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# Understanding the Role of Poly(vinylpyrrolidone) in Stabilizing and Capping Colloidal Silver Nanocrystals

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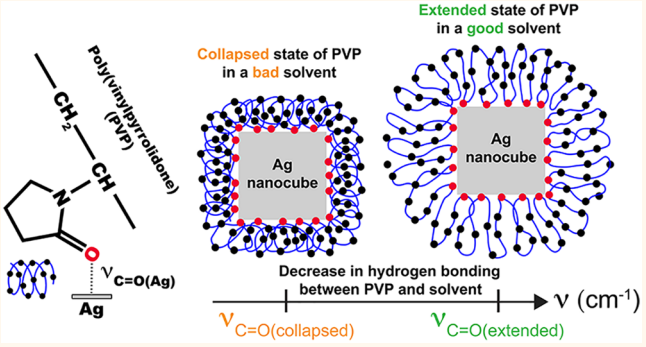
**ABSTRACT:** The ligands anchored to the surface of metal nanocrystals play an important role in controlling their colloidal synthesis for a broad spectrum of applications, but it remains a daunting challenge to investigate the ligand−surface and ligand−solvent interactions at the molecular level. Here, we report the use of surface-enhanced Raman scattering (SERS) to extract structural information about the binding of poly(vinylpyrrolidone) (PVP) to Ag nanocubes as well as its conformational changes in response to solvent quality. When a PVP chain binds to the surface of a Ag nanocube through some of its carbonyl groups, the segments between adjacent binding sites are expelled into the solvent as loops. As a result, the carbonyl peak ($\nu_{C=O}$) resolved in the SERS spectrum includes the contributions from those anchored to the surface and those residing on the loops, with their frequencies located at $\nu_{C=O(Ag)}$ and $\nu_{C=O(free)}$, respectively. While $\nu_{C=O(Ag)}$ remains at a fixed frequency due to the coordination between the carbonyl groups with Ag surface, the spectral position of $\nu_{C=O(free)}$ is dependent on the solvent. As the strength of hydrogen bonding between PVP and solvent increases, the peak position of $\nu_{C=O(free)}$ shifts toward lower frequencies. When exposed to bad and good solvents in an alternating manner, the PVP loops undergo conformational changes between collapsed and extended states, altering the separation between the free carbonyl groups and the Ag surface and thereby the intensity of the $\nu_{C=O}$ peak.




**KEYWORDS:** *poly(vinylpyrrolidone), quality of solvent, polymer−solvent interaction, silver nanocrystals, surface-enhanced Raman scattering*



The past two decades have witnessed the successful synthesis of colloidal nanocrystals with well-controlled sizes, shapes, and other properties for a broad spectrum of applications.[1−6] The success of such a synthesis critically relies on the involvement of a surface ligand capable of adsorbing on the surface of nanocrystals to keep them from aggregation, while helping maneuver their sizes and shapes.[7−10] Among the surface ligands reported in the literature, poly(vinylpyrrolidone) (PVP) easily stands out as the most powerful and versatile one, and it has been applied to the colloidal synthesis of nanocrystals made of essentially all noble metals. Because PVP contains a hydrophobic alkyl backbone and hydrophilic pyrrolidone rings as the side groups, it works well with both aqueous solutions and polar solvents used for the colloidal synthesis of noble-metal nanocrystals.[7−12] In a typical process, the oxygen atoms on some of the pyrrolidone rings coordinate with metal atoms to anchor the polymer chain to the surface through multiple binding sites. At the same time, the segments between adjacent binding sites are expelled from the surface to form loops extending into the solvent. As a result, PVP can act as a colloidal stabilizer to prevent the nanocrystals from aggregation by leveraging the steric hindrance effect arising from the loops that interact strongly with the solvent molecules.[11] In addition, as exemplified by the polyol synthesis of Ag nanocubes, PVP can serve as a facet-selective capping agent to stabilize the {100} facets and thus promote the formation of nanocrystals enclosed by this type of facet.[2,13−16]

Despite the widespread use of PVP in the colloidal synthesis of nanocrystals, it remains elusive about the configurations of

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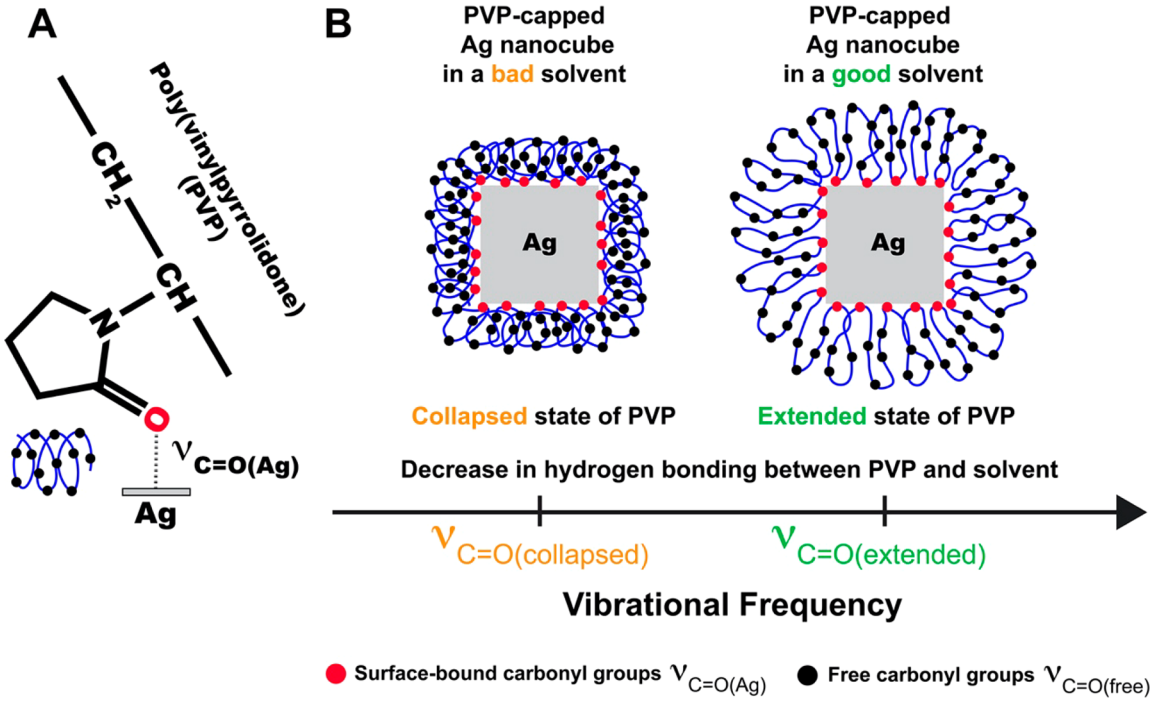


**Figure 1. (A) Schematic illustration showing the oxygen atom of the carbonyl group located on a pyrrolidone ring could coordinate with Ag surface. (B) Schematic illustration showing the difference in vibrational frequency for the $\nu_{C=O}$ band of PVP when a PVP-capped Ag nanocube is dispersed in a bad and good solvent, respectively.**

PVP adsorbed on the surface of a nanocrystal, let alone the interactions between the adsorbed PVP and solvent molecules. Part of the challenge arises from the lack of tools capable of characterizing the solution-phase adsorption of PVP onto a solid surface and the behaviors of PVP chains in response to different solvents. Most of the documented attempts have been based upon theoretical studies, with an emphasis on understanding the roles played by PVP oligomers in directing the shape evolution of Ag nanocrystals.[11,17−19] For example, using atomic-scale molecular dynamics (MD) simulations, Fichthorn and co-workers extensively investigated the interactions between PVP oligomers and different types of Ag surfaces in ethylene glycol (EG) to understand the formation of Ag nanocubes. In one study, they reported that there was a favorable free-energy change when a PVP oligomer adsorbs onto Ag(100) in EG.[17] They acknowledged that the Ag−solvent and PVP−solvent interactions could both affect the binding energy between PVP and Ag surfaces in a solution phase. In another study, they confirmed the preferential binding of PVP to Ag(100) relative to Ag(111) in the case of EG.[18] Although not all of the carbonyl oxygen atoms in PVP could simultaneously adsorb onto the Ag surface due to steric hindrance, they argued that those within the bonding range in proximity to the surface would account for the facet selective binding of PVP. On the other hand, Kalugin and co-workers studied the effect of PVP oligomers adsorbed on the surface of Ag nanoparticles in an aqueous solution.[11] They argued that the PVP chains could anchor to Ag surface through the nonbonding electrons of the carbonyl oxygen atom at the expense of hydrogen bonding between PVP and water. They also suggested that PVP oligomers with a relatively long chain could cover the surface of Ag nanocrystals in multiple layers to protect them from aggregation. Altogether, these theoretical studies support experimental findings in that the growth of Ag nanocrystals could be controlled with PVP of different chain lengths to generate either cubes or cuboctahedra.[2,13−16] However, it should be pointed out that these calculations were based on PVP oligomers instead of PVP polymers. As such, they were unable to include the contributions from the conformations of PVP, neither the interactions between PVP and the solvent molecules. Despite these developments, we still lack the experimental capability to directly analyze the PVP−surface and PVP−solvent interactions at the molecular level.

Herein, we use surface-enhanced Raman scattering (SERS) to analyze how PVP binds to the surface of Ag nanocubes while interacting with the solvent molecules. Although other studies have used SERS to confirm the presence of PVP on the surface of Ag nanocubes and Ag nanowires,[20−22] none of them used *in situ* SERS to investigate the conformations of PVP and its interactions with different solvents. In particular, we discover that both the frequency and intensity of the SERS peak associated with the stretching mode of the carbonyl group ($\nu_{C=O}$) are sensitive to the solvent. Specifically, the peak position of $\nu_{C=O}$ shifts toward higher frequencies when the PVP-capped Ag nanocubes are suspended in water, EG, and ethanol, respectively, due to the decrease in the strength of hydrogen bonding between PVP loops and solvent molecules. On the other hand, when suspended in a bad solvent such as water, the PVP loops collapse into a compact structure, resulting in an increase in peak intensity because of the residence of more free carbonyl groups in close proximity to the surface. In comparison, when suspended in a good solvent such as EG or ethanol, the PVP loops take an extended conformation, increasing the separation between the free carbonyl groups and Ag surface and thus decreasing the peak intensity. Our SERS analysis also demonstrates that the PVP loops can switch between the collapsed and extended conformations in a reversible manner when the nanocubes are alternatingly dispersed in bad and good solvents. We further demonstrate that SERS is capable of revealing the


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difference between PVP with different chain lengths when they adsorb on the surface of Ag nanocubes.

Given the PVP with a molecular weight of 55 000, we argue that the loops should be in dominance while there are some tail configurations.[23] A major conclusion of this work is that SERS can be used to differentiate the collapsed and extended conformations of PVP. In this case, it should not matter if the PVP is in loop or tail configuration. To our knowledge, there is no report on the potential role of solvent in affecting the conformation of PVP adsorbed on Ag nanocubes and therefore its effectiveness in controlling the development of {100} facets and cubic shape. Essentially, all the protocols reported for the synthesis of Ag nanocubes are based on the PVP-EG pair.[24−27] Likely, people have tried the PVP-water or PVP-ethanol pair but failed for the reason related to the insights gained in the present study. Taken together, we believe this work will have a major impact on the colloidal synthesis of noble-metal nanocrystals with well-controlled sizes, shapes, and other properties.

## RESULTS AND DISCUSSION

It is well-documented that PVP can use the oxygen atoms of its carbonyl groups located on the pyrrolidone rings to coordinate with the surface atoms of a Ag nanocrystal, as illustrated in Figure 1A.[11,14,20,28] As such, some of the carbonyl groups on a PVP chain are anchored to the surface through chemical bonding, while the polymer segments between adjacent anchor points are expelled into the solvent as loops. The free carbonyl groups residing on the loops can interact with the solvent molecules through different mechanisms, including dispersion forces, polar interactions, and hydrogen bonding. For the $\nu_{C=O}$ peak displayed in the SERS spectrum, it should include the contributions from both the anchored and free carbonyl groups, with their vibrational frequencies located at $\nu_{C=O(Ag)}$ and $\nu_{C=O(free)}$, respectively. Figure 1B illustrates how the position and intensity of $\nu_{C=O}$ can serve as a sensitive probe to elucidate the structural information about the PVP adsorbed on a Ag nanocube when it is dispersed in different solvents. By assuming that the PVP molecules anchored to the surface of a Ag nanocube would reach equilibrium with the free polymers in the solvent,[11,14,20,28] we hypothesize that the total numbers of the anchored and free carbonyl groups should remain the same when switching between different solvents because the interaction between PVP and Ag is stronger than that between solvent and Ag. We also argue that $\nu_{C=O(Ag)}$, corresponding to the surface-bound carbonyl groups anchored to Ag, should remain at a fixed frequency, whereas the spectral position of $\nu_{C=O(free)}$ arising from the interaction between the unbounded carbonyl groups and solvent is dependent on the solvent involved. As demonstrated in a previous Raman spectroscopy study of the interaction between PVP powders and water vapor, the frequency of $\nu_{C=O(free)}$ was continuously down-shifted by up to 26 $cm^{-1}$ as the mole fraction of water absorbed by the polymer increased to 0.8% due to the increase in hydrogen bonding between water molecules and the carbonyl groups on PVP.[29] Kitano and co-workers also observed a down-shift for the $\nu_{C=O(free)}$ band of PVP in $D_2O$.[30] They attributed the down-shift to two factors:[31] (i) the hydrogen bonding between the carbonyl group on PVP and $D_2O$ molecules and (ii) change to the electronic state of the carbon atom of the carbonyl group on PVP, as a result of the distortion of the ring by the formation of hydrogen bonds between the nitrogen atom and $D_2O$ molecules. Based on these previous studies, we anticipate that the vibrational frequencies of $\nu_{C=O}$ in the SERS spectra will decrease as the strength of hydrogen bonding between the free carbonyl groups and different solvent molecules increases.

On the other hand, the intensity of the $\nu_{C=O}$ peak in the SERS spectrum provides useful information regarding the conformation of the loops. When the PVP-capped Ag nanocube is dispersed in a bad solvent, the loops will collapse into a compact structure, with all of its free carbonyl groups residing in close proximity to the surface to give a strong SERS signal for $\nu_{C=O(free)}$.[11] When a good solvent is involved, the loops will be extended into the solvent. Because of their increased separation from the Ag surface, the SERS signal corresponding to the free carbonyl groups positioned in the terminal regions of the loops will drop significantly. As a result, we argue that the intensity of the $\nu_{C=O}$ peak in the SERS spectrum can be used to monitor the conformational changes of the loops between the collapsed state in a bad solvent and the extended state in a good solvent.

In this study, we first synthesized the Ag nanocubes in EG with the assistance of PVP55k.[27] Figure S1 shows a transmission electron microscopy (TEM) image of the PVP-capped Ag nanocubes with an average edge length of 39.7 ± 1.4 nm. We then dispersed the PVP-capped Ag nanocubes in different solvents, followed by SERS measurements (see details in the Experimental Section). In general, one can evaluate the quality of a solvent and even predict the solubility of a polymer in a solvent using their solubility parameters ($\delta$). It is well-established that $\delta$ is governed by three types of interactions, including dispersive forces ($\delta_d$), polar interactions ($\delta_p$), and hydrogen bonding ($\delta_h$). Based on the Hansen solubility parameters theory,[32,33] the difference between the solubility parameter of a polymer ($\delta_P$) and that of a solvent ($\delta_S$), $\Delta\delta$, can be calculated as follows:

$$\Delta\delta = [(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2]^{1/2}$$

When $\Delta\delta$ is minimized, the solubility of the polymer in the solvent will be maximized. Using the solubility parameters of PVP and different solvents reported in the literature,[32,33] we obtained $\Delta\delta$ values at 35.1, 18.7, and 13.1 when PVP is paired with water, EG, and ethanol, respectively (Table 1). As such, the quality of the solvent for PVP increases in the order of water < EG < ethanol. Accordingly, the PVP loops on Ag nanocubes are expected to take a more extended conformation when moving from water to EG and ethanol.

**Table 1. Solubility Parameters for PVP and the Three Commonly Used Solvents, Including Water, Ethylene Glycol, and Ethanol**

| | $\delta_d$ | $\delta_p$ | $\delta_h$ | $\Delta\delta^c$ |
|---|---|---|---|---|
| PVP[a] (theoretical) | 18.8 | 13.4 | 7.5 | |
| water[b] | 15.5 | 16.0 | 42.3 | 35.1 |
| EG[b] | 17 | 11 | 26 | 18.7 |
| ethanol[b] | 15.8 | 8.8 | 19.4 | 13.1 |

[a]Ref 26. [b]Ref 27. [c]The results calculated using the data from refs 26 and 27.

Figure 2A shows the SERS spectra recorded from the PVP-capped Ag nanocubes dispersed in water, EG, and ethanol, respectively. We resolved the $\nu_{C=O}$ peak of PVP (marked by red dots), confirming the presence of PVP on the surface of the Ag nanocubes. We also used UV−vis spectroscopy to


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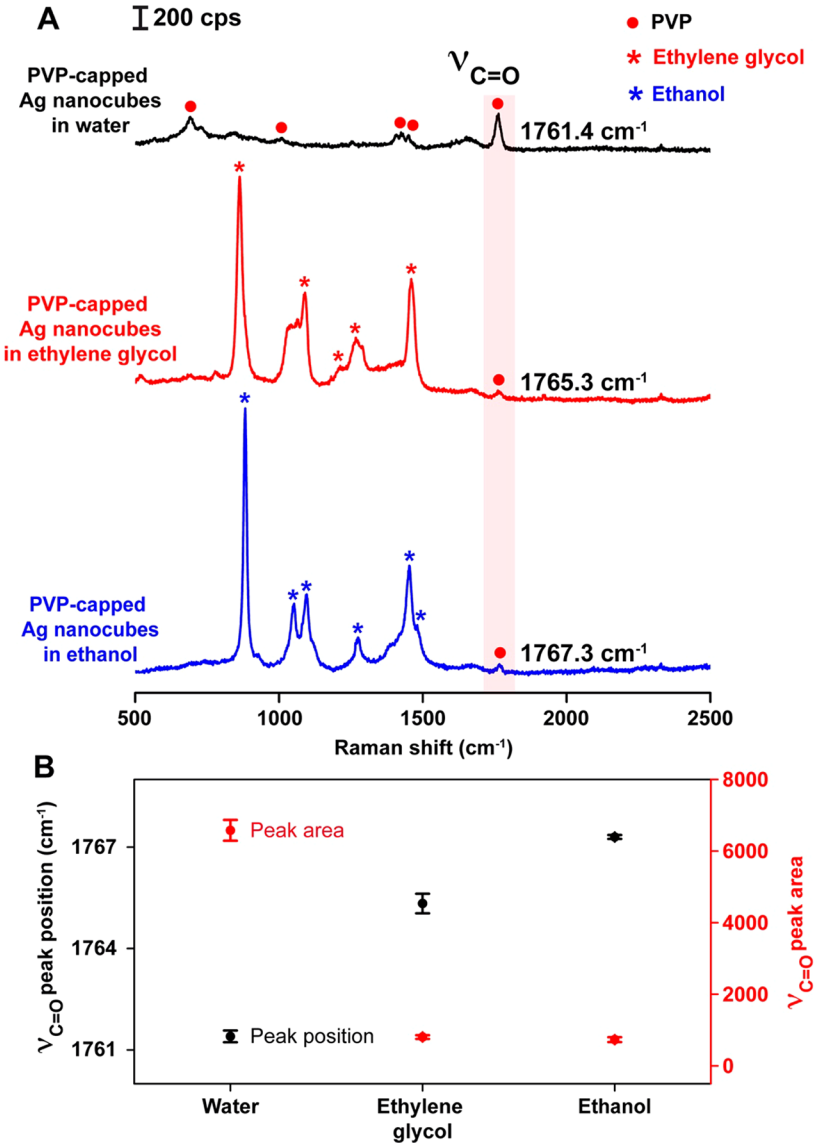


**Figure 2. (A) SERS spectra recorded from the PVP-capped Ag nanocubes dispersed in water, EG, and ethanol, respectively. (B) Comparison of the position and area of the $\nu_{C=O}$ peak of PVP adsorbed on Ag nanocubes when they were dispersed in water, EG, and ethanol, respectively.**

characterize the localized surface plasmon resonance (LSPR) of the Ag nanocubes when they were dispersed in these three solvents. As shown in Figure S2, the major LSPR peaks of the Ag nanocubes were located at 432, 448, and 426 nm, respectively, indicating that the nanocubes were well dispersed in all these solvents.[34] Evidently, the PVP adsorbed on the surface of the Ag nanocubes could serve as an effective colloidal stabilizer in all these cases regardless of the exact conformation of the PVP loops.[11]

By fitting the $\nu_{C=O}$ peak of PVP using a Gaussian–Lorentzian function, we obtained its exact position and area, as summarized in Figure 2B. Specifically, the peaks of $\nu_{C=O(water)}$, $\nu_{C=O(EG)}$, and $\nu_{C=O(ethanol)}$ were positioned at 1761.4, 1765.3, and 1767.3 $cm^{-1}$, respectively, confirming the upward shift in vibrational frequency due to the decrease in hydrogen bonding between PVP and the solvent in the order of water, EG, and ethanol. When analyzing the peak area, we noticed that the $\nu_{C=O(water)}$ peak was 8–9 times stronger than that of $\nu_{C=O(EG)}$ or $\nu_{C=O(ethanol)}$. This trend is consistent with the proposed involvement of loops when PVP adsorbs onto the surface of Ag nanocubes (see Figure 1). When the PVP loops collapsed in water to take a collapsed structure, most of the free carbonyl groups would reside in close proximity to the surface of the Ag nanocubes, giving rise to a much stronger intensity for $\nu_{C=O(water)}$. In contrast, when the PVP loops were extended into EG or ethanol to take an extended conformation, more free carbonyl groups would be kept away from the surface of the Ag nanocubes, resulting in a decrease in peak area for $\nu_{C=O(EG)}$ or $\nu_{C=O(ethanol)}$. To further validate the different conformations of PVP loops in these three solvents, we measured the hydrodynamic size of the corresponding Ag nanocubes using dynamic light scattering (DLS). Although the Ag nanocubes had an average edge length of 39.7 ± 1.4 nm as revealed by TEM, their hydrodynamic diameters in water, EG, and ethanol were found to be 74.1 ± 1.1, 84.6 ± 1.3, and 95.8 ± 1.4 nm, respectively, confirming that the PVP loops were indeed further extended as the quality of the solvent was improved.


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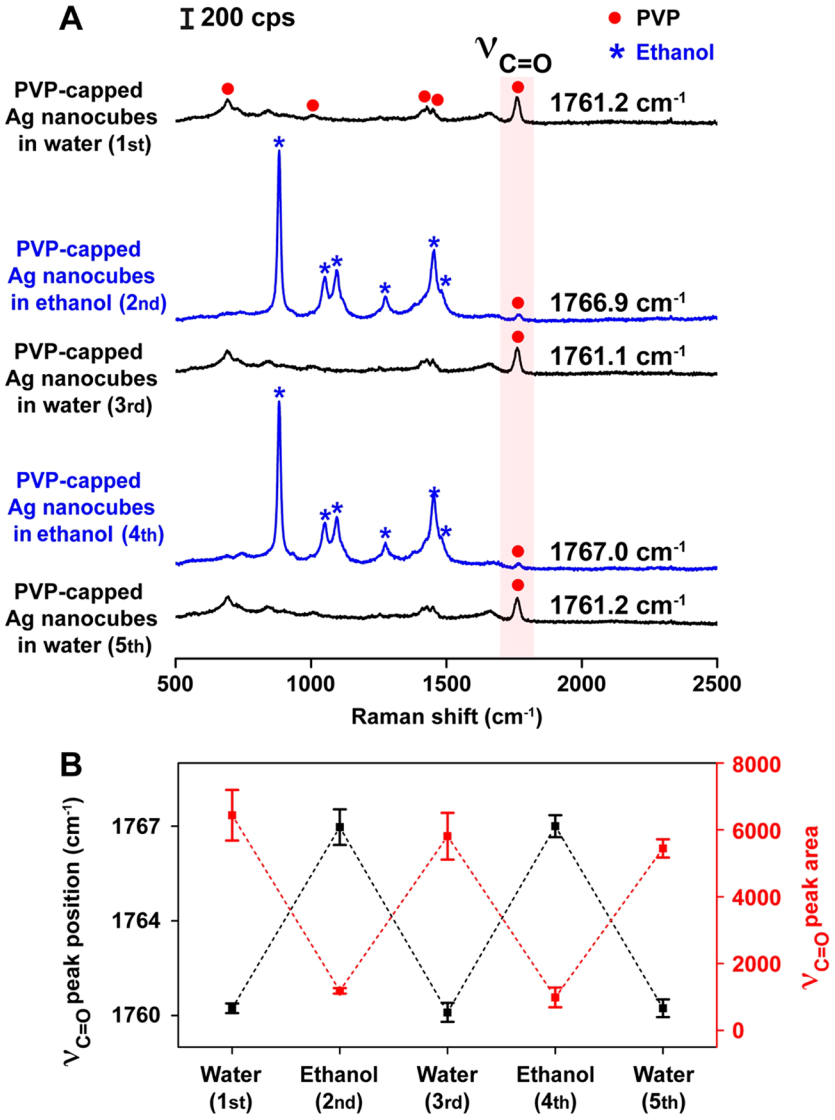


**Figure 3. (A) SERS spectra of PVP-capped Ag nanocubes when they were alternatingly dispersed in water and ethanol. (B) Plots of the position and area for the $\nu_{C=O}$ peak of PVP derived from the SERS spectra shown in (A).**

Different from water, EG, and ethanol, acetone is a less polar solvent.[35,36] As a result, PVP is expected to be insoluble in acetone. Figure S3 shows the photographs of four vials containing the solutions prepared by adding 70 mg of PVP powder into 3.5 mL of water, ethanol, EG, and acetone, respectively, under magnetic stirring for 30 min. The results indicate that PVP is soluble in water, ethanol, and EG, but not acetone. From the UV−vis spectrum of the PVP-capped Ag nanocubes dispersed in acetone (Figure S4), we observed a very broad peak extending from 500 to 800 nm, completely different from the UV−vis spectra of Ag nanocubes dispersed in water, EG, or ethanol (see Figure S2). Although we could still resolve the major LSPR peak of Ag nanocubes at 426 nm, the appearance of the broad peak was indicative of significant aggregation.[34,37] We also collected a SERS spectrum from the PVP-capped Ag nanocubes dispersed in acetone. As shown in Figure S5A, we only resolved the peaks associated with acetone, not those assigned to PVP. Likely, because of the aggregation and the consequent precipitation of nanocubes in acetone, there was a significant decrease in the number of Ag nanocubes in the SERS detection zone. As a result, the $\nu_{C=O}$ band of PVP became very weak and buried in the shoulder peak of acetone around 1749 $cm^{-1}$. To confirm the presence of PVP on the surface of the Ag nanocubes, we drop-casted the Ag nanocubes in acetone on a silicon substrate. After the evaporation of acetone under ambient condition, we collected another SERS spectrum from the Ag nanocubes dried on silicon. As shown in Figure S5B, we could indeed resolve the characteristic peak of $\nu_{C=O}$ band at 1767.6 $cm^{-1}$. Altogether, our results suggest that PVP could remain on the surface of Ag nanocubes in acetone, but it could no longer serve as a colloidal stabilizer due to the unfavorable interaction between the polymer and the solvent. In fact, a common practice for the collection of Ag nanocubes in a postsynthesis route is to introduce acetone into the original reaction solution in EG. We believe that the poor solubility of PVP in acetone would result in a major reduction in the steric effect, leading to the aggregation of Ag nanocubes owing to the particle collisions driven by Brownian motion.[38]

We conducted a set of control experiments to validate our assumption that the PVP molecules are able to maintain their binding to the surface of Ag nanocubes without involving


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desorption or additional adsorption when dispersed in different solvents or PVP solutions. Specifically, we introduced the PVP-capped Ag nanocubes into pure EG or a PVP solution in EG at a concentration of 3.84 mg/mL (the concentration involved in the synthesis of Ag nanocubes), followed by the collection of SERS spectra at different time points up to $t$ = 120 min (Figure S6A). By fitting, we obtained the position and area of the characteristic band of PVP ($\nu_{C=O}$) at different time points (Figure S6B). When benchmarked against the peak position and area in the case of pure EG, we observed essentially no change to this band regardless of the duration of time dispersed in the PVP solution in EG. We then performed another set of experiments by replacing EG with water while keeping the other experimental parameters unchanged. Figure S7 summarizes the results, in agreement with those shown in Figure S6. Altogether, these results suggest that the PVP molecules bind to the Ag surface more strongly than the solvent molecules, making it possible to retain the binding when switched to different pure solvents. These results also indicate that the surface of as-prepared Ag nanocubes in this study was already saturated with PVP and no additional polymer could be introduced onto the surface on the time scale of our experiments (up to 120 min), even when there was plenty of free PVP in the EG or aqueous solution.[39]

To validate our hypothesis that the total number of carbonyl groups anchored to the surface of a Ag nanocube would remain the same when switching between solvents, we collected a series of SERS spectra (Figure 3A) by successively dispersing the same sample of PVP-capped Ag nanocubes in water (first), ethanol (second), water (third), ethanol (fourth), and water (fifth). When the nanocubes were initially dispersed in water, we resolved the $\nu_{C=O(water)}$ band at 1761.2 cm$^{-1}$, consistent with the result shown in Figure 2A. Upon collecting the solids from water and redispersing them in ethanol, the $\nu_{C=O(ethanol)}$ band was blue-shifted to 1766.9 cm$^{-1}$, while its intensity became much weaker, in agreement with the observation shown in Figure 2A. For the next three measurements, the spectra gave SERS bands located at 1761.1 cm$^{-1}$ ($\nu_{C=O(water)}$), 1767.0 cm$^{-1}$ ($\nu_{C=O(ethanol)}$), and 1761.2 cm$^{-1}$ ($\nu_{C=O(water)}$), respectively, together with the alternating changes in peak intensity. From fitting, we obtained the position and area of the $\nu_{C=O}$ band of PVP (Figure 3B), confirming the reversible changes in both position and area for $\nu_{C=O}$ when the solvent was switched between water and ethanol. These results suggest that essentially all the PVP chains were able to retain their binding sites with the surface of a Ag nanocube during the repeated centrifugation and redispersion processes. These results also demonstrate that it is possible for the PVP loops anchored to the surface of Ag nanocubes to reversibly switch between the collapsed and extended conformations when repeatedly exposed to solvents with different solubility parameters.

To further support our argument, we performed another set of SERS measurements by dispersing the PVP-capped Ag nanocubes in binary mixtures of ethanol and water with different volume fractions of ethanol, that is, $X_{ethanol} = V_{ethanol}/(V_{ethanol} + V_{water})$. Figure 4A shows a series of SERS spectra that were recorded from the dispersions in a series of solutions, with their $X_{ethanol}$ tuned to 0, 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, and 1, respectively. Based on the SERS spectra recorded from the Ag nanocubes dispersed in water and ethanol, we assigned the vibrational frequencies of $\nu_{C=O(water)}$ and $\nu_{C=O(ethanol)}$ to 1761.2 and 1767.4 cm$^{-1}$, respectively. When dispersed in the

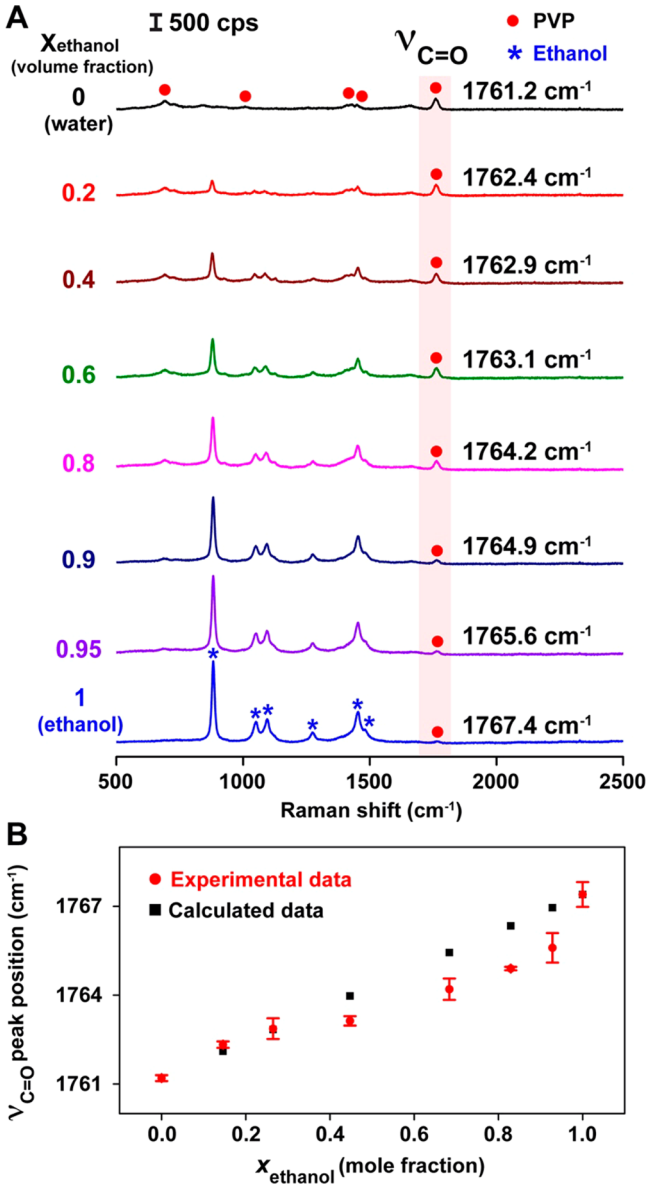


**Figure 4. (A) SERS spectra of the PVP-capped Ag nanocubes when they were dispersed in the ethanol−water binary solutions with different volume fractions of ethanol, $X_{ethanol}$. (B) A plot of the peak position of the $\nu_{C=O}$ band of PVP as a function of mole fraction of ethanol, $x_{ethanol}$, together with the values calculated using mathematical principle of superposition.**

ethanol−water binary mixtures, the $\nu_{C=O}$ band was progressively blue-shifted from 1761.2 ($\nu_{C=O(water)}$) to 1767.4 cm$^{-1}$ ($\nu_{C=O(ethanol)}$) as $X_{ethanol}$ was increased, together with a decrease in peak intensity. Based on mathematical principle of superposition,[40] we calculated the peak position of $\nu_{C=O(mixture)}$ for the mixture by following $\nu_{C=O} = \nu_{C=O(water)}(1 - x_{ethanol}) + \nu_{C=O(ethanol)}x_{ethanol}$, where $x_{ethanol}$ is the mole fraction of ethanol. Figure 4B shows a comparison of the experimental values and calculated ones. Although the data points above $x_{ethanol}$ = 0.5 are lower than the calculated values, together with larger deviation, we argue that this simple mathematical model could still be used to predict the trend of Raman shift ($\nu_{C=O}$) in the binary mixture. The linear relationship between $\nu_{C=O}$ and $x_{ethanol}$ suggests that it is possible for the PVP loops to interact with both the water and ethanol molecules. These


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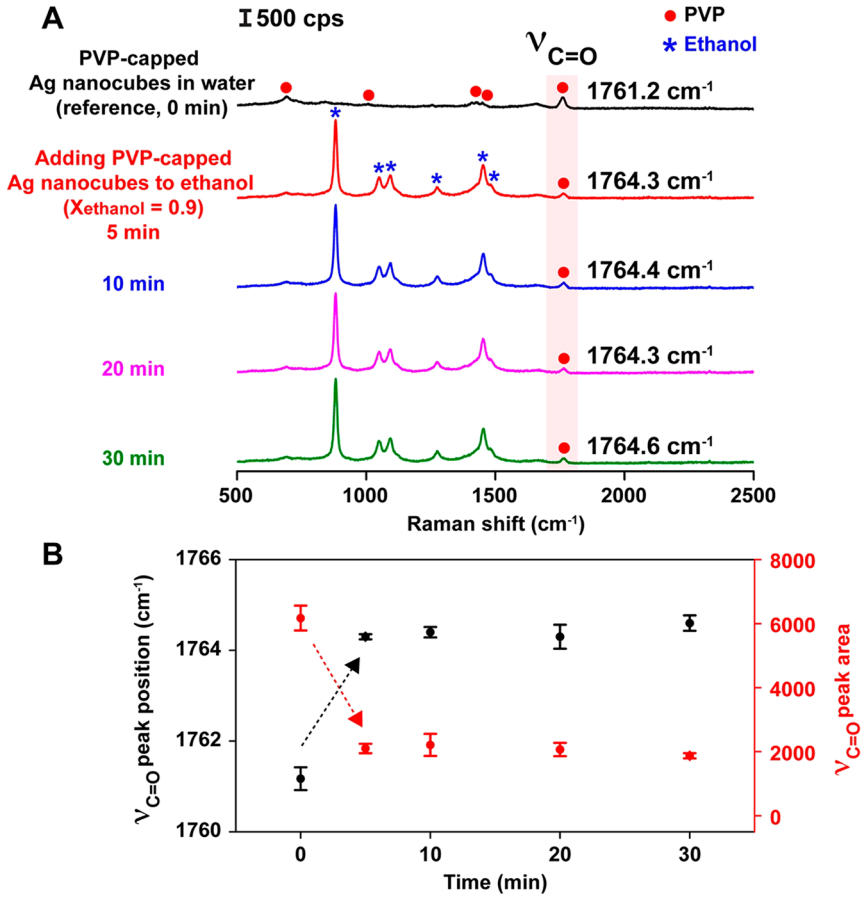


**Figure 5. (A) SERS spectra recorded at different time points after 30 $\mu$L of an aqueous suspension of the PVP-capped Ag nanocubes had been dispersed in 270 $\mu$L of ethanol. The reference SERS spectrum marked at $t$ = 0 min was collected from a sample obtained by mixing 30 $\mu$L of the aqueous suspension of the PVP-capped Ag nanocubes with 270 $\mu$L of water. (B) Plots of peak position and area for the $\nu_{C=O}$ band of PVP at different time points.**

results further support our argument that the total number of binding sites of PVP on the Ag nanocube should remain the same when dispersed in different binary mixtures.

We also investigated the dynamics of the transition between the collapsed and extended PVP loops by *in situ* SERS measurements. Specifically, we first collected the reference SERS spectrum (marked $t$ = 0 min) from a sample obtained by dispersing an aqueous suspension PVP-capped Ag nanocubes in water. We then dispersed an aqueous suspension of the PVP-capped Ag nanocubes in ethanol, followed by the collection of SERS spectra *in situ* at time points of $t$ = 5, 10, 20, and 30 min, respectively (Figure 5A). By fitting, we obtained the position and area of the characteristic band of PVP ($\nu_{C=O}$) (Figure 5B). When the Ag nanocubes were initially dispersed in water, the $\nu_{C=O}$ band of PVP was positioned at 1761.2 cm$^{-1}$, consistent with our prior results. Upon dispersion in ethanol to obtain a final binary mixture with $X_{ethanol}$ = 0.9, we noticed a blue shift for the $\nu_{C=O}$ peak position to 1764.3 cm$^{-1}$ at $t$ = 5 min, together with a decrease in peak area. At $t$ = 10, 20, and 30 min, the peaks remained at 1764.4, 1764.3, and 1764.6 cm$^{-1}$, respectively, while the peak area also stayed at the same level. These results indicate that the collapsed PVP loops on the surface of Ag nanocubes could change to the extended conformation in <5 min when the majority of the solvent molecules were switched from water to ethanol.

Because the molecular weight of PVP can affect its binding to Ag nanocubes and thus its capability to cap the surface and stabilize the colloidal suspension,[11,14] we examined the use of SERS to analyze the adsorption of PVP with different molecular weights onto Ag nanocubes when suspended in water. In the first step, we used $NaBH_4$ to remove the originally attached PVP55k from the surface of Ag nanocubes by following the protocol described in the Experimental Section. Figure S8 shows the SERS spectra of the PVP-capped Ag nanocubes in water before and after the addition of aqueous $NaBH_4$ solution at a final concentration of 0.05 mg/mL. At $t$ = 10 min, we observed a new peak located at 2396.5 cm$^{-1}$, with its assignment to the B−H stretching band of $BH_4^-$ ($\nu_{BH}$),[41,42] while the $\nu_{C=O(water)}$ band of PVP at 1761.6 cm$^{-1}$ became extremely weak. This result suggests the adsorption of $BH_4^-$ and desorption of PVP. Interestingly, at $t$ = 20 min, the $\nu_{C=O(water)}$ band reappeared, while the $\nu_{BH}$ band remained essentially the same in the SERS spectrum, suggesting the readsorption of PVP back to the surface of Ag nanocubes. There was little change to the SERS spectrum by $t$ = 30 min. When further increased to $t$ = 40 min, we noticed the peak intensity of $\nu_{BH}$ was decreased, while that of $\nu_{C=O(water)}$ was increased. From $t$ = 60 min up to 24 h, we could no longer observe the $\nu_{BH}$ band, while the $\nu_{C=O}$ band remained essentially unchanged in the SERS spectra. We performed another set of experiments by increasing the final concentration of $NaBH_4$ to 0.1 mg/mL. Figure S9 shows the time-


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elapsed SERS spectra. Upon the introduction of $NaBH_4$, at $t$ = 10 min, the $\nu_{C=O(water)}$ band located at 1761.2 $cm^{-1}$ disappeared, while the $\nu_{BH}$ band emerged at 2393.9 $cm^{-1}$. From $t$ = 10 to 80 min, the $\nu_{BH}$ band remained in the SERS spectra, with a slight decrease in peak intensity. By $t$ = 100 min and later up to 24 h, we could not detect any peaks in the SERS spectra, suggesting no readsorption of PVP back into the Ag nanocubes. Taken together, these results suggest that we can optimize the concentration of $NaBH_4$ to promote the desorption of PVP from the Ag nanocubes and delay the readsorption of PVP back to the surface, consistent with previous studies.[43,44] It should be pointed out that the driving force responsible for the desorption of PVP still deserves further study in the future. For the system involving 0.1 mg/mL $NaBH_4$ at $t$ = 100 min to 24 h, the good suspension of the Ag nanocubes suggests the presence of species other than $BH_4^-$ and PVP on the surface to keep the particles from aggregation. It has been argued that the PVP could also be replaced by hydride ions derived from $NaBH_4$ due to a stronger binding of this ligand to Ag surface.[44] Unfortunately, we were unable to resolve the vibrational band of the metal hydride to confirm the presence of hydride on the Ag surface.

In the next step, we introduced a certain amount of the aqueous suspension of Ag nanocubes treated with 0.1 mg/mL $NaBH_4$ for 24 h into an aqueous solution of PVP10k or PVP55k at a concentration that was 69.4 times greater than that of $NaBH_4$. After incubation for 3 h, we collected the PVP-treated Ag nanocubes and redispersed them in water or an ethanol–water mixture with $X_{ethanol}$ = 0.7 for SERS measurements. Figure 6A compares the SERS spectra collected from the PVP10k-treated or PVP55k-treated Ag nanocubes dispersed in water and ethanol–water mixture, respectively. In both cases, we observed the characteristic $\nu_{C=O}$ band of PVP, confirming the adsorption of PVP10k or PVP55k onto the surface of the Ag nanocubes. More specifically, we noticed that the peak position of $\nu_{C=O(water)}$ was located at 1761.1 and 1761.5 $cm^{-1}$, respectively, when aqueous solutions of PVP10k and PVP55k were involved. These results suggest that the molecular weight of PVP had essentially no impact on the hydrogen bonding between the free carbonyl groups on PVP loops and water molecules, resulting in a similar peak position for the $\nu_{C=O(water)}$. In comparison, when switched to an ethanol–water mixture with $X_{ethanol}$ = 0.7, the peak position of the $\nu_{C=O}$ band was blue-shifted to 1763.2 and 1764.1 $cm^{-1}$ for PVP10k and PVP55k, respectively. Because the loops of both PVP10k and PVP55k are expected to extend into the water–ethanol mixture, we argue that a larger portion of the carbonyl groups would form hydrogen bonds with the solvent molecules for PVP55k than for PVP10k. As a result, it is reasonable to observe more contribution from the free carbonyl groups of PVP55k and thus a higher vibrational frequency for $\nu_{C=O}$.

By fitting the $\nu_{C=O}$ bands of PVP10k and PVP55k, we plotted the peak areas of $\nu_{C=O}$ for the two different solvents in Figure 6B. It was found that the peak area of PVP55k was 1.6 times greater than that of PVP10k when both were dispersed in pure water. This result suggests the presence of more free carbonyl groups located in proximity to the Ag surface for PVP55k when the loops collapsed in water, leading to a stronger SERS signal. When converted to the area ratio between the mixed solvent and water, $I_{X=0.7}/I_{water}$, we noticed that the ratio for the PVP55k-treated Ag nanocubes was lower than that for the PVP10k-treated Ag nanocubes (0.35 *vs* 0.51). Likely, the longer loops of PVP55k on the Ag nanocubes

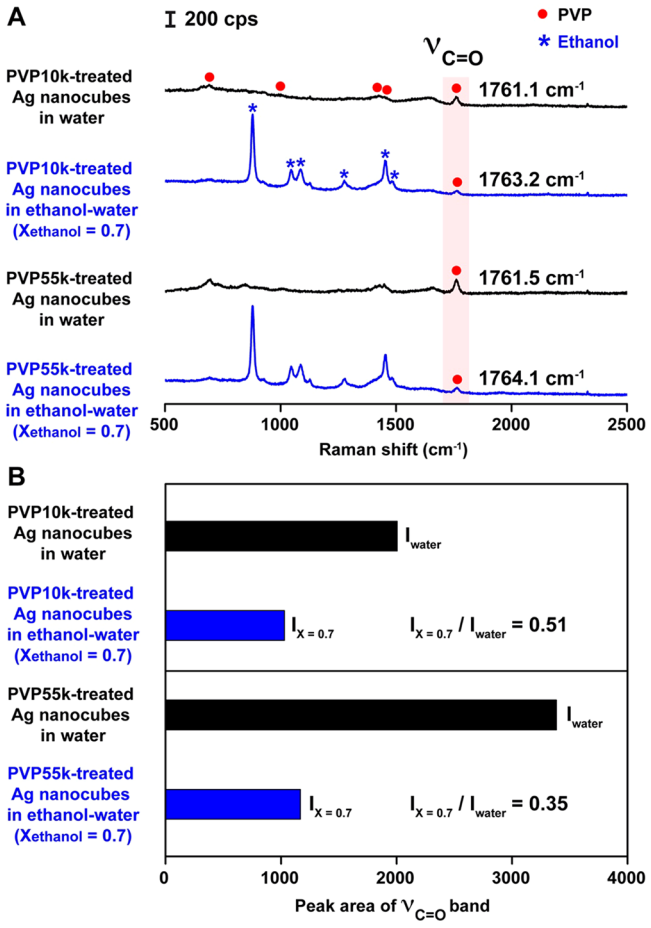


**Figure 6. (A) SERS spectra of PVP10k- or PVP55k-treated Ag nanocubes when dispersed in water and an ethanol–water binary solution at $X_{ethanol}$ = 0.7, respectively. (B) Plot of peak area for the $\nu_{C=O}$ bands of PVP10k or PVP55k adsorbed on Ag nanocubes that were dispersed in water and the ethanol–water binary solution, respectively.**

would extend further from the surface into the solution, leaving fewer numbers of free carbonyl groups in close proximity to the Ag surface for a significant decrease in SERS signal during the transition from water to water–ethanol mixture, consistent with our prior argument. Taken together, SERS is also a sensitive tool for distinguishing the behaviors of PVP with different molecular weights. As demonstrated by Xia and co-workers, the coverage density of PVP on Ag nanocubes in EG could affect the evolution of a Ag nanocube into other shapes.[14] We believe that SERS can be used to extract the information about the conformation of PVP in different solvents, helping to predict the coverage density of PVP on Ag nanocrystals and moving toward the rational syntheses of Ag nanocrystals with different shapes.

## CONCLUSIONS

In summary, we have demonstrated the use of SERS to investigate the binding of PVP to Ag nanocubes and the conformational changes of its loops in response to solvent quality. Our success relies on the detection of the $\nu_{C=O}$ band of the carbonyl group located on the pyrrolidone ring of PVP. When PVP binds to the Ag surface through some of its carbonyl groups, the segments between adjacent binding sites are expelled into the solvent as loops. We discovered that the


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$\nu_{C=O}$ peak displayed in the SERS spectrum was highly sensitive to the solvent involved. For example, the peak position of $\nu_{C=O}$ shifted toward higher frequencies when the PVP-capped Ag nanocubes were suspended in water, EG, and ethanol, respectively, due to the decrease in hydrogen bonding between PVP loops and solvent molecules. On the other hand, when switching between bad and good solvents, the PVP loops underwent conformational changes between collapsed and extended states, altering the separation between the free carbonyl groups and Ag surface and thereby the intensity of the $\nu_{C=O}$ peak. We further demonstrated the use of $\nu_{C=O}$ to monitor the reversible change of PVP loops between collapsed and extended states by switching between a bad and a good solvent. We also demonstrated that SERS embraced the sensitivity for characterizing the behaviors of PVP with different molecular weights in response to different solvents. Collectively, this work not only provides a deep understanding of the interactions among the surface of Ag nanocubes, the PVP polymer, and the solvent but also offers useful guidelines for identifying the right combination of polymer and solvent to suit a particular nanocrystal synthesis. Taking the synthesis of Ag nanocubes as an example, our results suggest that PVP and EG should be a better combination than PVP and water due to the more extended conformation of PVP in EG than in water under ambient conditions. Our observation may explain why most of the reported protocols for Ag nanocubes were based on PVP and EG rather than PVP and water.[24−27] It is worth mentioning that the typical synthesis of Ag nanocubes in the PVP-EG system is often performed at an elevated temperature, and as a result, the PVP−surface and PVP−solvent interactions could be further influenced by temperature. In comparison, when the synthesis involves aqueous solution, one typically has to introduce other components into the system, either preformed seeds or halide ions, in order to obtain the cubic products.[45,46] In principle, the SERS analysis reported in this article could be extended to other systems involving different types of capping agents and solvents.

## EXPERIMENTAL SECTION

**Chemicals and Materials.** Poly(vinylpyrrolidone) (PVP) with an average molecular weight of 10000 (PVP10k) and 55000 (PVP55k), silver trifluoroacetate ($CF_3COOAg$, ≥99.99%), sodium hydrosulfide hydrate ($NaSH{\cdot}xH_2O$), aqueous hydrochloric acid (HCl, 37 wt.%), ethanol (≥99.5%), and sodium borohydride ($NaBH_4$, ≥99%) were all obtained from Sigma-Aldrich. Ethylene glycol (EG) was ordered from J. T. Baker. Acetone (≥99.5%) was acquired from Alfa Aesar. All chemicals were used as received. Aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ·cm at room temperature.

**Synthesis of Ag Nanocubes.** We used polyol reduction for the synthesis of Ag nanocubes with an average edge length of 39.7 ± 1.4 nm, in which PVP55k served as both a capping agent and a colloidal stabilizer.[27] The as-prepared Ag nanocubes with PVP55k adsorbed on their surface (denoted PVP-capped nanocubes) were crushed out with acetone and then collected by centrifugation, followed by washing with water before they were redispersed in water at a final concentration of $6.0 \times 10^{12}$ particles/mL for future use.

**Raman Measurements.** We used a Renishaw inVia Raman Spectrometer integrated with a Leica microscope to record Raman spectra. We calibrated the Raman spectrometer using Si(100) as a standard sample every time before the start of SERS measurements. Based on 10 separate measurements over a period of about 1 month, the spectrometer consistently gave the Raman shift of Si at 520.18 $cm^{-1}$, with a standard deviation of 0.15 $cm^{-1}$ (Table S1). In a typical SERS measurement, we transferred an aliquot of 25 μL from the sample into a polydimethylsiloxane cell, covered the cell with a glass coverslip, and placed the cell on the sample stage of the microscope. We then collected the SERS spectra using an excitation wavelength of 532 nm, 100× objective lens, laser power of 50% (with maximum at 50 mW), and collection time of 10 s. For the SERS spectra recorded from Ag nanocubes on Si wafer, we used 100× objective lens, laser power of 10%, and collection time of 10 s.

**SERS Measurements of PVP-Capped Ag Nanocubes Dispersed in Different Solvents.** In a typical experiment, we withdrew 12 μL of PVP-capped Ag nanocubes from an aqueous suspension and redispersed them in 1 mL of a specific solvent, such as water, EG, ethanol, acetone, or ethanol−water binary mixture. After collection of the solids by centrifugation, we redispersed them in 100 μL of the same solvent for 30 min prior to SERS measurements. All SERS measurements were performed at least three times for analyzing peak positions and peak areas with error bars.

**SERS Measurements of PVP-Capped Ag Nanocubes Alternatingly Dispersed in Water and Ethanol.** By following the standard protocol described above, we collected a series of SERS spectra of the sample containing PVP-capped Ag nanocubes by successively dispersing the same sample in water (first), ethanol (second), water (third), ethanol (fourth), and water (fifth), respectively. In the first step, we dispersed 12 μL of the aqueous suspension of PVP-capped Ag nanocubes in 1 mL of water. After collecting the solids by centrifugation, we redispersed them in 100 μL of water (first) for 30 min before the first SERS spectrum was recorded. In the second step, we collected the solids from the previous SERS sample and then dispersed them in 1 mL of ethanol. After the collection of solids, they were redispersed in 100 μL of ethanol (second) for 30 min before the second SERS spectrum was recorded. The additional three steps were repeated using water (third), ethanol (fourth), and water (fifth) as the solvent to take three additional SERS measurements.

**SERS Measurements of Ag Nanocubes Capped by PVP with Different Molecular Weights.** In the first step, we dispersed 36 μL of the PVP-capped Ag nanocubes in 3 mL of water, followed by the addition of 0.6 mL of ice-cold aqueous $NaBH_4$ solution (0.6 mg/mL) to attain a final concentration of 0.1 mg/mL in the suspension. After 24 h, we withdrew 0.75 mL of the suspension and mixed it with 0.7 mL of an aqueous solution containing PVP10k or PVP55k (7.2 mg/mL). The final concentrations of $NaBH_4$ and PVP were kept at 0.05 and 3.47 mg/mL, respectively. After 3 h, we collected the solids through centrifugation and then redispersed them in 50 μL of water or a mixture of water (15 μL) and ethanol (35 μL) for SERS measurements.

**Instrumentation and Characterization.** The nanoparticles were collected using an Eppendorf 5430 centrifuge (Eppendorf North America, Hauppauge, NY). The concentration of Ag nanocubes was measured using an inductively coupled plasma mass spectrometer (ICP-MS, NexION 300Q, PerkinElmer, Waltham, MA). The UV−vis spectra were recorded using a Cary 50 spectrometer (Agilent Technologies, Santa Clara, CA). Hydrodynamic diameters were determined using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK). The Raman and SERS spectra were collected using a Renishaw inVia Raman Spectrometer (Wotton-under-Edge, UK) integrated with a Leica microscope (Wetzlar, Germany). TEM images were collected using a Hitachi HT7700 microscope (Hitachi, Japan) operated at 120 kV.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c01668.

TEM image of the Ag nanocubes used in the present study and a histogram of the particle size distribution; UV−vis spectra of the PVP-capped Ag nanocubes in water, EG, and ethanol; photos of vials containing 3 mL of PVP solution in water, ethanol, EG, and acetone,



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resepctively; UV−vis spectrum of the PVP-capped Ag nanocubes when dispersed in acetone; SERS spectrum recorded from the PVP-capped Ag nanocubes dispersed in acetone; SERS spectrum recorded from the PVP-capped Ag nanocubes deposited on a Si wafer; SERS spectra recorded at different time points after introducing 30 $\mu$L of the aqueous suspension of the PVP-capped Ag nanocubes into 270 $\mu$L of PVP solution in EG at a concentration of 3.84 mg/mL and the plots of peak position and area for the $\nu_{C=O}$ band of PVP at different time points; SERS spectra recorded at different time points after the introducing 30 $\mu$L of the aqueous suspension of the PVP-capped Ag nanocubes into 270 $\mu$L of aqueous PVP solution at a concentration of 3.84 mg/mL and plots of peak position and area for the $\nu_{C=O}$ band of PVP at different time points; the SERS spectra recorded from an aqueous suspension of the PVP-capped Ag nanocubes before and after the addition of aqueous $NaBH_4$ solution to attain a final concentration of 0.05 mg/mL; the SERS spectra recorded from an aqueous suspension of the PVP-capped Ag nanocubes before and after the addition of aqueous $NaBH_4$ solution to attain a final concentration of 0.1 mg/mL; and the Raman peak of Si(100) at 520.18 $cm^{-1}$, which served as a standard for the calibration of Raman shift (Figures S1−S9 and Table S1) (PDF)

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### Notes

The authors declare no competing financial interest.

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