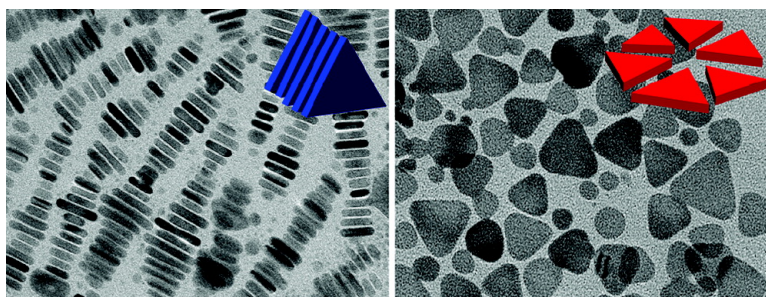


## Anisotropic Assembly of Ag Nanoprisms

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## Anisotropic Assembly of Ag Nanoprisms

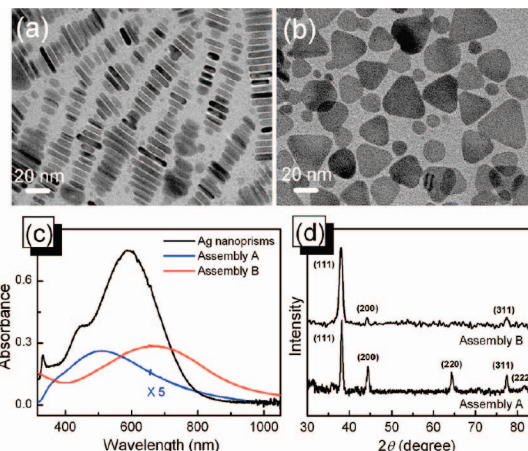
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Two-dimensional assemblies of nanometer-sized building blocks with ordered structures have been used for a variety of important applications as a result of their collective electronic, optical, and magnetic properties being distinctly different from the corresponding individual nanoparticles or the bulk solid.<sup>1</sup> However, most of studies have concentrated on the assemblies of isotropic spherical structures. Due to their anisotropic structure, anisotropic nano-objects such as nanorods and nanoprisms have shown interesting size- and shape-dependent properties, thus motivating interest in the controlled assembly of them into functional architectures.<sup>2,3</sup> Furthermore, anisotropic nanostructures should show different physical properties as the direction of measures, although anisotropic particles in the solution or assembled into random structures do not show anisotropic properties.<sup>4,5</sup> Anisotropic assembly of anisotropic nano-objects into controlled structures is therefore an important task because they show new and/or improved properties depending on the direction of assembly, spatial arrangement, and the degree of order among the individual building blocks.

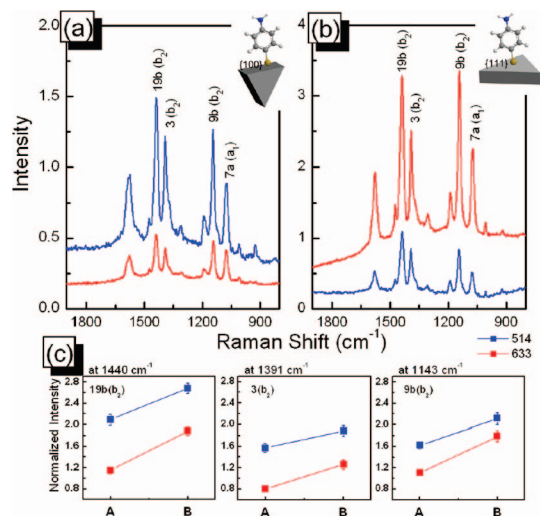
Here we report for the first time on the assembly of Ag nanoprisms with anisotropic orientation and the orientation-dependent properties of these assemblies. Ag nanoprisms were prepared by following the literature.<sup>6</sup> The almost Ag nanoprisms were truncated, and their average edge length was  $30 \pm 7$  nm. Although the edge lengths of nanoprisms were not homogeneous, their thicknesses (4.5 nm) were remarkably identical (Figure 1a,b). Using these Ag nanoprisms, two kinds of assembled structures were fabricated. One was fabricated simply by dropping Ag nanoprism solution onto the clean substrates (glass, indium–tin oxide (ITO) glass, Si and TEM grid) and drying slowly. During evaporation of nanoprism solution, almost Ag nanoprisms tend to stack face-to-face in rows with their edges perpendicular to the substrate (Figures 1a and S1a). The alignment of the nanoprisms was not affected by the type of substrate and always assembled with upright orientation on various substrates, indicating that the attractive force between nanoprism faces should be stronger than that between face and substrate.<sup>7</sup> This was further confirmed by the fact that we observed parallel alignment of nanoprisms when we used amine-terminated substrates to intentionally increase the interaction between nanoprism face and substrate (Figure S2). As shown in TEM images, small amounts of other particles with different shapes are present. However, these particles have no influence on the formation of assembly. It appears that strong attractive interaction between nanoprisms can also rule out a possible role of other particles. We called this assembled structure that consists of rows of stacked Ag nanoprisms “Assembly A”. The other was fabricated by using the interfacial entrapment method. We recently reported that the crown ether derivative mediates the transfer of Ag nanoprisms in water solution to the water/oil interface, directing the self-assembly of nanoprisms at the liquid/liquid interface in face-down fashion (Figures 1b and S1b).<sup>8</sup> It can be speculated that



**Figure 1.** TEM images of Assembly A (a) and B (b). (c) UV–vis spectra of Assembly A and B, and Ag nanoprisms in solution. (d) XRD patterns of Assembly A and B.

the parallel alignment of nanoprisms is due to the repulsion between crown ether derivatives adsorbed on the nanoprism faces which can overcome the tendency to stack in the face-to-face manner.<sup>8</sup> We named this structure “Assembly B”. In both assemblies, the nanoprisms were very close to each other.<sup>9</sup>

Ag nanoprisms in solution show three surface plasmon peaks at 600 (strong), 450 (medium), and 340 nm (weak but sharp) corresponding to in-plane dipole, in-plane quadrupole, and out-of-plane quadrupole resonances, respectively (Figure 1c).<sup>10</sup> In line with previous studies, the out-of-plane dipole resonance was not resolved in the spectrum because of its weak and broad feature.<sup>10,11</sup> While these plasmon modes are really dependent on the orientation of the Ag nanoprism, full angular averaging value is obtainable due to the random orientation of nanoprisms in solution.<sup>2,10</sup> However, the assembled nanoprisms on clean glass substrates exhibit the characteristic plasmon absorptions as the direction of the prisms in the assemblies (Figure 1c). Assembly B, composed of horizontally oriented Ag nanoprisms, exhibits only one peak at 670 nm, which can be assigned to an in-plane dipole resonance. Compared with the spectrum of nanoprisms in solution, this peak is red-shifted and broadened due to the resonance of surface plasmons of close-packed nanoprisms.<sup>2,8</sup> Assembly A, composed of vertically oriented Ag nanoprisms, shows one weak broadband centered at 504 nm with a shoulder at  $\sim 360$  nm. On the basis of the previous discrete dipole approximation calculations of the polarization-dependent extinction spectra of Ag nanoparticles<sup>4,11</sup> as well as its broad and weak spectral features, we can assign this band as plasmon resonance associated with out-of-plane polarization. The observed different optical properties of two assemblies can be understood by the assumption that incident light should excite mostly in-plane and out-of-plane plasmon modes for



**Figure 2.** SERS spectra of 4-ABT adsorbed on Assembly A (a) and B (b) with 514 and 633 nm excitations. (c) The relative intensities of the  $b_2$  modes of 4-ABT adsorbed on Assembly A and B.

Assembly B and A, respectively, due to the specific orientations of nanoprisms in the assemblies (Figure S4).

It is also interesting that Assembly A and B exhibit different XRD patterns (Figure 1d). The XRD pattern of Assembly B shows an overwhelmingly intensive diffraction peak from the (111) lattice plane with two very weak peaks from the (200) and (311) planes of fcc Ag (JCPDS No. 4-0783). Assembly A, however, shows a different pattern: peaks from (111), (200), (220), (311), and (222) can be observed clearly, and the intensity ratio of (200) to (111) diffraction increased to  $\sim 0.5$ . Considering the reported geometrical model of the Ag nanoprism, in which each nanoprism is bound by two {111} planes as the top and bottom faces and three {100} planes as the side faces,<sup>12</sup> this observation indicates that the {111} planes tend to be preferentially oriented parallel and perpendicular to the supporting substrate for Assembly B and A, respectively, due to the directional alignment of the nanoprisms (see insets of Figure 2a,b), thus demonstrating that exposed crystallographic planes as well as optical properties can be controlled by the anisotropic assembly of Ag nanoprisms.

We have also investigated the surface-enhanced Raman scattering (SERS) properties of the assemblies by using 4-aminobenzenethiol (4-ABT) as a model compound. 4-ABT molecule adsorbs strongly on the Ag surface by forming a Ag–S bond and shows vibrational mode-selective SERS enhancement owing to the charge transfer from metal to molecule.<sup>13</sup> The SERS intensities of 4-ABT on Assembly A and B depend on the excitation wavelength (Figure 2a,b). Assembly A exhibits stronger enhancement at 514 nm excitation than at 633 nm, whereas Assembly B shows an opposite trend. This can be ascribed to the different optical absorption characteristics of the two assemblies. It is widely accepted that the SERS effect is the result of enhancement of the localized electromagnetic field due to surface plasmon resonance.<sup>14</sup> As shown in Figure 1c, surface plasmon bands of Assembly A and B largely overlap with 514 and 633 nm excitation, respectively. To investigate the selective Raman enhancement of 4-ABT, normalized intensities of three  $b_2$  mode peaks at 1440, 1391, and 1143  $\text{cm}^{-1}$  with respect to the  $a_1$  mode at 1077  $\text{cm}^{-1}$  were monitored for each assembly (Figure 2c). The  $b_2$  modes of 4-ABT on Assembly B exhibit stronger relative intensities than on Assembly A with both excitations. It is well-known that these symmetric  $b_2$  modes of 4-ABT adsorbed on Ag are selectively enhanced in SERS via the

charge transfer from Ag to 4-ABT. This charge transfer is a resonance Raman-like process and is thus affected by the excitation wavelength and Fermi level ( $E_f$ ) of the Ag surface.<sup>13</sup> Due to the different exposed crystallographic planes for Assembly A and B, the 4-ABT molecules can be assumed to adsorb mostly on Ag(100) and Ag(111) surfaces for Assembly A and B, respectively (insets of Figure 2a,b). Therefore, the extent of charge transfer should be different between assemblies and result in different relative enhancement of  $b_2$  modes. From the observed higher SERS intensities of  $b_2$  modes for Assembly B, it may be supposed that the degree of resonance between excitation energies and the energy gap between  $E_f$  and the electronic level of 4-ABT is larger for Assembly B than for Assembly A. The different adsorption characteristics of 4-ABT were revealed by the XPS measurements. On Assembly A and B, the S 2p<sub>3/2</sub> binding energies are 161.7 and 159.6 eV, respectively (Figure S5). On the basis of the fact that thiol molecules generally adsorb at the highest coordination site on a given surface and thiol will have a greater S 2p binding energy if it is adsorbed at a higher coordination site,<sup>15</sup> the observed greater binding energy on Assembly A indicates that the binding site of 4-ABT on Assembly A has a higher coordination number than on Assembly B. This is consistent with the fact that the highest coordination sites of Ag(100) and Ag(111) surfaces are 4-fold and 3-fold hollow sites, respectively.<sup>15</sup>

In summary, we have demonstrated a method for anisotropic assembly of Ag nanoprisms. The Ag nanoprisms with controlled arrangements show distinct optical, crystallographic, and SERS properties depending on their orientation in the assemblies. Our results suggest that the controlled assembly of anisotropic nanostructures can be used as a powerful tool for studying their physicochemical properties and for the creation of new classes of functional materials.

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**Supporting Information Available:** Experimental details, SEM and XPS data, section analysis, and excitation scheme. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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