ORIGINAL CONTRIBUTION

Morphology and size-controlled synthesis of silver nanoparticles in aqueous surfactant polymer solutions

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Abstract We have employed a number of reducing and capping agents to obtain Ag(0) metallic nanoparticles of various sizes and morphologies. The size and morphology were tuned by selecting reducing and capping agents. Spherical particles of 15 and 43 nm diameter were obtained when 1 wt% aqueous starch solution of $AgNO_3$ precursor salt was reduced by D(+)-glucose and NaOH, respectively, on heating at 70 °C for 30 min. Smaller size particles obtained in the case of D(+)-glucose reduction has been attributed to the slow reduction rate by mild reducing agent D(+)-glucose compared to strong NaOH. Conducting the reduction at ambient temperature of silver salt in liquid crystalline pluronic P123 and L64 also gave spherical particles of 8 and 24 nm, respectively, without the addition of any separate reducing agent. NaOH reduction of salt in ethylene glycol (11 g)/polyvinyl pyrolidone (PVP; 0.053 g) mixture produced large self-assembled cubes of 520 nm when smaller (26–53 nm) star-shaped sharp-edged structures formed initially aggregated on heating the preparation at 190 °C for 1 h. Increasing the amount of PVP (0.5 g) in ethylene glycol (11 g) and heating at 70 °C for 30 min yielded a mixture of spherical and non-spherical (cubes, hexagons, pentagons, and triangle) particles without the addition of an extra reducing agent. Addition of 5 wt% PVP to 1 wt% aqueous starched solution resulted in the formation of a mixture of spherical and anisotropic structures when solution heated at 70 °C for 1 h. Homogeneous smaller sized (29 nm) cubes were synthesized by NaOH reduction of $AgNO_3$ in 12.5 wt% of water-soluble polymer poly (methyl vinyl ether) at ambient temperature in 30 min reaction time.

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Introduction

The preparations of nanomaterials have been conducted [1] for academic and application purposes for the last two decades. The metal nanoparticles have a number of applications from electronics and catalyst to pharmaceutical and medical diagnosis. In review articles [2, 3] and the references cited therein, the authors have covered in

detail the synthesis, characterization, properties, and applications of nanometals. Researchers have been synthesizing these materials based on the principle of capturing the atoms in the early stage of reaction and stabilizing them by capping or stabilizing agents. Normally, surfactants molecules or polymers are used as stabilizing agents to keep material floated in the solvent. In the last one decade, the materials got much attention from researchers all over the world, and now, they are being studied in the new subject of nanoscience or nanotechnology which were not known before, although the materials were prepared and studied for a long time. Barnickel [4] and Petit et al. [5] synthesized Ag nanoclusters stabilized by surfactant molecules in water-in-oil microemulsions (W/O). Reduction of precursor salts occurred in the core of microemulsions at different water content (W_0) of the systems. Ag nanometal particles in the size range 3.3–4.4 and 1–14.8 nm were prepared, respectively. W/O reaction media used for nanomaterial synthesis consist of an aqueous core stabilized by a layer of surfactant molecules dispersed in organic solvent bulk phase. Several other methods using toxic organic solvents and reducing agents have been applied to prepare the nanomaterials [6, 7]. The preparation of these materials in green solvents such as water and other non-toxic solvents are becoming popular. Among the non-toxic and green solvents used until recently, liquid or supercritical carbon dioxide [8, 9], water [10], and polyols [11] are the most common. Because of the requirement of high-pressure vessels, the liquid and SC CO_2 have not become the favorite media for nanomaterial preparations. In addition, the synthesis of nanomaterials in superheated water has not attracted much attention because of high temperature and subsequent development of high pressure in the reactor. Thus, the aqueous solutions containing capping or stabilizing agents remained the attractive media for nanomaterial preparations to date. Solvent-induced shape evolution of polyvinyl pyrolidone (PVP)-protected spherical Ag(0) nanoparticles into triangular nanoplates and nanorods were reported [12]. PVP acted as reducing agent for $AgNO_3$ precursor salt in PVP/pyridine reaction mixture. Shape of nanomaterial changed from spherical and polyhedral to quadrilateral, triangular plates, truncated and non-truncated triangular plates, nanorods, and circular disks by adjusting the precursor salt to PVP monomer units ratio. Microwave-assisted synthesis of Pt and Ag nanoparticles was conducted [13]. Reduction of precursor salts in ethylene glycol–PVP mixture was conducted by NaOH as reducing agent and the application of microwave heating. The molecular weight of PVP effected the morphology of the particles. Pt nanoparticles of 100–400 and 50–150 nm were obtained with PVP molecular weights (M_w) 8,000 and 10,000, respectively.

When $AgNO_3$ was reduced in the presence of 8,000, 10,000, and 40,000 M_w of PVP, the strings of Ag metal were produced. The growth of strings decreased as the molecular weight of PVP increased. Using PVP of M_w 1,300,000 without NaOH addition formation of discrete Ag nanoparticles of 100 nm were reported. Au core–Ag shell nanomaterials were formed [14] in ethylene glycol–PVP mixture by the application of microwave. First, the smaller seeds of Au nanometals of mixed geometries were prepared by microwave heating for 2 min of $HAuCl_4 \cdot 4H_2O$ precursor salt in ethylene glycol–PVP mixture. Addition of $AgNO_3$ salts to the Au seeds' solution and heating by microwave again for 2 min produced the desired Au shell–Ag core of mixed morphologies. Authors have stated that the formation of the core-shell structure is the two-step mechanism using seeded growth method. When they reduced the mixture of the two precursor salts in one step, then the core-shell structures did not form using similar method. Authors [15] have synthesized Ag nanomaterial of different morphologies by adjusting the concentration of precursor salt, amount of PVP in N,N-dimethylformamide (DMF) or ethanol, temperature, and reaction time. Importantly, these nanomaterials exhibited tunable surface plasmon resonance properties in the visible to near-infrared regions.

In this presentation, we describe the results of the preparation of nano-sized Ag metallic [Ag(0)] particles with special emphasis on the effect of reducing and capping agents on the size and morphology of the preparation. The work has been conducted to develop one pot, cost-effective, monodispersed preparations at low temperature and in short reaction time, 5 min to 1 h. Along with the preparation of spherical particles, we have tried to produce non-spherical (anisotropic) materials as well, as the structural complexity enables greater function [16]. Recently, researchers are giving emphasis to control size, morphology, and composition of the materials for the development of new nanotechnologies. The anisotropic nanostructures are more important from the bioscience viewpoint where the development has occurred via the bottom-up approach with long successful history where complex building blocks of biomolecules yielded diverse structural and functional relationships. In this work, the stabilizing agents water-soluble starch containing the carbohydrate component amylose, PVP, and poly(methyl vinyl ether) (PVE) were tested. Two triblock copolymers poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) L64 and P123 were also employed as capping agents. Reducing agents NaOH, D(+)-glucose were used. The molecular structures of the capping agents are given below. Out of these capping agents, PVP, P123, and L64 also acted as reducing agents.
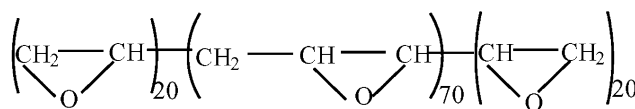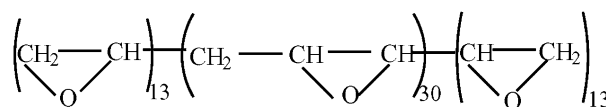
Water soluble starch

$-[CH(OCH_3)-CH_2]_n-$
Poly(methyl vinyl ether) PVE

$HO-(CH_2-CH)_n-OH$
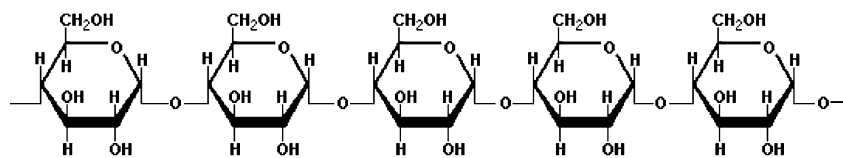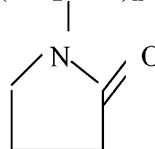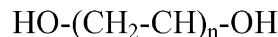
Polyvinyl Pyrolidone (PVP)

Pluronic P123

Pluronic L64

Experimental

Ultra pure water, precursor AgNO$_3$ (99.99%) salt, and D(+)-glucose (dextrose, anhydrous) were purchased from Wako Pure Chemical Industries. Starch, soluble ACS reagent, and PVP (M_w=29,000 and 55,000) was from Sigma-Aldrich. PVE 50 wt% water solution was procured from Aldrich. For all the experiments, freshly prepared AgNO$_3$ stock solution was used. The nanomaterials were prepared using glass vials, and solution was stirred continuously at the experimental temperature. The digital pictures of the preparations were taken from a digital still camera of Sony (Cyber-shot DSC-T1). UV–vis absorption spectra were recorded by Jasco V570 spectrophotometer. For transmission electron microscopy (TEM) recording, the nanomaterial preparations were diluted either with acetone or ethanol, while some preparations were dissolved in water. After putting a drop of diluted preparation on copper grid, the sample was left overnight before recording the picture by Hitachi H-800 TEM apparatus operating at 200 kV. The concentrations of precursor salt, capping, and reducing agents were adjusted as per the preparation given in the

text. The reaction time and temperature have also been mentioned in the "Results and discussion" with the description of each preparation. For all the PVP preparations, the polymer of M_w=55,000 was used except PVP–starch preparation where the M_w of PVP was 29,000. For plotting the histograms of the TEM images, all the particles shown in the pictures were counted. The number of particles considered for histograms are the same as shown in each TEM image. In TEM picture Fig. 4b, more than 100 particles were captured, and average size of the particles was determined by counting all the particles shown in the TEM image.

Results and discussion
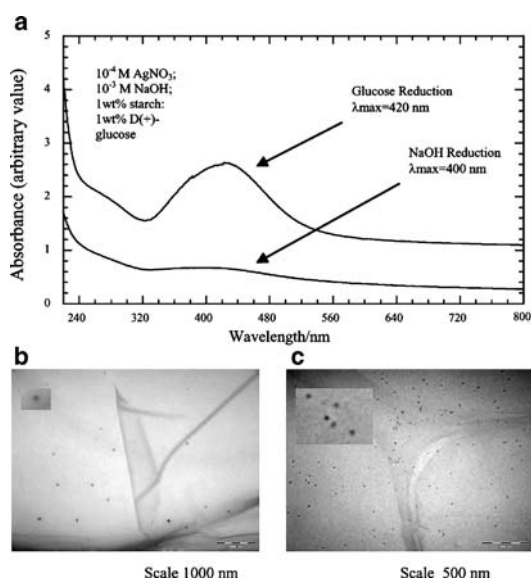
Preparation of monodispersed spherical particles

A 10^{-4} M solution of AgNO$_3$ was reduced in aqueous gel solution of 1 wt% water soluble starch using D(+)-glucose and NaOH as reducing agents. Complete reduction of Ag+ occurred to Ag(0) as colorless (Fig. 1a) AgNO$_3$ solution

Fig. 1 a–g Pictures showing the prep-
aration of Ag(0) colloidal nanoparticles.
a precursor AgNO$_3$ solution of 10^{-4} M;
b the preparation in 1 wt% starch using
1 wt% D(+)-glucose as reducing agent; **c**
the preparation in 1 wt% starch using
10^{-3} M NaOH as a reducing agent; **d**
reduction in neat copolymer pluronic P
123 where copolymer acted as both
reducing as well as capping agent; **e**
preparation of anisotropic (cubes and
stars) Ag(0) nanoparticles (4×10^{-3} M)
in ethylene glycol (11 g)/PVP (0.053 g)
mixture obtained by the addition of
NaOH (4×10^{-2} M) and heating at
190 °C for 1 h; **f** Ag(0) nanoparticles
(0.045 M) of mixed geometries of
spheres, cubes, hexagons, triangles, and
pentagons formed in ethylene glycol
(11 g)/PVP (0.5 g) mixture by heating
solution at 70 °C for 30 min; **g** Ag(0)
(0.045 M) formed in 10 ml water
containing 0.5 g PVP (29,000 M_w) and
0.1 g starch on overnight heating of the
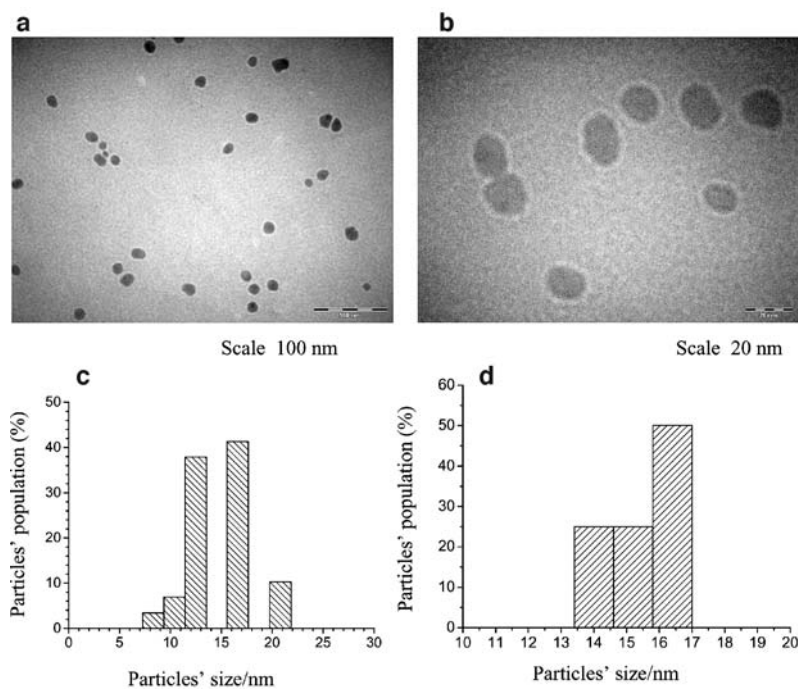mixture at 70 °C
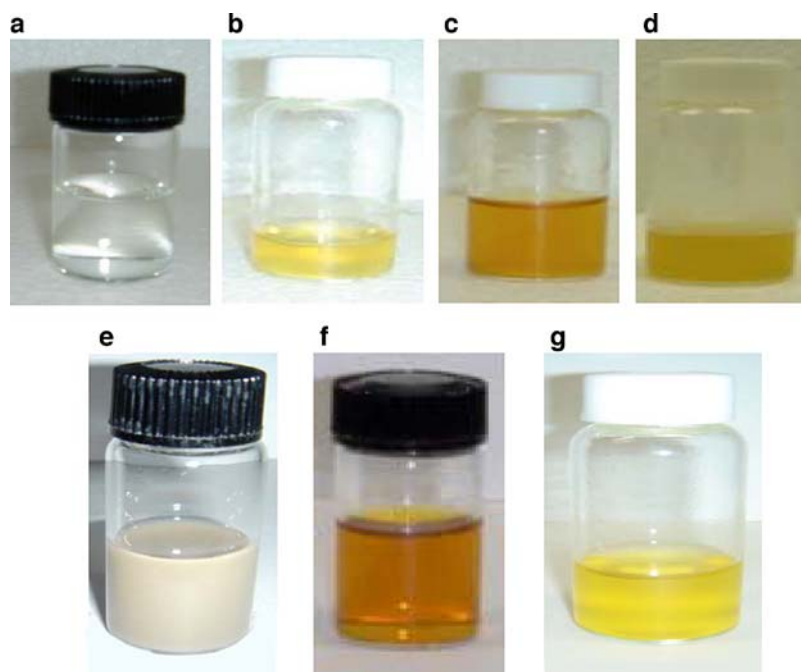
changed to golden yellow color (Fig. 1b and c). Surface
plasmon resonance band observed (Fig. 2a) in the UV–vis
spectra at 400 and 420 nm for NaOH and glucose
reduction, respectively, are the characteristics of the
formation of silver metallic nanoparticles. TEM micro-

Fig. 2 **a** Surface plasmon resonance bands of Ag(0) prepared in
starch solution by the reduction of silver precursor salt using D(+)-
glucose and NaOH as reducing agents. **b** and **c** TEM images of the
silver nanomaterial synthesized in 1 wt% starch solution using NaOH
(**b**)and D(+)-glucose (**c**) as reductants, respectively. The average
particle size is 43 and 15 nm for NaOH and D(+)-glucose, respectively.
The component's concentrations were similar to those given in Fig. 1.
Insets in both pictures are four times the magnification of the particles;
the length of the scale shown in the picture and its value are
multiplication of four for the magnified inserts

graphs (Fig. 2b and c) showed that the spherical particles of
43 and 15 nm were formed using NaOH and D(+)-glucose
as reducing agents, respectively. A diffused and low
intensity visible band noticed (Fig. 2a) in the case of
NaOH reduction compared to the sharp band for glucose
also suggests that the particles sizes are larger if strong
NaOH, rather than mild glucose, is used as reducing agent.
Reaction rate is faster if strong reducing agent, compared to
mild reducing agent, is used, leading to the formation of
large size crystals. A similar visible absorption band
broadening was noticed by Chaudhary et al. [17] when
silver particle size grew by the addition of increased
amount of salt anilinium nitrate to the sodium dodecyl
sulfate template assisted preparation. Kelly et al. [18] cited
that the reason of radiative damping originated from
radiation's spontaneous emission by increasing induced
dipole with increasing the particles' size which resulted in
the broadening of the plasmon resonance band. Figure 3a
and b are the magnified representative TEM images of Ag
(0) nanoparticles prepared in starch solution reduced by
glucose. Homogeneous spherical particles of 15-nm aver-
age size were obtained. Size distribution histogram
(Fig. 3c) of micrograph Fig. 3a shows that most of the
particles are of the size 12.5 and 16.6 nm; however, the
distribution range is 8.3 to 20.8 nm. Figure 3b is a further
magnified image of Fig. 2c, and Fig. 3d is the histogram of
Fig. 3b. The histogram (Fig. 3d) shows that there are three
different sizes of particles: 14, 15.2, and 16.4 nm, with
average size of 15 nm. Triblock copolymer pluronic L64
(poly(ethylene oxide)-poly(propylene oxide)–poly
(ethylene oxide) (PEO$_{13}$ PPO$_{30}$ PEO$_{13}$)) and P123 (PEO$_{20}$
PPO$_{70}$PEO$_{20}$) were also tested for the preparation of Ag(0)

Fig. 3 **a** and **b** Enhanced resolution of the TEM micrographs. **c** and **d** Size distribution, respectively, of Fig. 2c showing the spherical Ag(0) metallic nanoparticles obtained in starch solution by glucose reduction. Reaction conditions are similar to the one given in Fig. 1


nanomaterial in liquid crystalline phase of these polymers. When a 10^{-4} M AgNO$_3$ salt was added to these neat copolymers, the colorless solution was changed to light golden yellow color (Fig. 1d) without the addition of extra reducing agent. Thus, the copolymers L64 and P123 acted both as reducing and stabilizing agents. The TEM images (Fig. 4a and b) recorded for these preparation showed particles' size 8 and 24 nm in P123 and L64, respectively. As shown in Fig. 4c, a sharp and high intensity UV–vis band (λ_{max}=407 nm) observed in P123 compared to a broad and red shifted band (λ_{max}=440 nm) in L64 also confirmed that the particles' size is larger in L64 than in P123 polymer. A similar broadening and red shift in the visible spectra were noticed for Ag(0) preparation obtained [19] by reducing AgNO$_3$ with ascorbic acid in Daxad 19 stabilizing agent. Ag(0) size grew with reaction time followed by the broadening and red shift in the absorption spectra similar to the one observed in our preparation of Ag(0) in L64 compared to P123. P123 is a bulky polymer than L64; therefore, the former acted as mild reducing agent than the latter. Thus, the particle size is smaller in P123 than in L64.

The mechanism of nanocrystal formation is that during the initial stage of reduction of Ag+ to Ag(0), the hydroxyl and oxygen moieties of amylose component of water-soluble starch pacify the high surface energy of metallic silver nanocrystals consisting of a few atoms as noticed in the TEM images of the preparation. Similarly, in the case of P123 and L64 polymer surfactants, the ethylene and propylene oxides' oxygen capped the synthesized crystals in earlier stage of the formation, thus, prohibiting the metal to grow into larger crystals.

Preparation of non-spherical anisotropic materials

Reduction of silver precursor salt (4×10^{-3} M) was conducted in a solvent mixture of ethylene glycol (11 g) and PVP
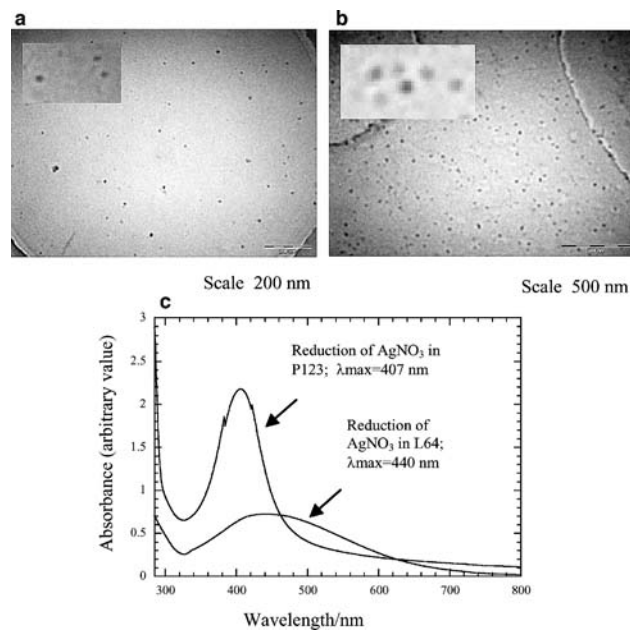
Fig. 4 **a** and **b** TEM images of Ag(0) nanoparticles prepared in pluronic P123 (**a**) and L64 (**b**). The scale bars are 200 nm (**a**) and 500 nm (**b**). The average size the particles are 8 and 24 nm in P123 and L64, respectively. *Insets* in the pictures are four times the magnified particles; the length of the scale and its value shown in the picture are the multiplication of four for the magnified inserts. **c** UV–vis absorption spectra of the material prepared by conducting reduction in P123 and L64 surfactant polymers

Fig. 5 a UV–vis spectrum of the preparation of Ag(0) nano-materials; the reaction conditions are the same as described in Fig. 1e. The asymmetric band observed at 407 nm confirmed the formation of anisotropic cubes and stars of Ag(0) nano-materials. TEM micrographs (b, c, e–g) and histogram (d) of Ag (0) material prepared in ethylene glycol/PVP mixture under the conditions given in Fig. 1e
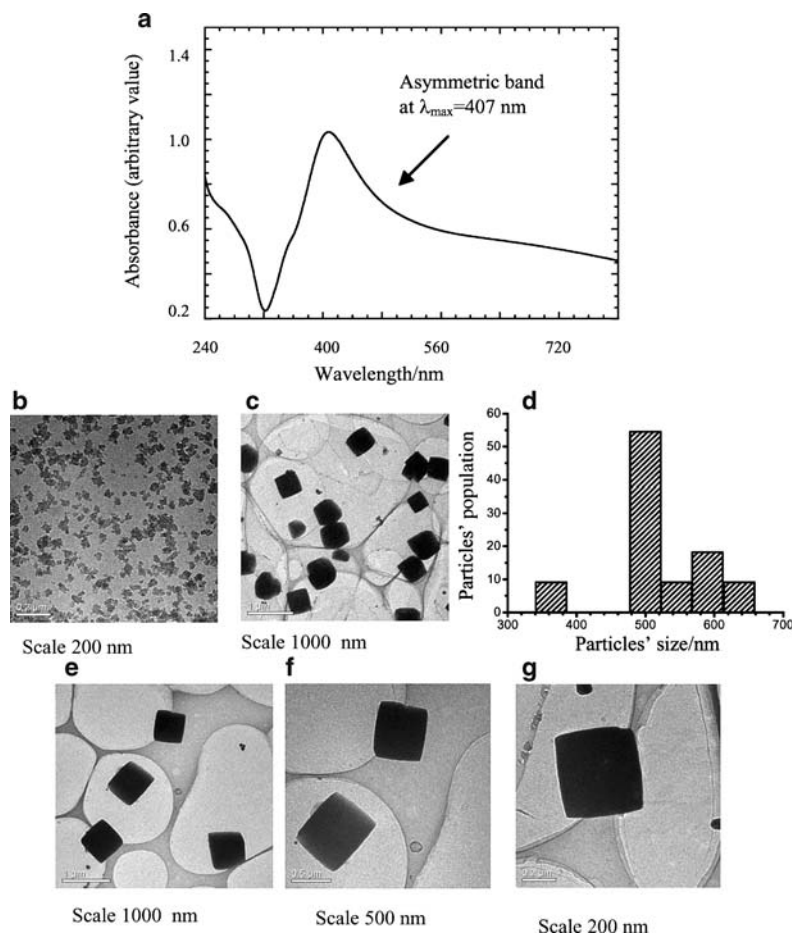

(0.053 g) using NaOH (4×10^{-2} M) as a reducing agent. First, the solvent mixture containing precursor salt was heated at 190 °C. Then, the measured amount of NaOH was added. On the addition of NaOH, the solution turned into a milked tea color (Fig. 1e), an indication of the formation of Ag(0) nanomaterial stabilized in the ethylene glycol/PVP mixture. The preparation was heated at 190 °C for 1 h before recording TEM and UV–vis spectrum of the sample. Asymmetric nature of the band (Fig. 5a) observed in the UV–vis absorption spectrum of the preparation appeared due

to anistropic nature of the synthesized material. Figure 5b, c, e–g are the TEM micrographs and histogram (Fig. 5d) of the preparation. This preparation consisted of mixed morphologies of star-shaped sharp-edged structures of 26–53 nm size (Fig. 5b) and homogeneous cubes (Fig. 5c) of average size 520 nm. The size distribution bars for cubes (Fig. 5d) show that 55% particles are of 500 nm; however, other particles are in the range of 363–636 nm. Figure 5e–g are the magnified images of Fig. 5c. Most probably, the large-sized cubes are formed by the method of self-assembly of smaller

Fig. 6 a TEM micrograph showing that nanoparticles of various shapes are formed in the preparation as given in Fig. 1f. b The histogram of the micrograph (a) showing the population of various geometries
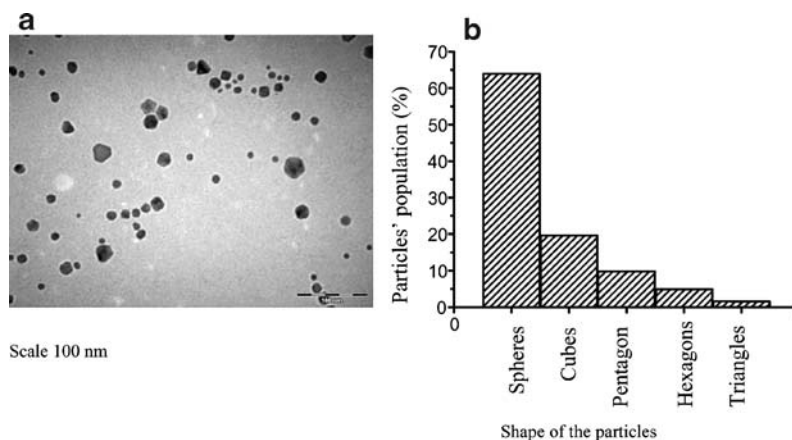
Fig. 7 a TEM micrograph of the preparation shown in Fig. 1g. A mixture of nanoparticles of spherical, ellipsoid, hexagons, pentagons shapes are formed. **b** and **c** Single asymmetric hexagon and symmetric hexagon. Along with the above geometries, sharp-edged structure also existed as shown in **d**
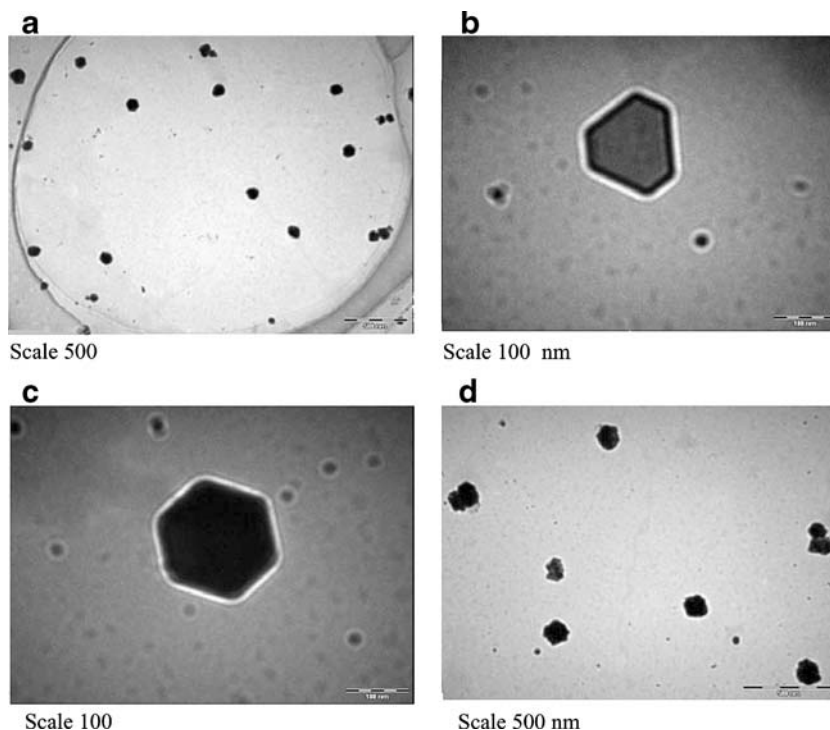
star-shaped particles. Although, the exact mechanism of morphology direction and size control of these structures have not been established and mentioned in the literature for the preparation of a number of self-assembled structures reported [20, 21]. However, it is known that the surfactants or polymer capping agents direct the morphology and size of nanomaterials.

A 0.045 M AgNO$_3$ solution was reduced by PVP in ethylene glycol (11 g)/PVP(0.5 g) mixture, a colorless precursor solution changed to dark golden yellow (Fig. 1f) color on heating at 70 °C for 30 min. PVP–ethylene glycol mixture stabilized the nanomaterial while ethylene glycol acted as reducing agent. In this method, NaOH was not used as a reducing agent; instead, the amount of PVP was increased by tenfold than in earlier preparation where NaOH was used as a reducing agent. TEM micrograph (Fig. 6a) recorded of the preparation showed that Ag(0) nanomaterials of mixed morphologies: spheres, cubes, hexagons, triangles, and pentagons were formed. The particles' sizes were in the range of 7–30 nm. The shape distribution histogram (Fig. 6b) showed that most (64%) particles were spherical followed by cubes (19%), pentagons (10%), hexagons (5%), and triangles (2%).

Increased amount of PVP (29,000 M_w; 0.5 g) was also tested as a reducing and shape-modifying agent in 1 wt% 10 ml aqueous starch solution. A 0.045 M silver salt solution was reduced without a reducing agent on heating the preparation at 70 °C. After completion of reduction, a golden yellow color (Fig. 1g) solution of Ag(0) nanoparticles was formed. Mixed morphologies: spheres, regular
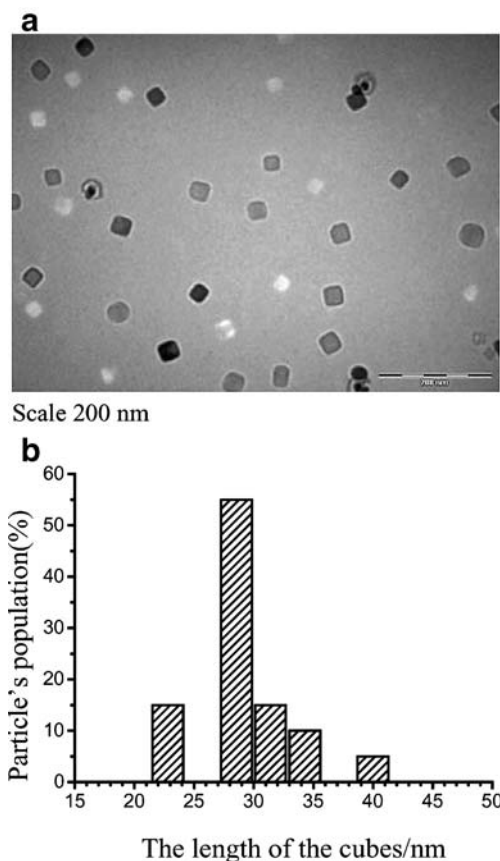
Fig. 8 a TEM cubes of Ag(0) nanocubes obtained on reduction of AgNO$_3$ (5×10^{-3} M) precursor salt by NaOH (2.5×10^{-2} M) in 12.5 wt % of PVE at room temperature in 30-min reaction time. The average length of the cubes is 29 nm. **b** Histogram of Fig. 8a showing the size distribution of the length of Ag (0) cubes

hexagon, asymmetric hexagon, oval, and triangle of the size range 50–100 nm were found in the TEM micrograph (Fig. 7a) of the preparation. Figure 7b and c are the isolated enlarged asymmetric and symmetric hexagons. Along with the above geometries, star-shaped sharp-edged structures (Fig. 7d) of the size 100–133 nm were also found in the same preparation.

Poly(methyl vinyl ether), commonly known as PVE, was also tested as Ag(0) nanomaterial stabilizing and shape-modifying agent. A 5×10^{-3} M precursor AgNO$_3$ solution in 12.5 wt% PVE was reduced using 2.5×10^{-2} M NaOH; reduction was confirmed by recording UV–vis spectrum of the sample which showed a strong band of Ag(0) nano-particles. TEM (Fig. 8a) recording of the sample showed the formation of homogeneous dispersed nanocubes of the average length of 29 nm. The size distribution bars (Fig. 8b) showed that 55% particles have a cube size of 28.57 nm; the particles 22.8 and 31.4 nm are 15% each. Ten percent particles have a size of 34.3 nm, while particles of 40 nm are the least with a 5% population.

Conclusions

We have shown that a number of morphologies of Ag(0) colloids can be prepared by adjusting the capping and reducing agents. The capping agents PVP and PVE also played a role of shape-modifying agents for the synthesis of pure cubes, stars, and mixed geometry preparation of Ag(0) nanomaterials, while reduction in water-soluble starch by D(+)-glucose and NaOH gave spherical particles. No extra reducing agent was required in neat triblock copolymer pluronic P123 and L64 for the reduction of precursor salt, as these polymers worked both as reducing as well as stabilizing agents. The work will give future directionality to improve the catalytic activity of other metallic nano-particles which are known to have high conversion and selectivity for difficult and high-valued organic synthesis.

References

1. Lianos P, Thomas JK (1986) Chem Phys Lett 125:299–302
2. De TK, Maitra A (1995) Adv Colloid Interface Sci 59:95–193
3. Liu J, Ikushima Y, Shervani Z (2003) Curr Opin Solid State Mater Sci 7:255–261
4. Barnickel P, Wokaun A, Sager W, Eicke HF (1992) J Colloid Interface Sci 148:80–90
5. Petit C, Lixon P, Pileni MP (1993) J Phys Chem 97:12974–12983
6. Hou Y, Kondoh H, Ohta T, Gao S (2005) Appl Surf Sci 241:218–222
7. Lee KJ, Jun BH, Kim TH, Joung J (2006) Nanotechnology 17:2424–2428
8. Bell PW, Anand M, Fan X, Enick RM, Robert CM (2005) Langmuir 21:11608–11613
9. Esumi K, Sarashina S, Yoshimura T (2004) Langmuir 20:5189–5191
10. Tian X, Wang W, Cao G (2007) Mater Lett 61:130–133
11. Luo C, Zhang Y, Zeng X, Zeng Y, Wang Y (2005) J Colloid Interface Sci 288:444–448
12. Deivaraj TC, Lala NL, Lee JY (2005) J Colloid Interface Sci 289:402–409
13. Komarneni S, Li D, Newalkar B, Katsuki H, Bhalla AS (2002) Langmuir 18:5959–5962
14. Tsuji M, Miyamae N, Matsumoto K, Hikino S, Tsuji T (2005) Chem Lett 34:1518–1519
15. Yang Y, Matsubara S, Xiong L, Hayakawa T, Nogami M (2007) J Phys Chem C 111:9095–9104
16. Wang D, Lieber CM (2003) Nat Mater 2:355–356
17. Chaudhary VR, Haram SK, Kulshreshtha SK, Bellare JR, Hasan PA (2007) Colloids Surf A 301:475–480
18. Kelly KL, Coronado E, Zhao LL, Schatz GC (2003) J Phys Chem B 107:668–677
19. Sondi I, Goia DV, Matijevic E (2003) J Colloid Interface Sci 260:75–81
20. Shi H, Wang X, Zhao N, Qi L, Ma J (2006) J Phys Chem B 110:748–753
21. Yang J, Qi L, Zhang D, Ma J, Cheng H (2004) Cryst Growth Des 4:1371–1375