Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Mechanism and modeling of Poly(Vinylpyrrolidone)(PVP) facilitated Synthesis of Silver Nanoplates

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1. Particle size distribution graph of Ag nanoplates

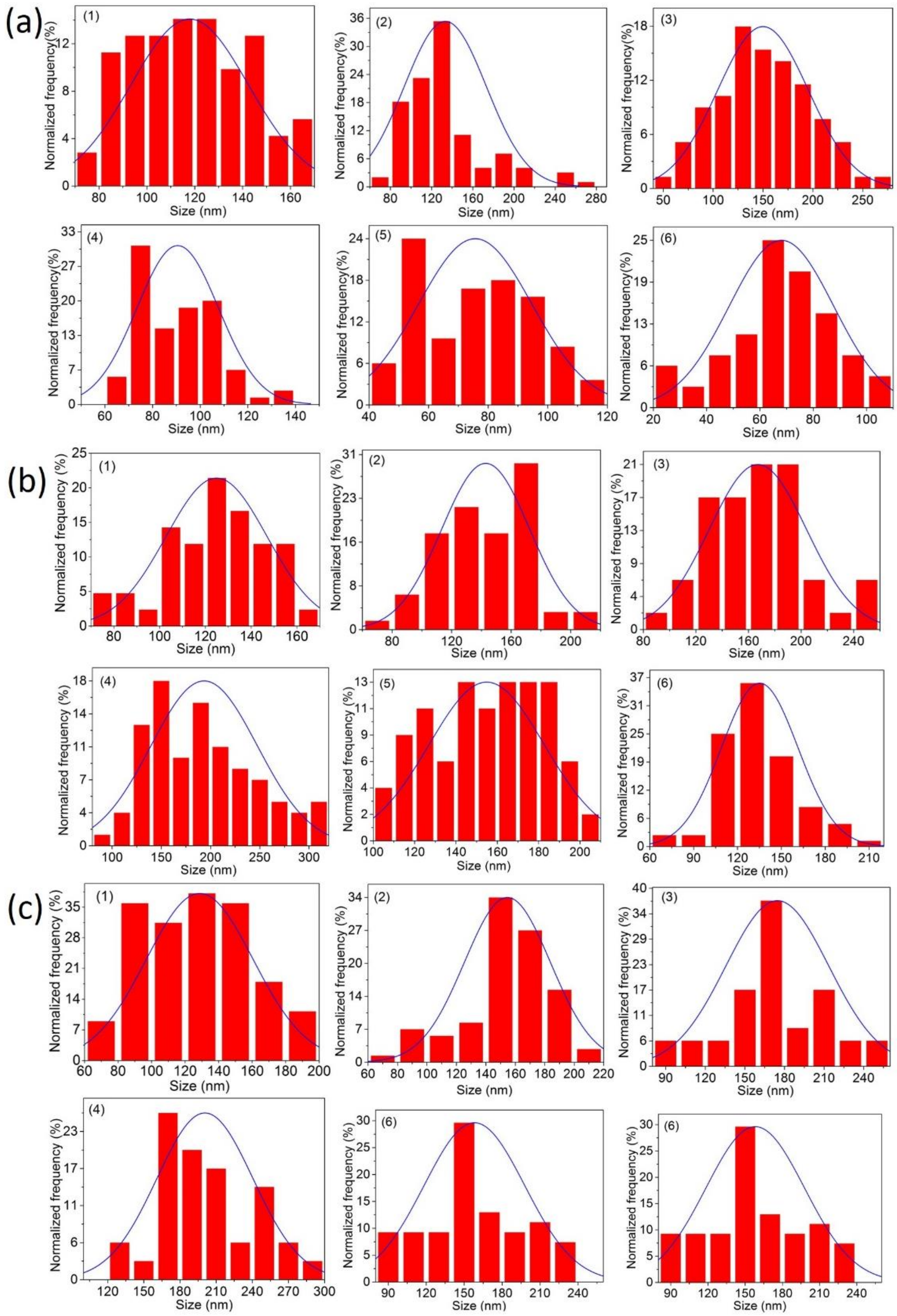

Fig. S1 Particle size distribution graph of Ag nanoplates with different molecular weight of PVP (a) 10 kDa, (b) 29 kDa and (c) 40 kDa. (1) - (6) corresponds to different molar ratio of PVP/$AgNO_3$ [P:S] as 5, 15, 22, 30, 38 and 48

2. FT-IR data for [P:S] ratio = 15

We performed the FT-IR analysis of nanoparticles stabilized with PVP of different molecular weight at [P: S] ratio = 15 and the results are shown in Figure S2. The magnitude of the band shift of C=O for PVP stabilized Ag nanoplates is 30 cm^{-1} for 10 kDa, 16 cm^{-1} for 29 kDa and 11 cm^{-1} for 40 kDa. These band shifts suggest that the strength of interaction follows the trend 10 kDa > 29 kDa > 40 kDa, and this observation is consistent with that of molar ratio of 30.

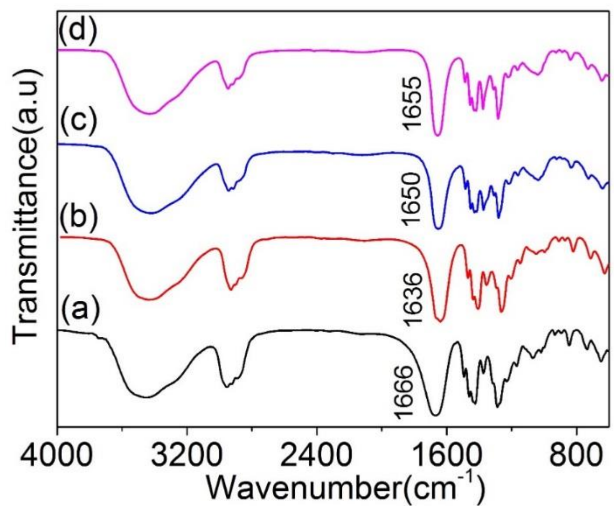

Fig. S2 FT-IR spectrum of (a) solid PVP (control) and Ag nanoplates stabilized with PVP of different molecular weight (b) 10 kDa, (c) 29 kDa and (d) 40 kDa at [P:S] ratio = 15.

3. Concentration of (-OH) ions at each molar ratio ([P:S])

Table S1: - Concentration of (-OH) ions: molarity ($Mx10^{-3}$)

[P:S]	10 kDa	29 kDa	40 kDa
5	2.845	0.981	0.711
15	8.71	3	2.17
22	13.06	4.5	3.26
30	17.02	5.86	4.25
38	21.7	7.5	5.44
48	27.3	9.41	6.22

4. Method to find reaction rate constant

The value of k_1 estimated from the kinetic data of Washio et al [1] for PVP of molecular weight 29 kDa at [P:S] ratio = 15. It is assumed that the number of silver atoms formed at each time period are completely utilized for nanostructure growth. The number of nanostructures formed in the reaction mixture are calculated based on the percentage conversion of $AgNO_3$ and number yield of nanostructure provided in the literature. The number of silver atoms constituting the nanostructures at different time periods are calculated by the following method. In FCC, the ratio of volume of atoms constituting the nanoparticle to the volume of nanoparticle is considered to be 74.1%. Therefore the number of Ag atoms (N) comprised in a nanostructure of size D_0 can be calculated by the $\frac{\mathrm{NV}}{\mathrm{V_{nanoparticle}}} = 74.1\%$, where the radius of the silver metal atom is 0.144 nm. For spherical particles, the number of atoms (N) is equal to $31.01D_0{}^3$ and for a triangular plate it is $25.66a^2w$, where w is the thickness and a is the edge length of the plate. Based on this, the concentration of remaining silver ions and hydroxyl ions of PVP in the solution are calculated at different time period with respect to their initial values. Equation has been fitted with this derived data from the literature by using both MATLAB solvers ode45 and fminsearch simultaneously. The estimated value of rate constant k1 is $2.242\mathrm{x}10^{-4}((\mathrm{mol/m}^3)^{-2}\mathrm{hr}^{-1})$.

We have estimated k_1 from our kinetic experiments (shown in Figure S3) using 40 kDa PVP at [P: S] ratio = 30. The new estimate of k_1 is 1.63 $\mathrm{x}10^{-4}$ $(\mathrm{mol/m}^3)^{-2}\mathrm{hr}^{-1}$, which is similar (in the order of magnitude) to the value obtained from Washio's data. The difference could be due to the use of polymers of different molecular weight in these two experiments.

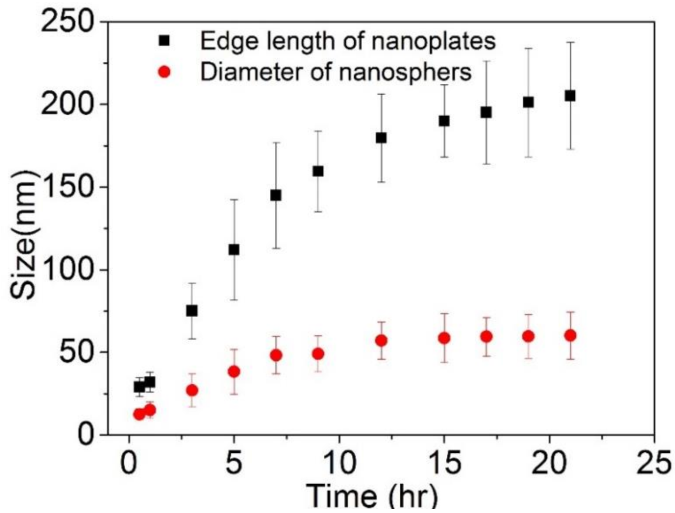

Fig. S3 Time evolution of edge length of Ag nanoplates and diameter of nanospheres derived from the experimental data

5. Method to find number of nanoplates and nanoparticles

The number of particles corresponds to a fixed volume of the reaction mixture. The number of plates and spheres are counted from several (~ 10) TEM images corresponding to the volume of sample used in the preparation of TEM grids, and then scaled to the total reaction mixture. The details of the calculation is given below.

Let A is area of the TEM grid, *a* is area of the frame and *n* is number of particles in area *a*.

Total number of particles in a grid, $\mathrm{N} = \frac{\mathrm{n \ x \ A}}{\mathrm{a}}$

Let V is volume of sample used for drop casting on TEM grids and V_t is the volume of the reaction mixture

Then the total number of particles in the whole reaction mixture, $N_t = \frac{\mathrm{Nx}V_t}{\mathrm{V}} = \frac{\mathrm{nA}V_t}{\mathrm{aV}}$.

This approach is followed to calculate number of nanoplates and nanospheres.

References

[1] I. Washio, Y.Xiong, Y.Yin and Y.Xia, Advanced *Materials,* 2006, 18, 1745-1749.