhibits good crystallinity, thus indicating that the dumbbells are single crystalline rather than aggregates of smaller constituents.

It has been found that the surface energies and crystallinity of the added initial seeds can be as important and instrumental in controlling the morphology of the final product as structure-directing agents such as PVP\[^{1a,b,2k,3a,8,10b,13a}\] and hexadecyltrimethylammonium bromide (CTAB).\[^{1v,9a,l,13a}\] To obtain more controllable shapes and sizes, a Au nanoparticle suspension has been directly added instead of using the aqueous C\(_6\)H\(_5\)O\(_7\)Na\(_3\)·2 H\(_2\)O solution. As shown in Table 1 and Figure 8a–d, the highly shape-selective synthesis of Au belts with an average length of up to 21 \(\mu\)m is achieved on a large scale. High-magnification SEM (Fig. 8b and c) and TEM (Fig. 8d) images reveal the belt-like nature of the obtained particles. The particles are monodisperse in terms of their lateral dimensions (ca. 130 nm) and surface smoothness, and are ca. 40 nm thick. As shown in Figure 8c and d, all the Au belts end in a 60° acute angle structure. This angular structure is identical in shape and angular value to the angular structure of regular triangular plates. Notably, this morphology is different from the previously reported Au belts that terminate in a rectangular structure.\[^{11a}\] The crystallographic structure of the belts has been further characterized by HRTEM. Figure 8e shows the HRTEM image and corresponding SAED pattern (inset) obtained from a belt lying flat on the support film with the electron beam perpendicular to the flat facets. The fringe spacing of 0.25 nm as well as the six-fold rotational symmetry displayed by the diffraction spots imply that all the lateral faces of the belts are surrounded by [111] planes. The appearance of (1/3)[422] reflections is consistent with a previous report of Ag belts\[^{11b}\] but is in marked contrast to a previous report of Au belts.\[^{11a}\]

By simultaneously using the Au nanoparticle suspension and aqueous C\(_6\)H\(_5\)O\(_7\)Na\(_3\)·2 H\(_2\)O, Au hexagons with an average edge length of 200 nm have been successfully prepared (see Table 1 and Fig. 8f). The diffraction spots in the corresponding SAED pattern (Fig. 8f, inset) obtained by aligning the electron beam perpendicular to the hexagonal facets of an individual particle display six-fold rotational symmetry, suggesting that the hexagonal faces are surrounded by [111] planes.

Figure 9 displays the absorption spectra for ethanol solutions of the above Au nanoparticles exhibiting various shapes including triangles, polyhedral spheres, rods, dumbbells, belts, and hexagons. The triangular Au particles exhibit a broad SPR peak around 870 nm. According to previous reports\[^{2p,3b,m,5}\] this band can be assigned to the in-plane dipole modes of the triangular gold plates, which are located between the in-plane dipole resonance bands of triangular Au plates with average edge lengths of 96 and 158 nm, corresponding to peak wavelengths of ca. 825 and 910 nm, respectively.\[^{3b}\] This is consistent with the average edge length (120 nm) of the triangular faces in the triangular Au sample. However, the broad size distribution and unique side structures of our triangular Au sample, as well as the presence of impurities such as decahedra (ca. 12 %), regular octahedra (ca. 8 %), and irregularly shaped particles (ca. 6 %), broaden the SPR band and quench the
2.3. Growth Mechanism of Anisotropic Au Nanoparticles

To evaluate whether the nucleation and growth of Au nanostructures occur along PVP and are directed by it, IR absorption spectra have been acquired for Au nanostructures with various shapes. These spectra are compiled in Figure 10. For comparison, the IR absorption spectra of pure PVP as well as Au octahedra after 4 h of annealing at 900 °C have also been recorded (octahedra 1). As shown in Figure 10, PVP displays some typical bond absorptions around 1284, 1427, 1666, 2925, and 3433 cm\(^{-1}\) arising from the absorptions of the N→H–O complex, the pyrrolidone ring, and bond vibrations from C=O, C–H, and O–H (from water impurities) moieties, respectively.\(^{[15]}\) The Au octahedra also show several typical absorption bands related to PVP. These characteristic bands disappear after the removal of PVP by annealing, confirming the adsorption of PVP on the octahedra. As compared to pure PVP, in octahedron 1, the band related to the C–H bonds remains unvaried in position since the hydrocarbon chain is inert to Au. However, bands arising from the N→H–O complex, the pyrrolidone ring, and the bond vibrations of C=O are red-shifted to 1248, 1388, and 1584 cm\(^{-1}\), respectively. These red-shifts can be attributed to bond weakening arising from the partial donation of O/N lone-pair electrons of PVP to vacant orbitals on the Au surface. Specifically, this relates to the coordination bonds formed between the O/N atoms of PVP and specific Au crystallographic planes. Analogously, characteristic PVP absorption bands are observed for Au particles of various shapes such as triangles, polyhedra, rods, dumbbells, belts, and hexagons. This clearly shows that the Au nanostructures are formed around PVP in this reaction, and that the shapes of the structures are defined by the interplay between PVP and Au or the adsorption of PVP on Au.

The role of PVP in our approach has been further revealed by using distilled water instead of the citrate solution in the syntheses of polyhedral, octahedral, triangular, dumbbell-like, and rod-like Au nanoparticles. It has been found that all the well-defined shapes can still be observed in the final products although the ratio of particles with the desired shape is greatly reduced. These results and the IR absorption spectra taken together suggest that PVP not only directs seed growth by adsorbing onto the seeds, but also takes part in the self-seeding process as the reductant; the main role of the citrate is to facilitate the formation of uniform Au seeds. In other words, varying the amount of PVP changes the number, surface energy, crystallinity, and PVP coverage of the initial nuclei, and can thus modify the way in which the nuclei grow, resulting in the growth of different Au structures. As demonstrated above, by keeping the amount of the aqueous citrate solution constant (1.7 mL, 0.5 %), and using 3.0, 2.4, 1.5, and 0.6 g of PVP, Au polyhedra, octahedra, rods, and octahedra 1 have been obtained. The transformation from polyhedra to dumbbells induced by stirring the reaction mixture might also arise from variations in the initial nuclei related to varying PVP coverage.

Besides changing the amount of PVP, adjusting the volume of water provides another approach to modify the initial nuclei by tuning the reduction ability of PVP. Varying the volume of water also alters the adsorption behavior of PVP on Au, thus yielding more controllable shapes (such as the triangles shown in Fig. 6a) and sizes (such as the octahedra with controllable sizes shown in Fig. 2b and d). As demonstrated by Xia and co-workers,\(^{[26]}\) the presence of stacking faults is critical for the growth of Ag and Au nanoplates. Clearly, our triangular Au plates (Fig. 6a) with unique symmetrical boundaries arise from the PVP-directed growth of initially formed nuclei possessing stacking faults.\(^{[36]}\) The hexagonal Au plates shown in Figure 8f...
can initially form as Au triangles, and subsequently grow equivalently along [110] instead of [100] directions when the [111] planes are passivated by PVP. The Au nanobelts (Fig. 8a–e) may be formed by the same mechanism reported previously for Ag nanobelts. The PVP adsorbed on the edge surfaces of the small initially formed triangles may be selectively removed upon heating, thus inducing the triangles to self-organize (antiparallel to each other) into 1D nanostructures, and finally to recrystallize into single-crystalline nanobelts without changing their flat surfaces. Indeed, the small surviving triangles observed in Figure 8c and d, as well as the unique 60° acute angle structure (identical to the angle of the small triangles) of the belt ends, also suggest that our Au belts likely arise from the self-assembly of small triangular plates.

2.4. Highly Shape-Selective Synthesis of Silica Spheres, Tubes, and Needles with Controlled Aspect Ratios

In contrast to previous uses of PVP reported in the literature, here PVP plays a rather unique role. Firstly, water “bound” to PVP is exploited for the first time to confine the reaction to the PVP surface rather than the entire reaction solution. This greatly enhances the ability of PVP to direct the reaction, thus facilitating the synthesis of highly pure, novel Au nanostructures. Secondly, the novel WPN system permits the volume of water to be adjusted, thus yielding control over the reaction speed and the reduction ability of PVP, and thereby improving the ability of PVP to kinetically control the nucleation and growth of Au. Finally, the WPN system allows the region-selective (rather than uniform) distribution of PVP and water. This also enhances the ability of PVP to direct the shape-selective synthesis of Au nanoparticles.

Our approach offers three advantages over previous methods based on PVP. 1) By adjusting the experimental parameters, a variety of shapes including octahedra, triangles, polyhedra, rods, dumbbells, belts, and hexagons can be prepared using the novel WPN system, whereas only one or two kinds of shapes have been obtained by most of the previous methods reported in the literature. 2) The products obtained by our approach are highly pure and adopt shapes that have not previously been observed for Au nanostructures. For example, this work represents the first synthesis of highly pure Au nanobelts with high aspect ratios and unique 60° acute angle ends. Furthermore, the synthesis of regular Au octahedra with controllable edge lengths and high purity of up to ca. 90% has been achieved for the first time. Thirdly, the unique tip structure of the Au nanorods synthesized here makes them distinctive from all previously reported Au rods. Finally, hexagonal Au plates with the highest reported purity have been synthesized using this approach although these structures are prepared with a maximum purity of only 45%. We believe that it will be possible to synthesize other highly pure novel Au nanostructures with controllable sizes by optimizing the experimental parameters of the WPN system. 3) The unique combination of PVP and “bound water” in the WPN system makes our method very versatile.

The WPN system has been successfully extended to realize the highly shape-selective synthesis of silica nanostructures by confining the hydrolysis of tetraethylorthosilicate (TEOS) along PVP using water “bound” to PVP. In a typical synthesis, 0.35 mL of the concentrated Au nanoparticle suspension is diluted with 2 mL of ethanol and added into 20 mL of an n-pentanol solution of PVP (0.1 g) in a conical flask with a stopper under stirring at room temperature. After 20 min, 0.45 mL of ammonia water is added. After another 30 min of stirring, 0.2 mL of TEOS is added. The reaction solution is then stirred for 12 h and centrifuged; the obtained product is washed three times with ethanol under centrifugation and ultrasonication. As shown in Figure 11a, the obtained product is dominated by Au/silica core/shell nanospheres. Upon increasing the PVP amount from 0.1 to 1.0 g, the products change in shape from spheres to needles with an average aspect ratio of 20 (Fig. 11b). The aspect ratio of the silica needles can be easily tuned by varying the volume of the concentrated Au nanoparticle suspension. As shown in Figure 11c, silica needles with an average aspect ratio of 3 have been obtained by using 0.65 mL of the concentrated Au nanoparticle suspension. In the synthesis of the silica needles shown in Figure 11b, silica nanotubes are predominantly obtained upon using the concentrated Au nanoparticle suspension without dilution by ethanol (Fig. 11d).

3. Conclusions

The synthesis of anisotropic Au nanostructures with highly controlled sizes, shapes, and plasmon resonances has been achieved in a two-phase WPN system. The WPN system has been designed to take advantage of “bound” water as well as the region-selective distribution of PVP and water, thus confin-
ing the synthesis reaction along the PVP surface. IR absorption spectra provide direct evidence that the synthesis reaction of the anisotropic Au nanostructures occurs around PVP and involves sensitive interplay between PVP and Au. The remarkable highly pure Au nanostructures produced here expand the ability to study the physicochemical properties and technological applications of Au nanostructures. Furthermore, due to the unique combination of “bound” water and PVP, the WPN system developed here can be extended to synthesize other nanostructures with controllable sizes. The present experiments have shown that the highly shape-selective synthesis of silica spheres, tubes, and needles with controlled aspect ratios can also be realized in the WPN system.

4. Experimental

H AuCl4·H2O (analytical reagent (AR), ≥ 99.95 %), PVP (number average molecular weight Mn = 30 000), C12H22O11·4H2O (AR, ≥ 99.0 %), TEOS (AR, SiO2 ≥ 97.9%), NH3 solution (AR, 25–28 %), and anhydrous ethanol (AR, ≥ 99.7 %) were used as received. TEM images were obtained on JEM-200CX (JEOL, Japan) or Tecnai F20 (Philips, The Netherlands) transmission electron microscopes. The sample colloids were placed on carbon-coated copper grids for TEM observation. SEM images were obtained on LEOS1530VP or XL30 (Philips, The Netherlands) instruments. Visible absorption spectra of samples dispersed in ethanol were recorded on a U-3410 spectrophotometer (Hitachi, Tokyo, Japan). IR absorption spectra of samples dispersed on a silicon substrate were collected using a far-field Fourier transform infrared (FTIR) spectrometer (Nicoleti 5700, USA). The surface tension of the WPN and PVP/n-pentanol solutions was measured using an optical surface tension instrument (CAM200, KSV).

Preparation of Au Nanoparticle Seeds (ca. 10 nm): 3 mL of aqueous HAuCl4·4H2O (0.03 M) and 6 mL of aqueous sodium citrate (1.0 %) were added sequentially into 360 mL of boiling water in a conical flask.

The as-prepared suspension was obtained after 15 min of boiling. For the synthesis of silica, the as-prepared suspension was concentrated to ten times its concentration.

Preparation of Anisotropic Au Nanoparticles: An aqueous C12H22O11·4H2O solution and/or the as-prepared Au seed suspension was added into 60 mL of an n-pentanol solution of PVP in a conical flask under stirring. The flask was sealed with a ground glass stopper during the entire reaction process except during the addition of reaction reagents. After stirring for 30 min, 1.5 mL of an ethanol solution of HAuCl4·4H2O was added under stirring over another 5 min. Subsequently, the mixture was heated at 95 °C in a constant-temperature oven for 24 h. When stirring was required for the synthesis, the reaction solution was heated in a silicon oil bath under magnetic stirring. The obtained product was washed with ethanol three times under centrifugation and sonication. The products synthesized under different conditions are summarized in Table 1.

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