Electronic Supplementary Material for PCCP

Electronic Supplementary Information

Real Time Monitoring of the *In situ* Growth of Silver Nanoparticles in a Polymer Film under Ambient Conditions

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Contents

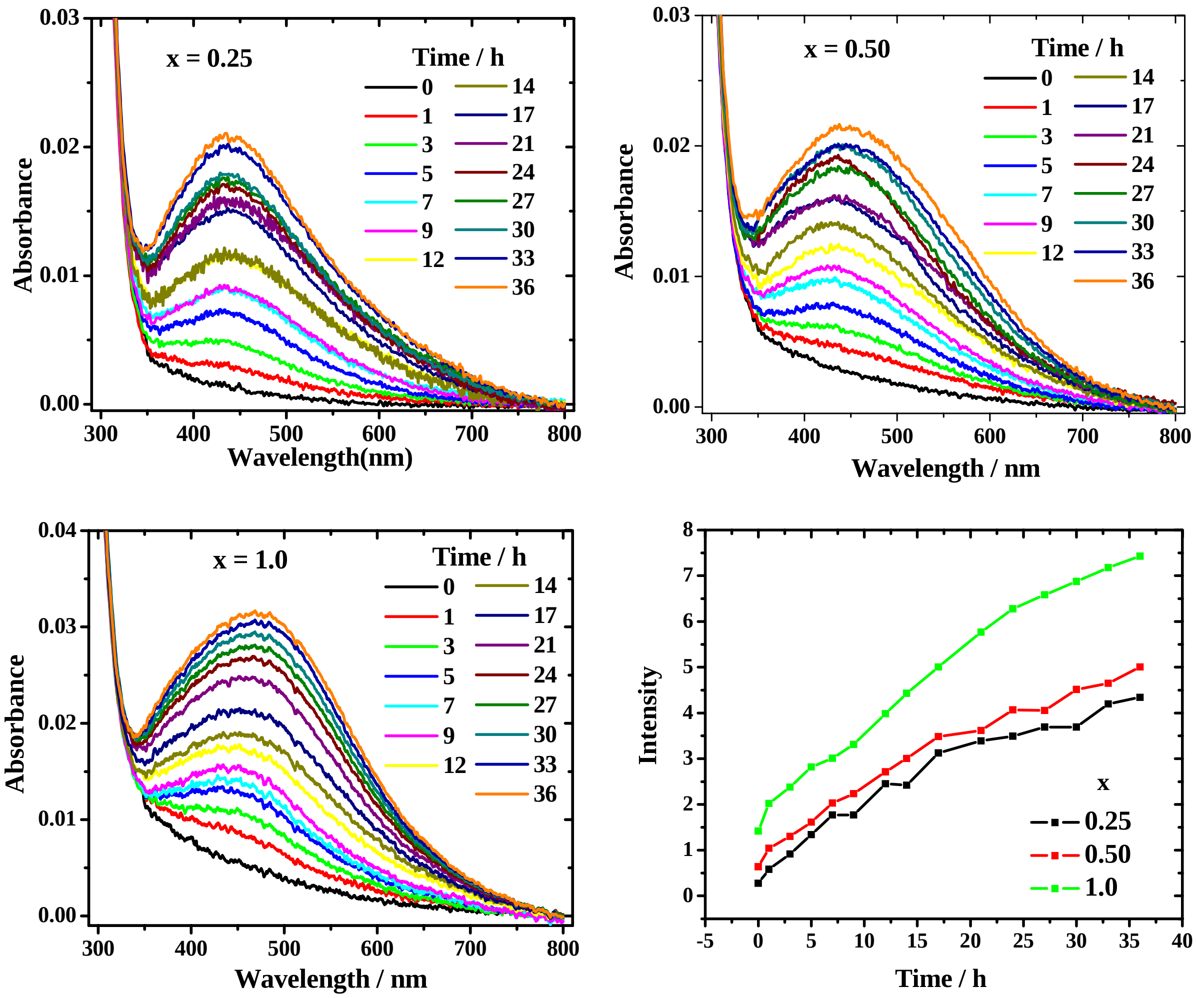
Additional supporting information

Movie showing the real time growth of the nanostructures: **tpr_movie.mpg**

Electronic absorption studies

Electronic absorption spectra of Ag-PVP films coated on glass substrates were recorded on a Cary 100 Bio UV-Visible Spectrophotometer. The glass substrates used had less than 0.001 absorbance at wavelengths above 350 nm. Spectra were deconvoluted using two Gaussian peaks one for the plasmon absorption and another for the absorption below 350 nm; the plasmon absorption intensities (integrated area that takes into account amplitude and possible width variations) and peak positions obtained are plotted against time in Figure 1b in the main text. In the last panel of the figure below, we provide the integrated (above 350 nm) intensities for the spectra as a function of time for films with different values of the Ag/PVP weight ratio, x.

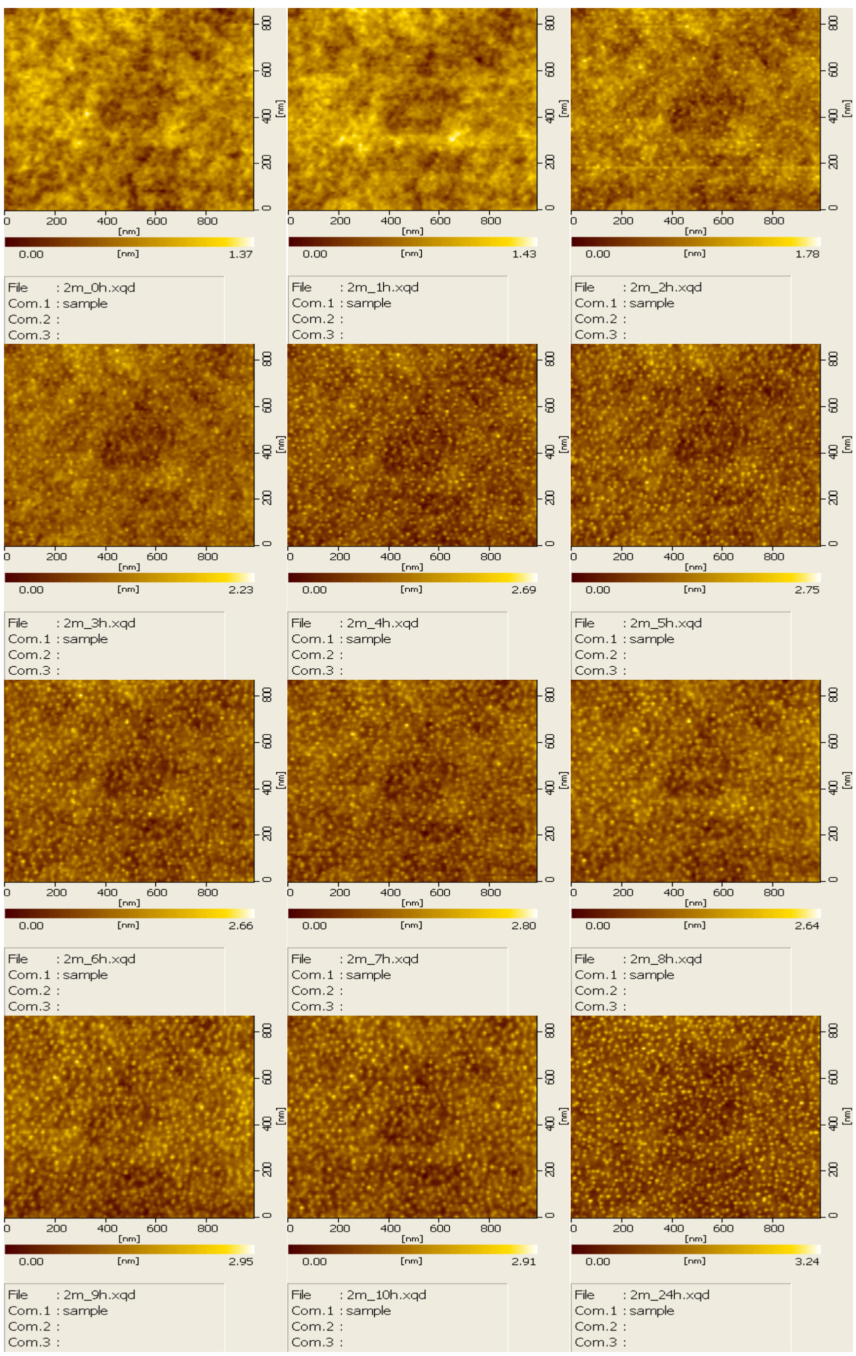
Spectra of Ag-PVP - time/composition variation



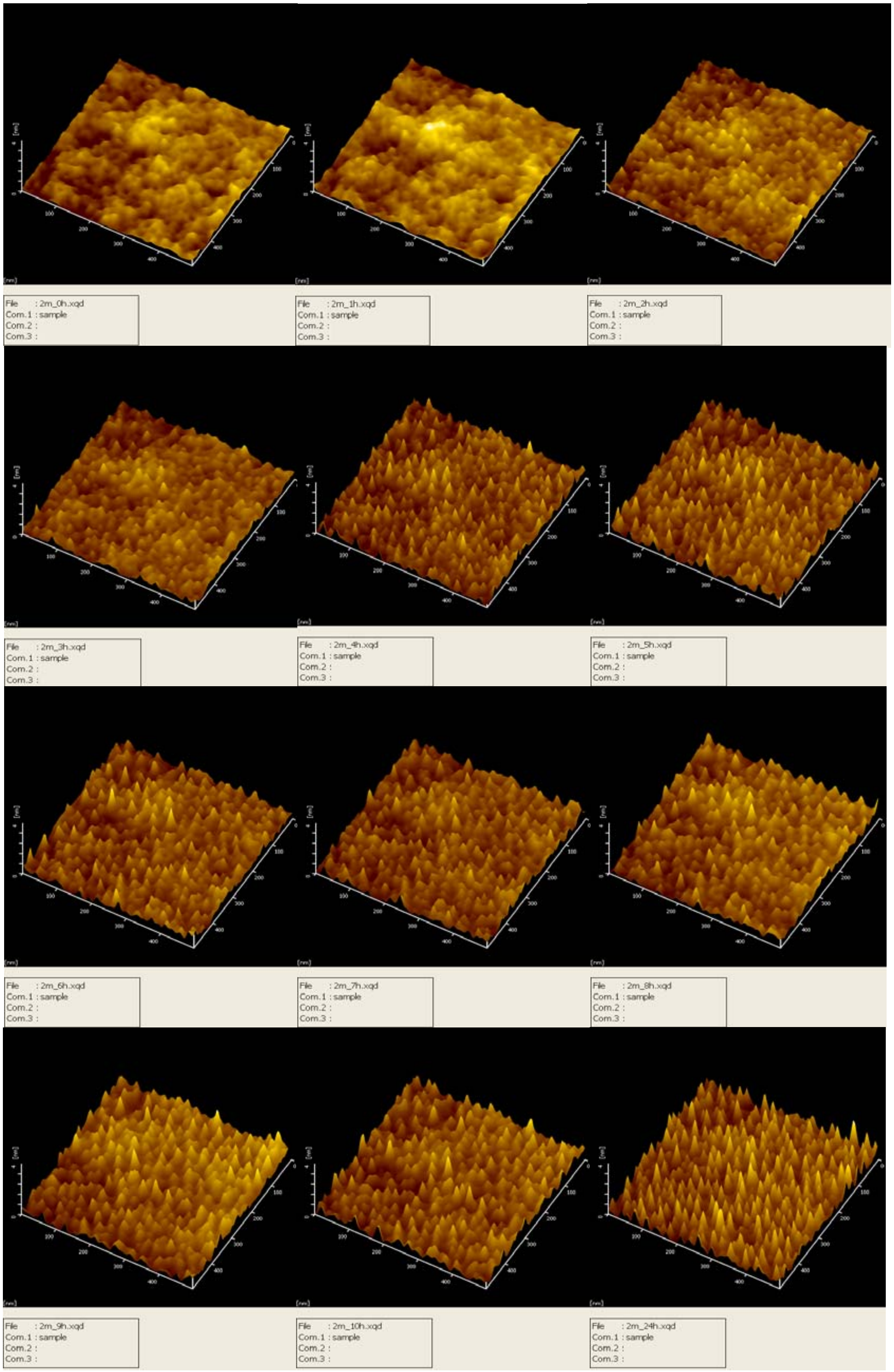
Atomic force microscopy

AFM images were recorded on Ag-PVP films (x = 1.0) coated on glass substrates, using a SEIKO Model SPA 400 atomic force microscope in the dynamic force mode using a cantilever having a force constant of 12 N/m. After each image scan the tip was retracted by 100 μm; approach was carried out again for the subsequent scan. Films coated on mica plates showed similar features as those on glass substrates ruling out any specific substrate effects. AFM imaging was carried out also on NT-MDT Model Solver Pro M microscope using semicontact mode; observations were similar.

2-D AFM images of Ag-PVP film corresponding to Figure 2 in main text: time elapsed in hours for each imaging after the first one is indicated in the file names.

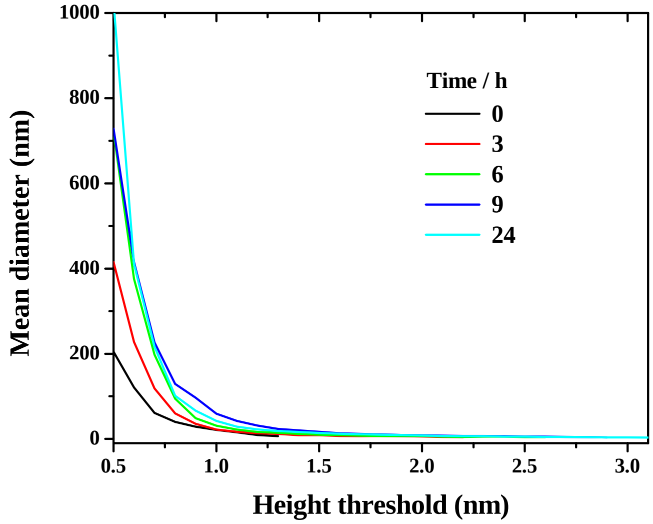


3-D AFM images of Ag-PVP film corresponding to Figure 2 in main text: time elapsed in hours for each imaging after the first one is indicated in the file names.

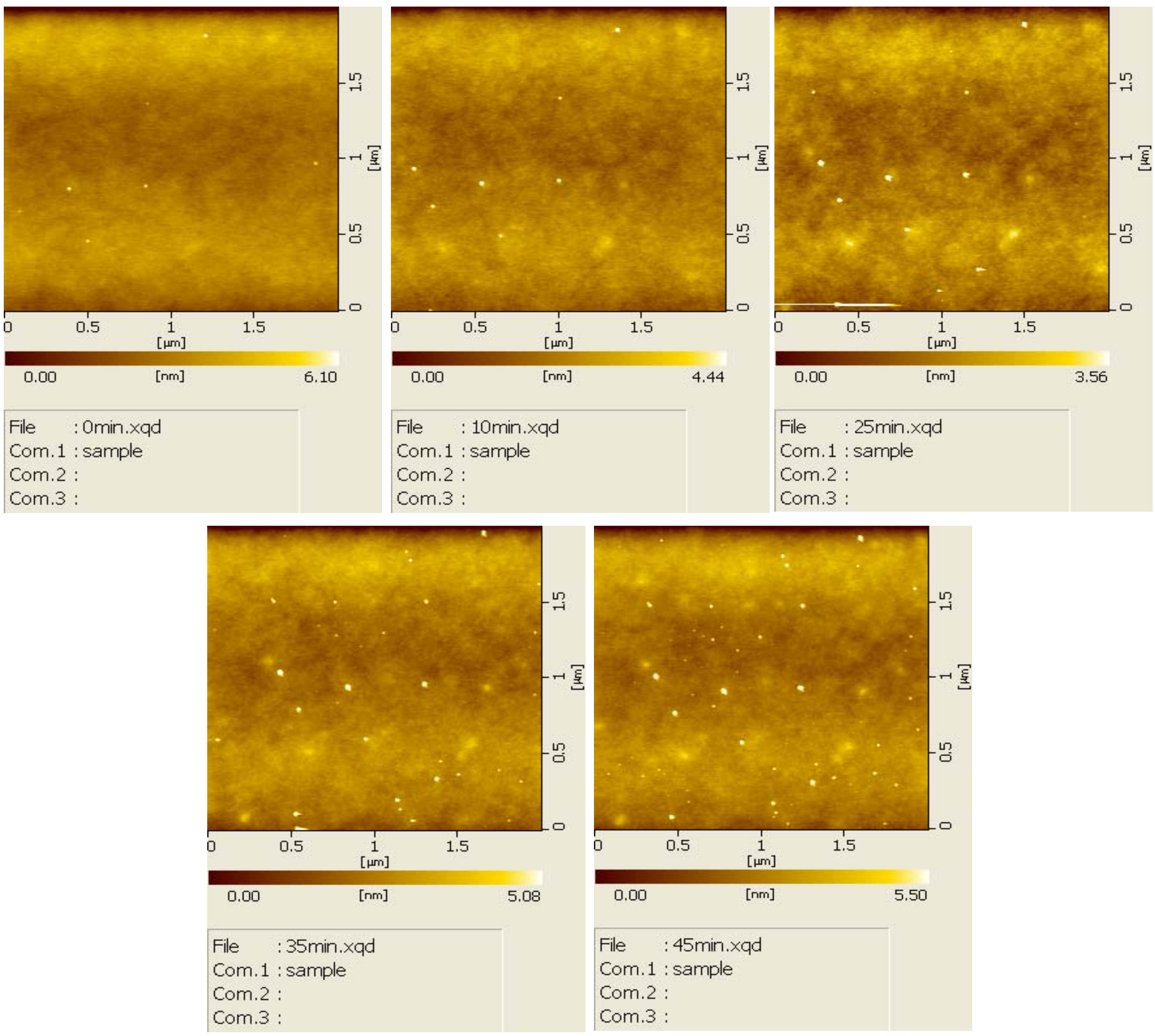


Grain size analysis

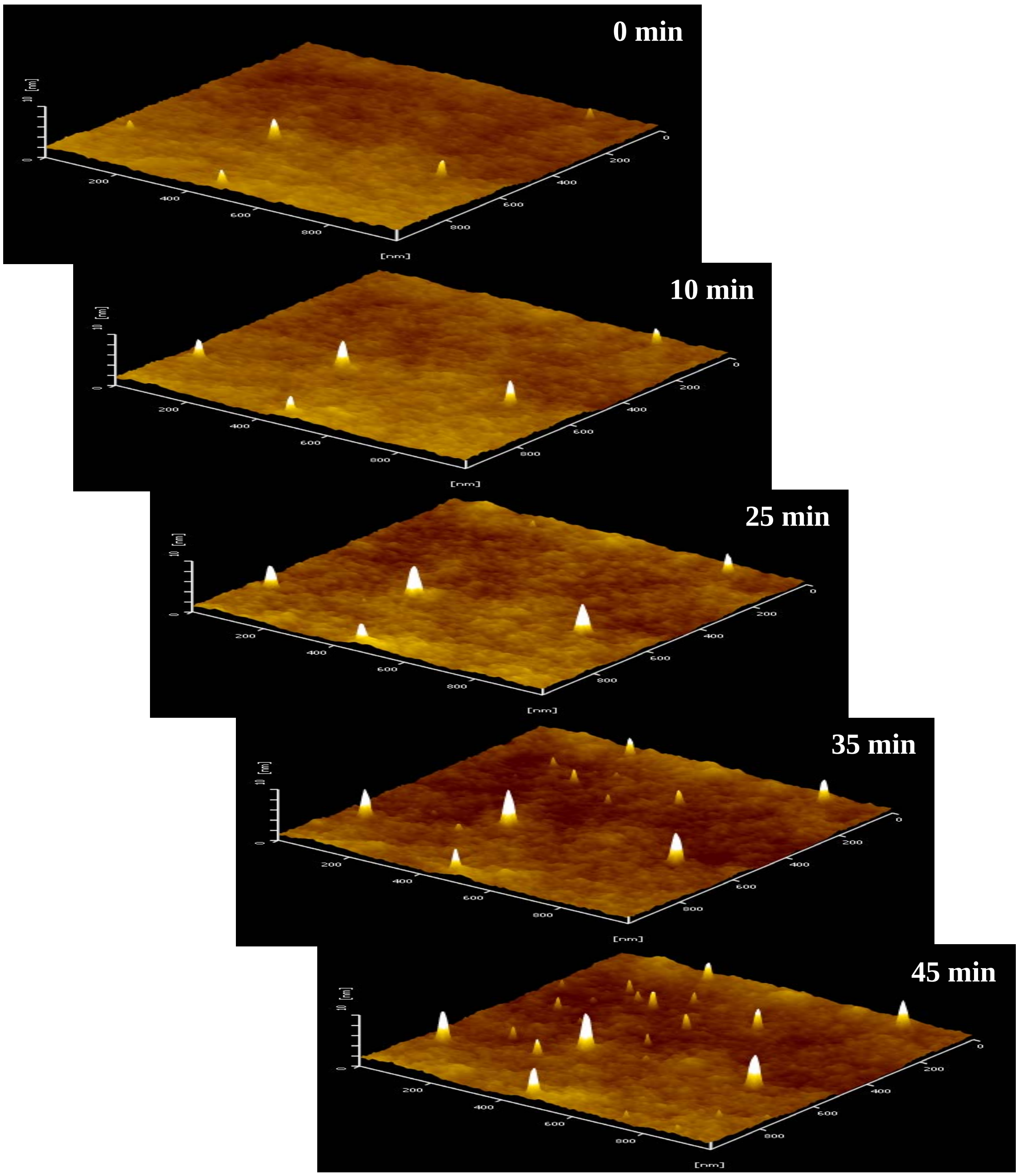
Grain size analysis was carried out using SPIWin Version 3.01 provided by the manufacturer of the SEIKO Model SPA 400 AFM. For each image, the grain size distribution was analyzed at different height thresholds with intervals of 0.1 nm, from 0.5 nm to 3.1 nm. Plot of the mean grain diameter at each height, for the images at different times is shown below.



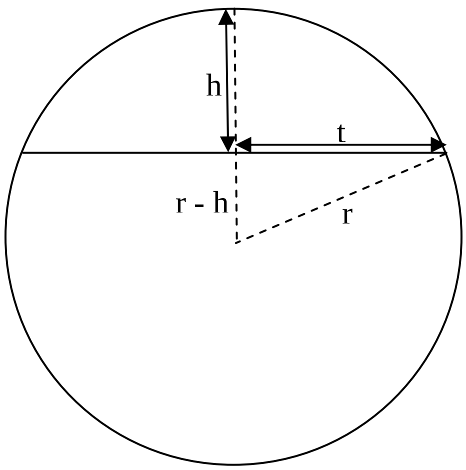
2-D AFM images of the thinner Ag-PVP film (Figure 4 in main text) : time elapsed in minutes for each imaging after the first one is indicated in the file names.



3-D AFM images of the thinner Ag-PVP film (Figure 4 in main text): time elapsed in minutes for each imaging after the first one is indicated.



The dimensions of the structures were examined to verify whether they represent segments of spheres. If a segment is part of a circle (cross section of sphere), the radius or half-length of the chord (t) and height (h) of different sections of the segments (preferably taken along different directions as well) will provide the same value of radius (r) of the circle (see figure and equation below). A consistent value of radius within ~ 10% variation was taken as evidence for the segment being part of a sphere. Based on this analysis, the structures in the above images are suggested to be parts of individual particles which are nearly spherical.



From the geometry of the circle shown in figure, the radius of the circle (r), height of the segment (h) and half-length of the chord (t) can be related as:

$$r^2 = (r-h)^2 + t^2$$

Rearranging the above equation, one gets the following relation,

$$r = \frac{t^2 + h^2}{2h}$$

Analysis of the the image at time = 45 min in Fig. 4 (right panel)

Radius of the section at different heights is noted and the radius estimated from each is shown below.

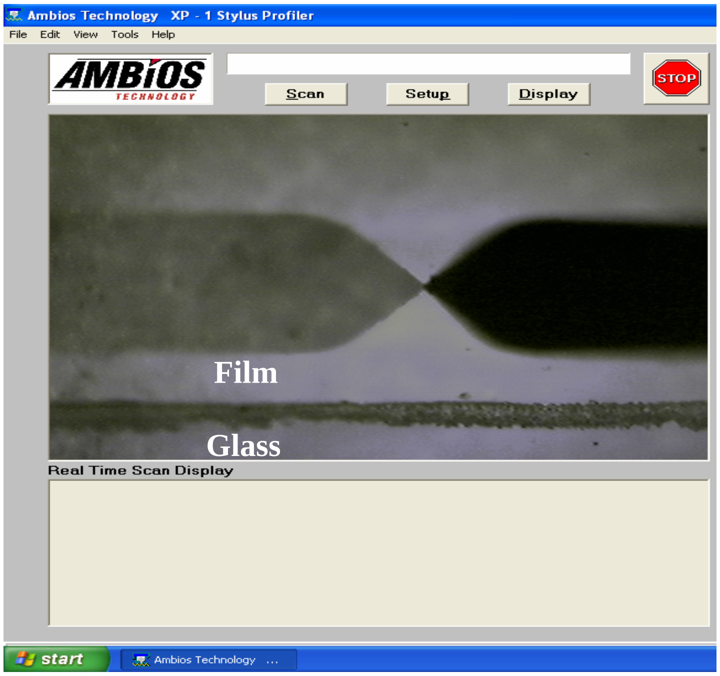
t (nm)	h (nm)	r (nm)
17.66	4.13	39.8
14.57	3.02	36.7
12.25	2.06	37.5
11.34	1.70	38.7
9.80	1.18	41.3
5.54	0.37	41.7

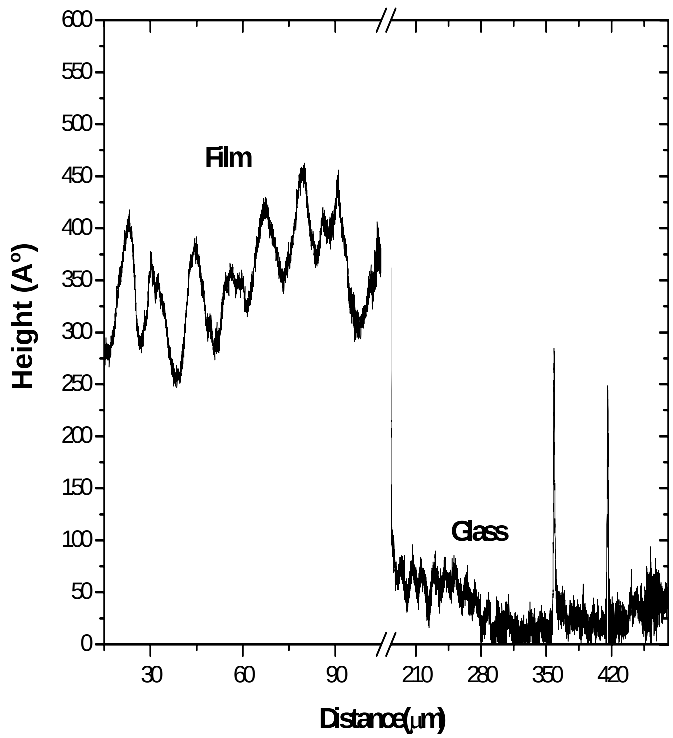
The data show that the segment is part of a circle (sphere in 3-D) with an average radius of 39.3(2.0) nm.

Film Thickness

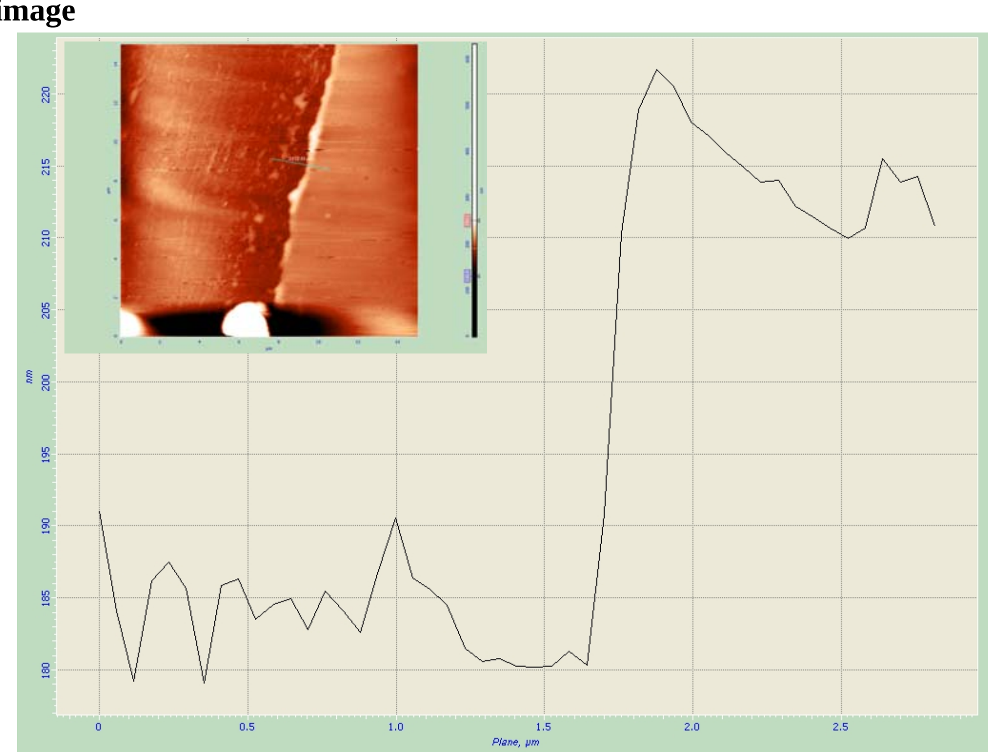
A sharp edge was created on the film. Several samples were checked. Typical image in the profilometer along with its trace and the AFM image with the relevant line profile are shown below.

Profilometer trace





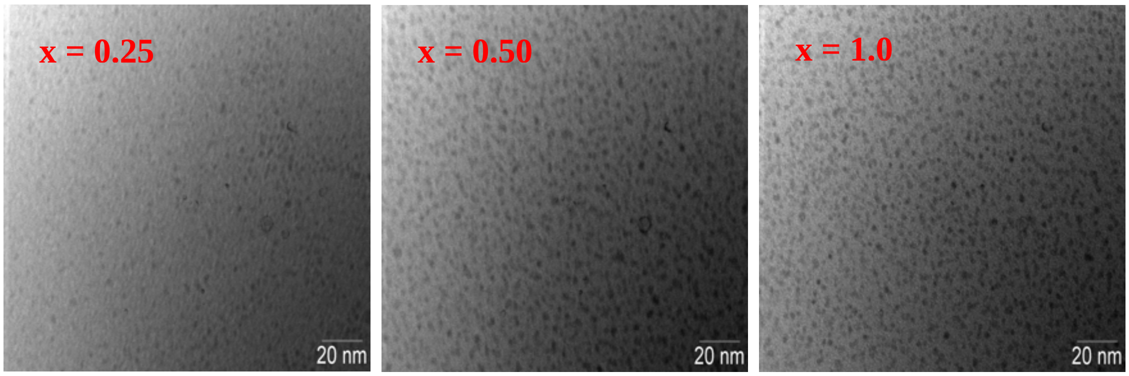
AFM image



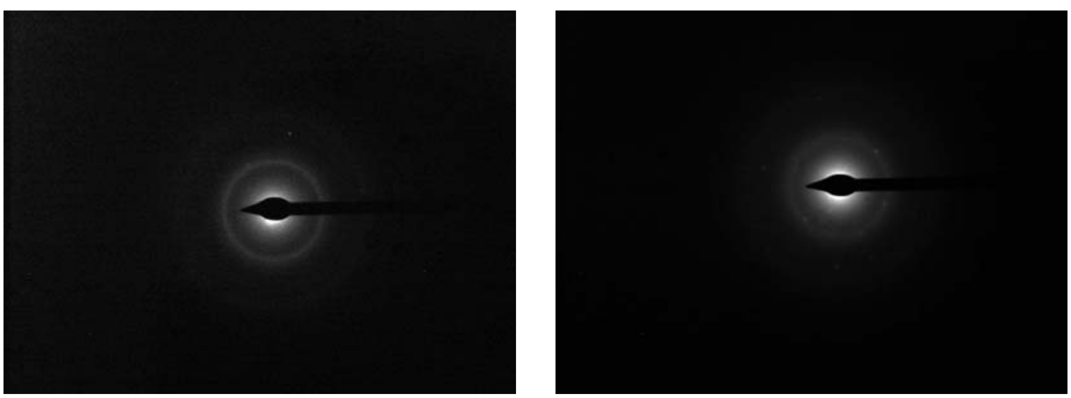
Transmission electron microscopy

The samples were examined in TECNAI G^2 FEI F12 transmission electron microscope at an accelerating voltage of 120 kV.

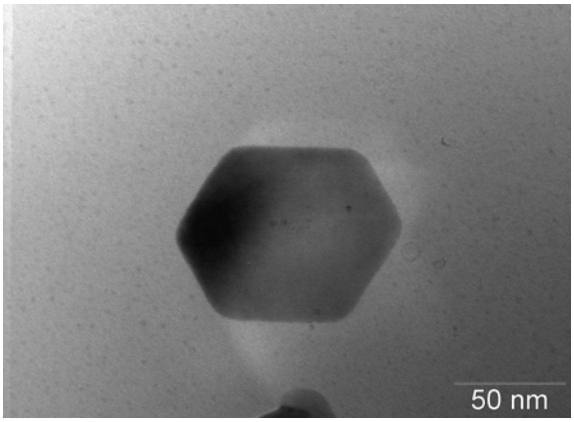
TEM images of films with different Ag/PVP composition

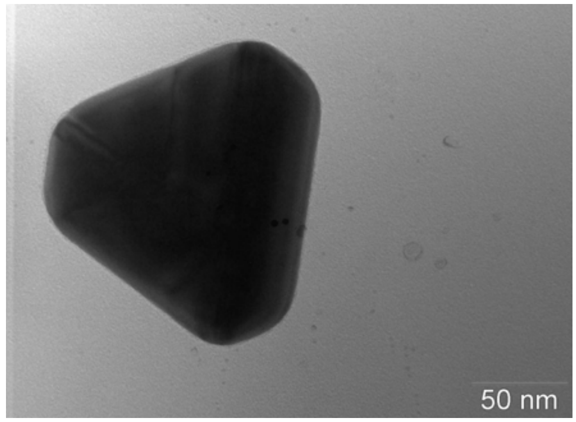


Electron diffraction patterns for film with x = 1.0

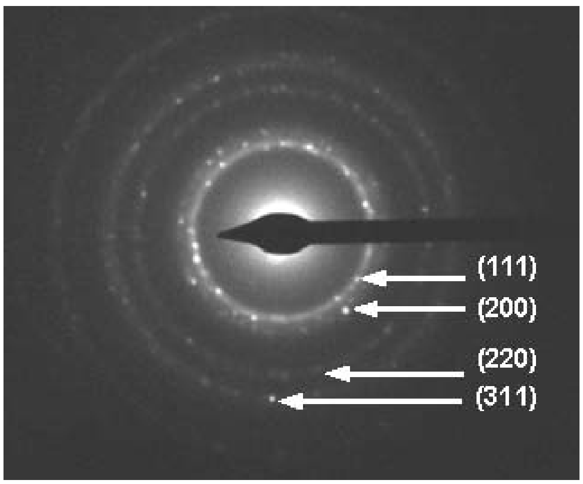


TEM images of film with x = 1.0 showing some well-formed large particles





Electron diffraction images of the well-formed structures

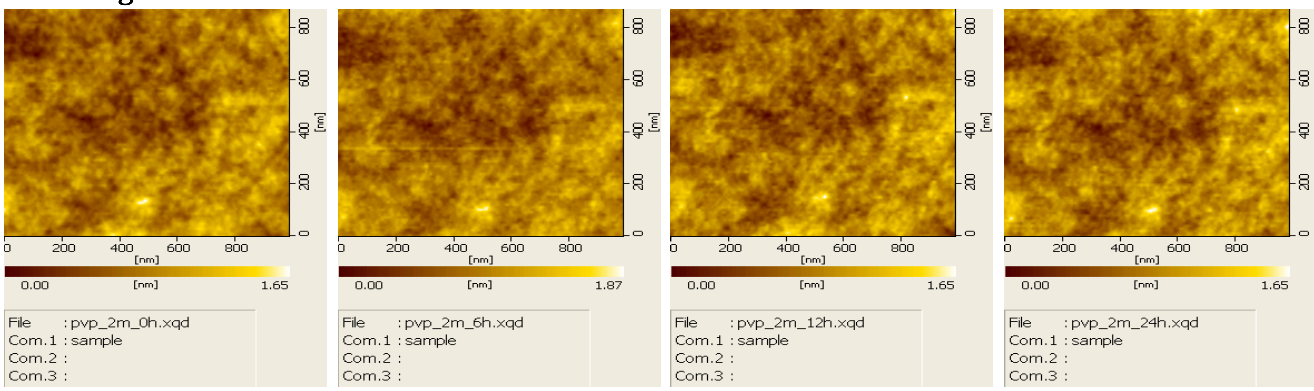


Control Experiments

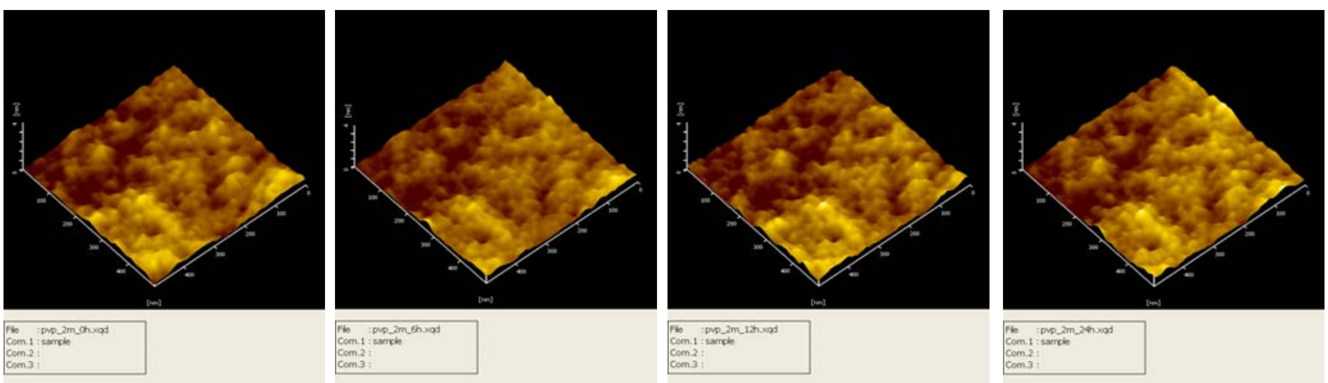
AFM imaging of pure PVP films spin-coated on glass

The following AFM images (0, 6, 12, 24 h) show no growth of nanostructures upto 24 h, proving that the growths observed in the Ag-PVP films are associated with the formation of Ag nanoparticles.

2-D images

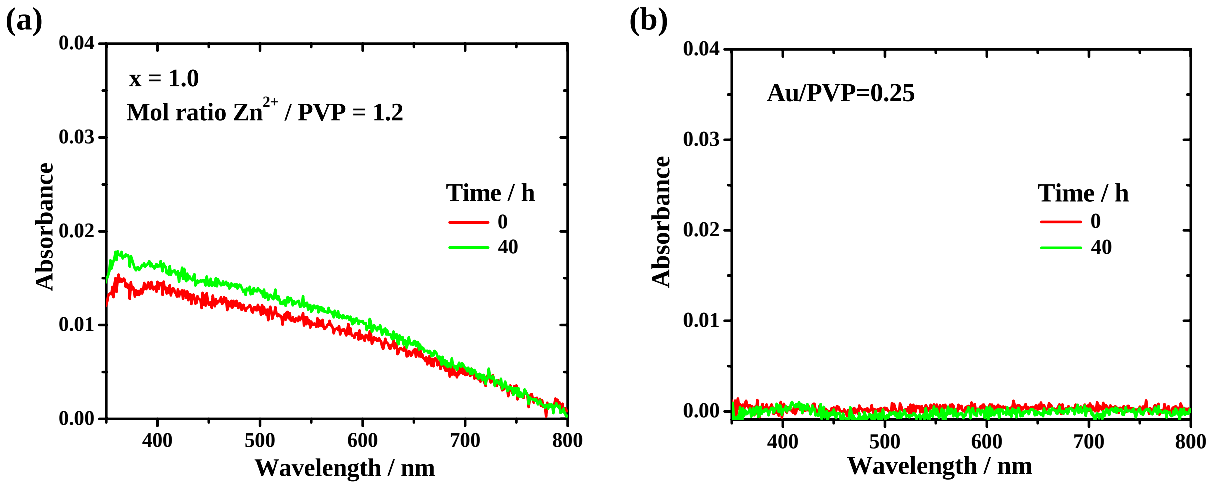


3-D images



Absorption spectra: (a) $AgNO_3$-PVP films with added Zn^{2+}, (b) $HAuCl_4$-PVP films

(a) Films were prepared using aqueous solutions of PVP in which $Zn(NO_3)_2$ was added first, followed by $AgNO_3$. The spectra of fresh films and those kept for 40 h are shown below. The broad and weak absorption is due to the zinc salt; there is no sign of formation of silver nanoparticles even after 40 h. (b) Similar is the situation in the case of PVP films with $HAuCl_4$. Due to the relatively lower solubility of $HAuCl_4$ in water containing PVP, films with x = 0.25 was studied; as films with similar ratios showed silver nanoparticle formation, it is concluded that the metal nanoparticle formation under ambient conditions does not occur with $HAuCl_4$.



A plausible mechanism of Ag^+ reduction in PVP film

A mechanism for the reduction of Ag^+ to Ag by PVP, inferred using the control experiments is presented below.