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SHORT COMMUNICATION

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Hyperbranch-polyethyleniminated functional polymers II: effect of polyethyleniminated polyoxypropylenediamines on copper nanoparticle formation in aqueous solution

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Abstract Colloidal aqueous solution of zerovalent copper (Cu(0)) nanoparticles were prepared from the Cu^{2+} ions coordinated with polyethyleniminated polyoxypropylenediamines ($D400(EI)_x$) followed by chemical reduction of $NaBH_4$. Aqueous solution of copper clusters formed in the presence of $D400(EI)_8$ with a loading ratio of $[EI]/[Cu^{2+}] = 3$ were stable without precipitation for standing more than 1 month. The protective effects of $D400(EI)_x$ and the particle size of the resulted Cu nanoparticle are regulated by the attachments of ethylenimine (EI) groups per polymer backbone and the normality ratio of $[EI]/[Cu^{2+}]$ used. It is found that the more EI-content per polymer backbone results in the smaller particle size and the narrower size dispersity of the colloidal Cu(0) particles, and the average particle size of 5.07 nm with standard deviation of 0.86 nm was obtained in the presence of $D400(EI)_8$ with the ratio of $[EI]/[Cu^{2+}] = 3$. As the polymer concentration of $D400(EI)_8$ increases (the increase of $[EI]/[Cu^{2+}]$), the average particle size of the prepared Cu(0) nanoparticle slightly changes, but interestingly, the size dispersity gradually decreases, where the standard deviation for the concentration at $[EI]/[Cu^{2+}] = 5$ is 0.82 nm approaching that for monodispersed nanoparticles (0.5 nm).

Keywords Ethylenimine · Nanoparticles · Polymer-metal complexes · Water-soluble polymers

Introduction

The ability to construct nanoscale objects in unlimited quantities is presently an ultimate challenge in contemporary materials research [1–3]. Nanoscale, zerovalent metal clusters with a high level of size/structure control would be of significant interest for use in catalysis [4, 5], optoelectronics [6], or other nano-devices [7]. Polymeric materials are used as media for metal nanoparticle formation by providing improved stabilization and controlling of nanoparticle growth [8–16].

Recently, some studies on double-hydrophilic block copolymers [17], consisting of one hydrophilic block to interact with appropriate inorganic materials and another hydrophilic block to promote solubilization in water, report that these copolymers effectively control on the morphology of inorganic crystals [18–20]. In our previous work [21], hydrophilic ethylenimine (EI) groups are anchored to polyoxypropylenediamine to form water-soluble ABA type triblock copolymers. These copolymers have been synthesized via a simple in situ ethylamination of polyoxypropylenediamine with 2-chloroethylamine hydrochloride, and have been found to be multidentate chelates to effectively coordinate with Cu^{2+} ions utilizing an average of three amino ligands per ion.

In this study, the water-soluble copolymers, polyethyleniminated polyoxypropylenediamines ($D400(EI)_x$) (Fig. 1) consisting of a solvating block of polypropylene glycol and two binding blocks of branched EI group of two terminals, are used as stabilizers being designed not only to chelate with Cu^{2+} ions to keep each ion separated but also to provide inhibition of direct agglomeration of Cu(0) nanoparticles after reduction by $NaBH_4$ in aqueous solution. Copper ions were chosen to demonstrate this concept, since the copper nanoparticles are well known to tend to aggregate very quickly [22, 23]. The protective effects of $D400(EI)_x$ on Cu(0) nanoparticle formation are regulated by the attachments of EI groups per polymer backbone and the normality ratio of $[EI]/[Cu^{2+}]$ used.

Experimental

Materials

Polyoxypropylenediamine, Jeffamine D400 (AHEW = 115 g/equiv.), was kindly supplied by Huntsman Corporation. Polyethyleniminated polyoxypropylenediamines, $D400(EI)_x$ (x = 4 and 8) (Fig. 1), were prepared as described in our previous work [21], and have the average EI number to be 4.2 and 7.8 for $D400(EI)_4$ and $D400(EI)_8$, respectively. Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, Aldrich) was used as received. The water used in this study was purified through a Milli-Q Plus system and degassed.

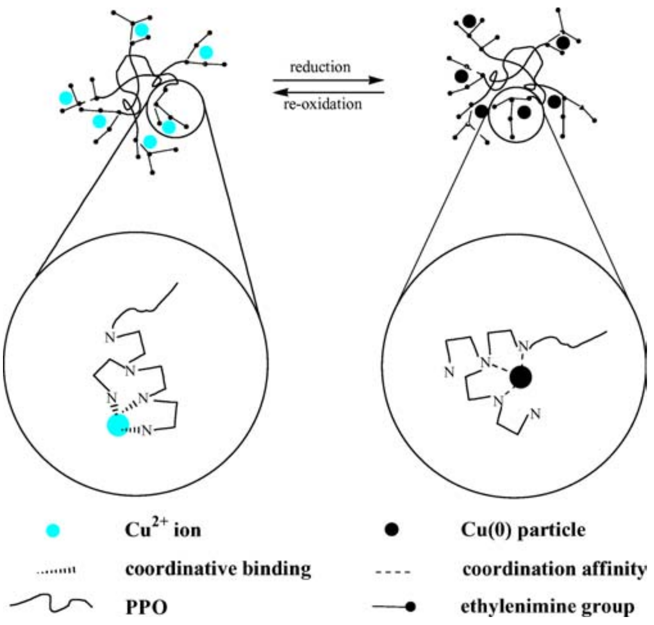
Methods

The $D400(EI)_x$–Cu^{2+} complexes (x = 0, 4 or 8) were synthesized in the same manner as described in the literatures [24–26]. To ensure that the proper stoichiometric ratios were obtained, the requisite amounts of aqueous solutions of $CuCl_2 \cdot 2H_2O$ and the corresponding $D400(EI)_x$ were mixed to result in a final Cu^{2+} concentration of 1.0 mM. The faint blue $CuCl_2$ solution turned to an intense blue upon mixing with the $D400(EI)_x$ solution. Cu(0) nanoparticles were formed by the reduction of $D400(EI)_x$–Cu^{2+} solutions with excess $NaBH_4$. The reduction resulted in a color change of the solution from blue to golden brown, indicating the formation of Cu(0) nanoparticles.

The specimens for the transmission electron microscopy (TEM) were prepared by spreading a small drop of the colloidal solutions onto standard copper grids coated with a thin amorphous Formvar carbon film and letting the drop dry completely in vacuum oven. The size and morphology of the particles were observed at room temperature on a JEOL JEM-1200EX electron microscopy operating at 80 kV. The size distribution was derived from histograms for about 150 particles. The standard deviation (σ) of the size distribution was calculated from the following equation:

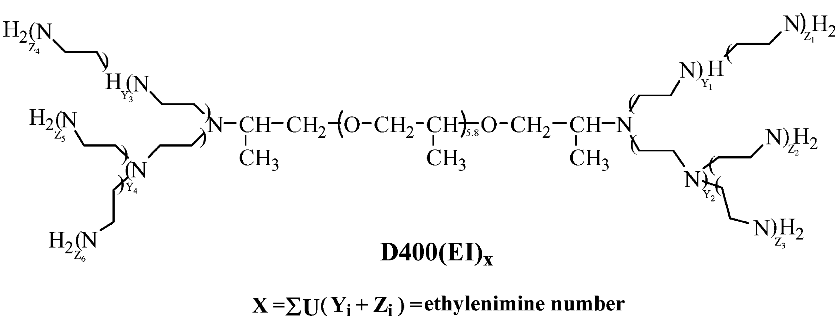
$$\sigma = \left[\sum n_i (D_i - D)^2/(N-1)\right]^{0.5}$$

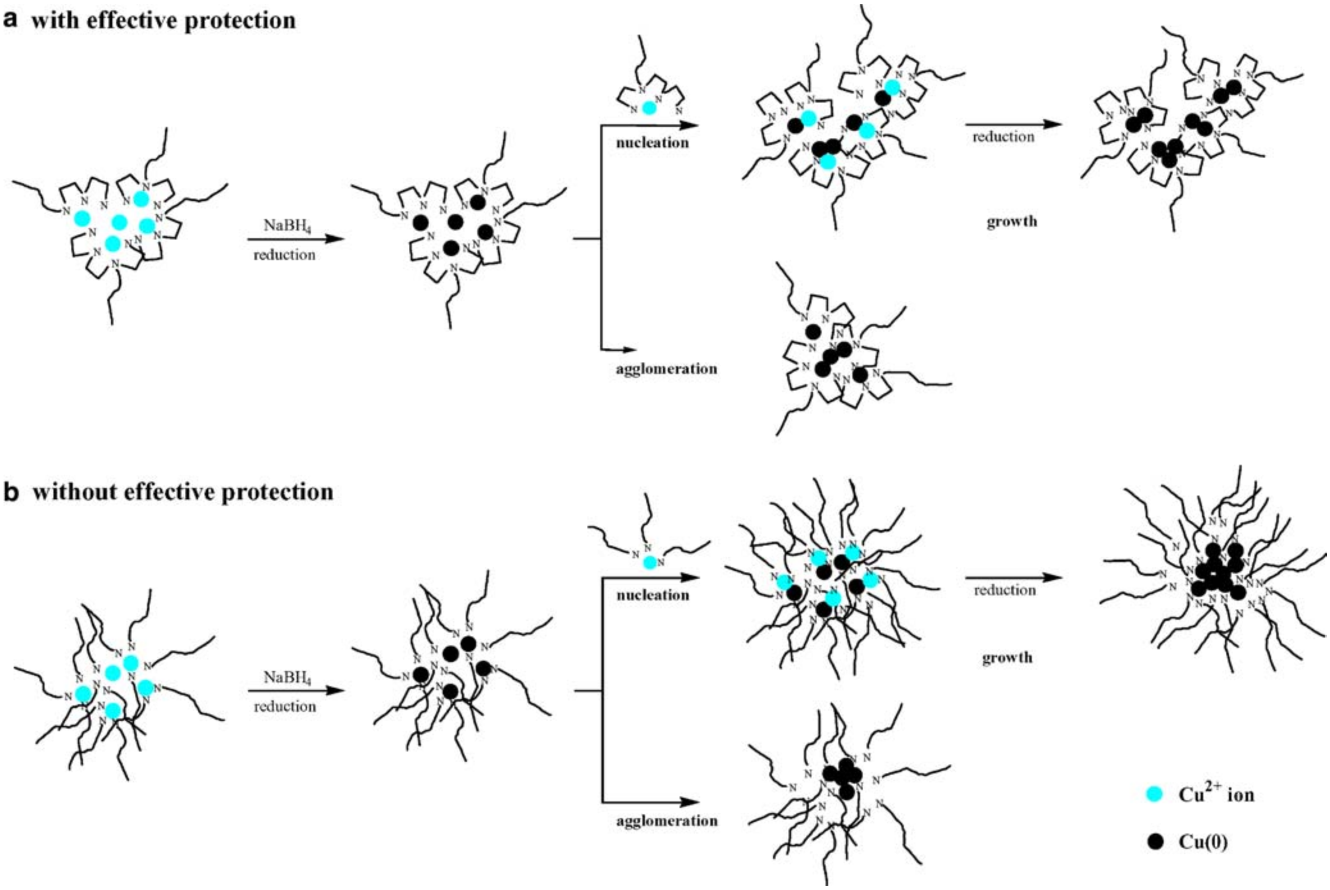
where n_i is the number of particles having diameter D_i. D is the average diameter [$= (\sum n_i D_i)/N$] and N is the total number of particles.



Sch. 1 The interactions between $D400(EI)_x$ and Cu^{2+} ion or Cu(0) particles

Fig. 1 The structures of polyethyleniminated polyoxypropylenediamines ($D400(EI)_x$) as protectors





Sch. 2 Schematic illustration of the formation of colloidal nanostructured Cu(0) particles with/without effective protection by D400(EI)$_x$. Only one binding block of branched EI group of D400(EI)$_x$ is drawn for clarity

Results and discussion

For the preparation of metal nanoparticles in homogeneous solution, general methods used are the chemical reductions of metal salts in the presence of stabilizers such as surfactants [27–30] and polymers [8–16] to control the growth of the initially formed nanoclusters and to prevent aggregation of the metals. In this study, the used protectors, D400(EI)$_x$, possess PEI groups which expect to exhibit two functions through donating the unpaired electrons on nitrogen atoms of EI groups: (1) nitrogen atoms interact with Cu^{2+} ions before reduction via coordinative binding including ionic, covalent, coordinative, and charge-transfer bonds; (2) nitrogen atoms interact with Cu(0) nanoparticles via coordination affinity including weak coordination bonds, charge-transfer and dipole–dipole interactions. Additionally, Hirai et al. [31] prepared the Cu(0) colloidal solutions using the poly(ethylene oxide) as protector and reached a conclusion for poly(ethylene oxide) of not having the protecting ability to Cu(0) particles. As a result, the existence of poly(propylene oxide) segments in D400(EI)$_x$ cannot be expected to effectively stabilize the Cu(0) nanoparticles in aqueous solution.

In order to investigate the stability of the colloidal Cu(0) nanoparticles in the presence of D400(EI)$_x$, those reduced solutions of D400(EI)$_x$/Cu(0) were kept air-free at lower temperature atmosphere (~5 °C). It was observed that the stability of the colloidal Cu(0) nanoparticles varied strongly depending on the functionalities and concentration of D400(EI)$_x$ used for preparing colloidal solution, i. e., the more functionalities and the higher concentration of D400(EI)$_x$ result in more stable colloidal Cu(0) nanoparticles. The Cu(0) clusters formed in the presence of D400(EI)$_8$ with a Cu^{2+} loading normality ratio of $[EI]/[Cu^{2+}] = 3$ were observed to be stable, and no observable agglomeration or precipitation was detected for standing more than 1 month. As this solution was exposed to the atmospheric condition, the oxidation caused by oxygen changed the solution color from golden brown (Cu(0)) through green (Cu(I) complexes) back to blue (Cu^{2+} complexes). Without a pro-

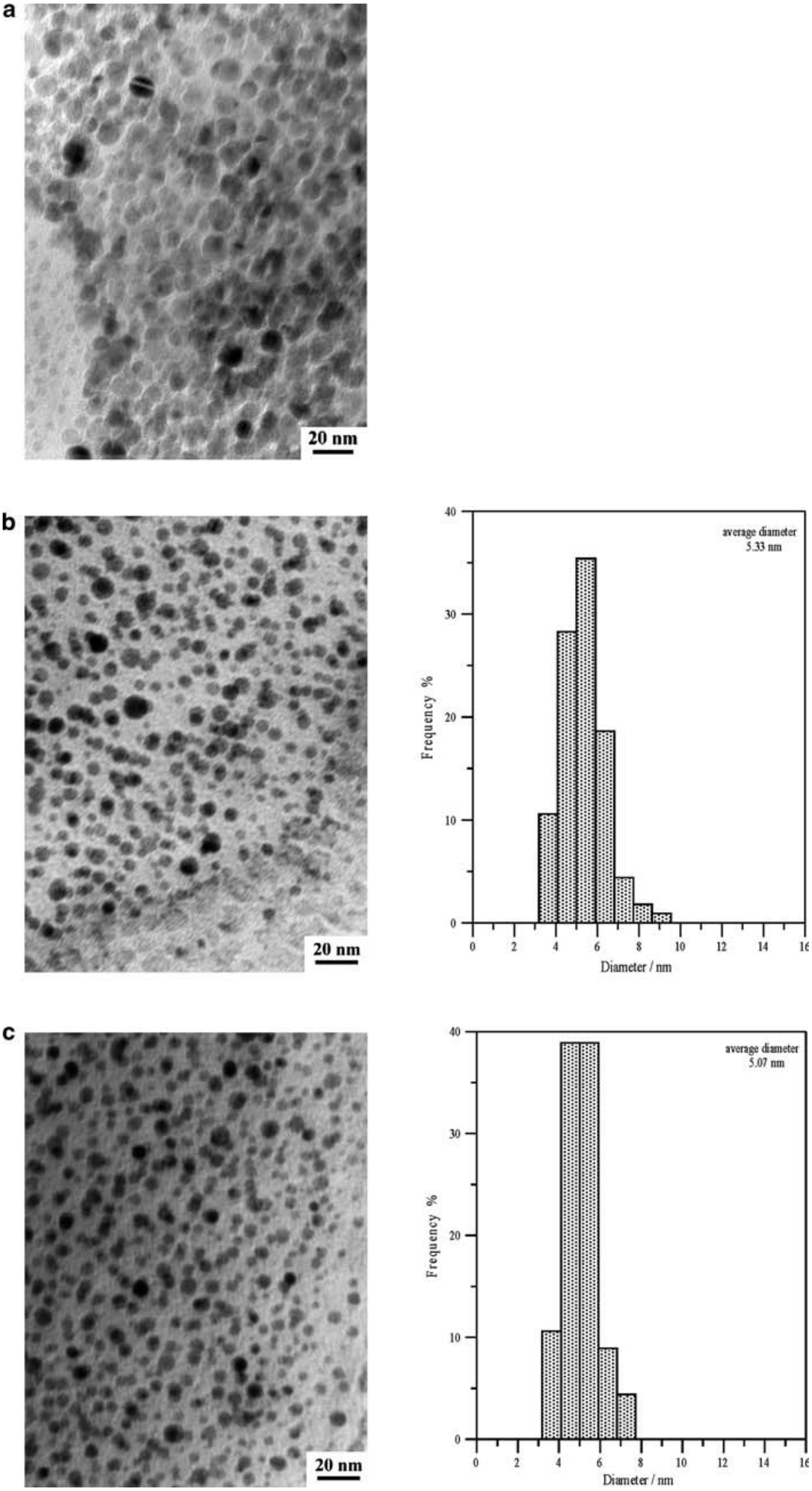


Fig. 2 TEM photographs (*left-hand side*) and particle size distributions (*right-hand side*) of **a** D400, **b** D400(EI)$_4$, and **c** D400(EI)$_8$-protected copper nanoparticles in the presence of [EI]/[Cu^{2+}] = 3 and [NaBH$_4$]/[Cu^{2+}] = 3

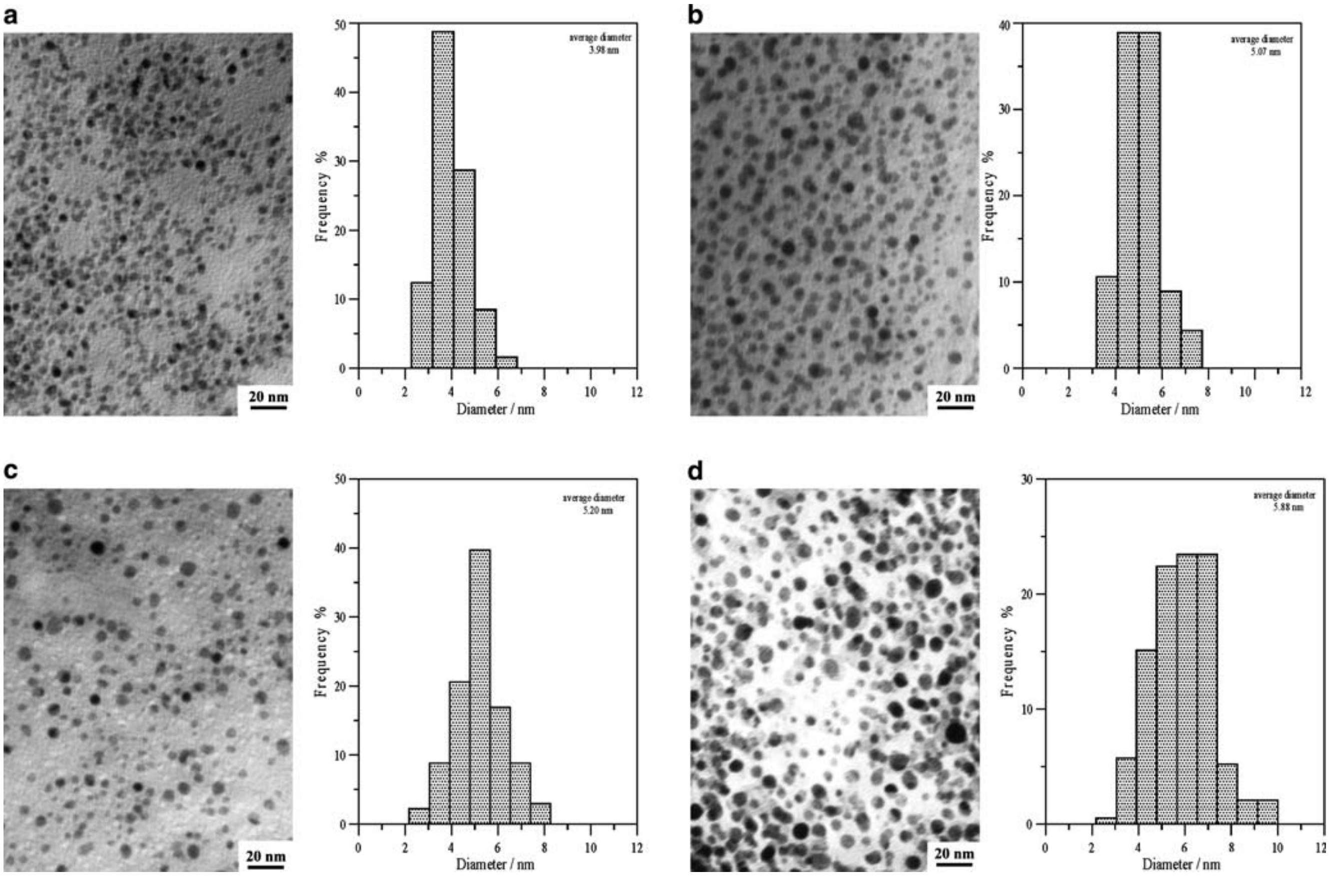


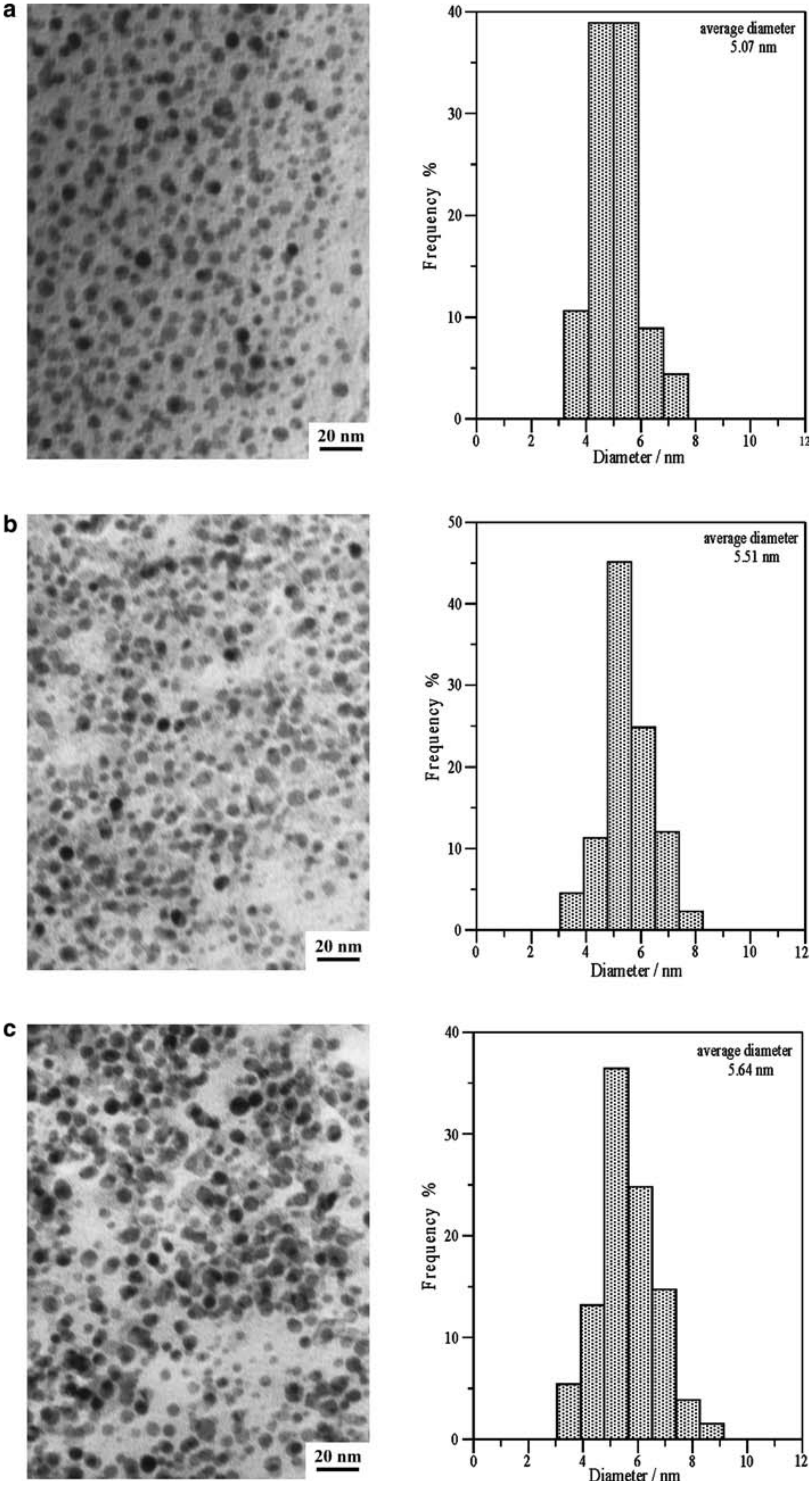
Fig. 3 TEM photographs (*left-hand side*) and particle size distributions (*right-hand side*) of D400(EI)$_8$-protected copper nanoparticles formed in the presence of [NaBH$_4$]/[Cu^{2+}] = 3.0 and at the ratio of [EI]/[Cu^{2+}] = 5 (**a**), 3 (**b**), 2 (**c**), and 1 (**d**)

tecting polymer, the similar solution of Cu(0) prepared at room temperature became dark, and precipitation occurred quickly. These results indicate that the EI group in D400(EI)$_x$ possesses the ability to prevent the formed Cu(0) nanoparticle from agglomeration.

Based on the above-mentioned observations, it is comprehensible that the coordination of metal ions to protective polymer plays an important role in the preparation of polymer-protected colloidal metal solutions by the NaBH$_4$-reduction method. A reasonable mechanism for the stepwise formation of nanoclusters is proposed to describe the simultaneously occurred nucleation, growth and agglomeration. Before chemical reduction by NaBH$_4$, each Cu^{2+} ion equally coordinates with three nitrogen atoms as quantitatively assessed by continuous variation analysis from UV spectroscopy [21]. In the embryonic stage of the nucleation after introducing NaBH$_4$, the Cu^{2+} ions are reduced to zerovalent Cu(0) atoms which further collide in solution with coordinated/or free Cu^{2+} ions or with Cu(0) atoms, or to form irreversible and stable Cu(0) nuclei of which the diameter depends on the strength of the metal–metal bonds and the difference between the redox potentials of metal salt and the reducing agent applied [32]. In the case of existing effective protection, the PEI groups show high coordination affinity both with Cu^{2+} ions and Cu(0) particles, as illustrated in Scheme 1. This strong interaction relatively stabilizes more the intermediates in the initial stage of reduction and the final Cu(0) nanoparticles via adsorptive interaction with the host. In contrast, without effective protection, the intermediates could not be stabilized and the nucleation rate is high. Thus, the required controlled growth of the particle formation does not take place, leading to the formation of bigger aggregates or even the precipitation. Scheme 2 illustrates the formation of colloidal nanostructured Cu(0) particles with and without effective protection by D400(EI)$_x$.

The size of Cu(0) nanoclusters prepared from the solution of metal-ligand complexes of D400(EI)$_x$ at different functionalities and concentrations were examined by TEM. As the normality ratio of [EI]/[Cu^{2+}] is fixed at 3, it is observed that in the presence of D400(EI)$_4$ and D400(EI)$_8$ as protector result in the formation of Cu(0) nanoparticles with the size of 5.33 ± 1.06 and 5.07 ± 0.86 nm, respectively. However, in

Fig. 4 TEM photographs (*left-hand side*) and particle size distributions (*right-hand side*) of D400(EI)$_8$-protected copper nanoparticles formed at the ratio of [EI]/[Cu^{2+}] = 3.0 and in the presence of [NaBH$_4$]/[Cu^{2+}] = 3 (**a**), 5 (**b**), and 10 (**c**)



the case of D400, the Cu(0) particles stuck together, as shown in Fig. 2(a), reflecting the poor protective effect of polymer against instantaneous dipole-induced dipole interactions among the particles, as illustrated in Scheme 2. At the normality ratio of [EI]/[Cu^{2+}] = 3, it can be concluded from Fig. 2 that the average particle size of the colloidal Cu(0) nanoparticles is in the order of D400$(EI)_8$ < D400$(EI)_4$ < D400, and the size dispersity of the Cu(0) particles is in the order of D400$(EI)_8$ < D400$(EI)_4$ < D400. These two trends demonstrate that the more EI-content per polymer backbone results in the smaller particle size and the narrower size dispersity of the resulted Cu(0) nanoparticles. It suggests that the more attachments of EI groups per polymer backbone causes the greater coordination affinity to either Cu^{2+} ions or Cu in zero-valence states to slow the migration and to prevent agglomeration of the metal particles in aqueous solution.

Surfactant concentration was used to control both the rate of particle growth and impart useful chemical behavior to the final nanocrystal product [33], and to affect the particle sizes and shapes [34]. The effect of the concentration of EI group on the formation of Cu(0) nanoparticles was investigated by changing the normality ratio of [EI]/[Cu^{2+}]. Figure 3 shows the TEM images in the sizes of the prepared particles using the D400$(EI)_8$ as protector at the different normality ratios of [EI]/[Cu^{2+}]. Due to the effective protecting ability of D400$(EI)_8$ for the colloidal Cu(0) nanoparticles, the increase of [EI]/[Cu^{2+}] only slightly changes the average particle size in the range of 3.98 ± 0.82 to 5.88 ± 1.33 nm. Nevertheless, the size dispersity of the resulted Cu(0) nanoparticle significantly decreases with increasing ratio of [EI]/[Cu^{2+}], where the standard deviation for the concentration at [EI]/[Cu^{2+}] = 5 is 0.82 nm approaching that for monodispersed nanoparticles (0.5 nm). By increasing the normality ratio of [EI]/[Cu^{2+}], the coordination affinity of polymer to metal ions and the protecting effect of polymer against the growth of particles are both increased, favoring the formation of particles with small size and narrow dispersity.

Figure 4 displays the TEM images for the prepared Cu(0) particles at different normality ratios of [$NaBH_4$]/[Cu^{2+}] in the presence of D400$(EI)_8$ at the ratio of [EI]/[Cu^{2+}] = 3. In this figure, it is noticed that increasing molar ratio of $NaBH_4$ from 3 to 10 does not remarkably induce the change in the size of Cu(0) particles from 5.07 ± 0.86 to 5.64 ± 1.09 nm, but prevents the rapid oxidation of the copper atoms back to Cu^{+} or Cu^{2+} ions.

Summary

Colloidal Cu nanoparticles protected by D400$(EI)_x$ were prepared in aqueous solution followed by the chemical reduction of Cu^{2+} ion with $NaBH_4$. The evidence of Cu(0) nanoparticle formation is directly demonstrated by the change in solution color from blue to golden brown immediately. It is found that the coordination of metal ions with protective polymers plays an important role in the synthesis of polymer-protected colloidal metal solutions. The protective effects of D400$(EI)_x$ and the particle size of the resulted Cu nanoparticle are regulated by the attachments of EI groups per polymer backbone and by the normality ratio of [EI]/[Cu^{2+}] used. From the TEM results, it is concluded that an increasing attachments of EI groups per polymer backbone as well as an increasing ratio of amine to Cu^{2+} ion decreases the size of the clusters, where the standard deviation for the concentration at [EI]/[Cu^{2+}] = 5 is 0.82 nm approaching that for monodispersed nanoparticles (0.5 nm).

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