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ARTICLE

Facile method for preparation of superfine copper nanoparticles with high concentration of copper chloride through photoreduction

Bowen Wang^{a,b}, Shuxi Chen^{a,b}, Jun Nie^{a,b}, Xiaoqun Zhu^{a,b*}

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Superfine copper nanoparticles were synthesized through direct photoreduction of high concentration of copper ion in ethanol solution with photoinitiator at room temperature in the presence of polyethylene imine (PEI). This synthetic method was very effective in decreasing the effect of copper ion concentration on copper particle size. The reaction process was monitored using UV–vis spectroscopy, and the obtained copper nanoparticles were investigated using transmission electron microscopy. The results show that PEI acted not only as a coordinating agent to the copper ion, but also as a polymer cage that reduced the chance of copper nanoparticle aggregation.

Introduction

Metal nanoparticles have elicited considerable attention because of their high surface area-to-volume ratio, size-dependent properties, and potential applications in biomedical, optical, magnetic, electronic, and catalytic fields¹⁻¹⁴. As metal nanoparticles, copper nanoparticles have been extensively studied because of their electronic, catalytic, optical, thermal conductivity, and antifungal/antibacterial properties¹⁵⁻²³. Various methods have been used to prepare ultrafine copper particles²⁴. These techniques include polyol processes²⁵⁻²⁷, thermal reduction²⁸⁻²⁹, chemical reduction in solution²⁸⁻²⁹, microemulsion techniques³¹⁻³³, sonochemical method³⁴, radiation methods³⁵⁻³⁹, flame synthesis reduction⁴⁰⁻⁴¹, metal vapor synthesis⁴², and vacuum vapor deposition⁴³⁻⁴⁴. Most of these reports rarely produced copper nanoparticles with sizes below 20 nm when high concentration of copper salt was used. Copper salt concentration below 10⁻³ M is typically used for the preparation of copper nanoparticles. The procedures used in previously reported methods were complicated and usually involved a number of steps.

Facile preparation of copper nanoparticles with high concentration of copper salt is significant for technological advancements and application. From the technical viewpoint, the quantity of particles increases per volume with increasing copper salt concentration, favoring the aggregation of small particles or their ripening into larger particles. Surface energy increases with decrease in the diameter of particles, resulting in the aggregation of small particles into larger particles⁴⁵. This

phenomenon is contradictory to the use of high concentration of metal salt for the preparation of superfine metal particles. From the application viewpoint, the preparation of superfine copper particles with high concentration exhibits high efficiency and relatively high yield. Therefore, new synthetic methods are necessary for controlling the synthesis of superfine copper nanoparticles with high concentration of copper salt without the need for complicated techniques.

We have reported a method for the preparation of copper nanoparticles and patterned surfaces with copper stripes through ultraviolet (UV) irradiation of a mixture solution of a photoinitiator and a copper–amine coordination compound at room temperature⁴⁶. The copper–amine compound, which prevented the production of insoluble cuprous ion, was formed by adding diethanol amine into an ethanol solution of copper chloride. Under UV irradiation, free radicals were generated by photoinitiator decomposition. Based on the foregoing, we developed a one-step photochemical method to prepare superfine copper particles with high concentration of copper salt. This method was designed from a homogeneous solution in the presence of a special capping agent, namely, polyethylene imine (PEI). PEI controls the size of copper nanoparticles in this photoreduction system, in contrast to other polymer capping agents such as polyvinyl pyrrolidone (PVP). The results indicate that PEI could control the size of copper particles due to the following two reasons: first, PEI is a polymer and the polymer chain in the solution was entangled. This curly chain could form numerous small cages for copper ion that are independent of each other. Second, PEI contained

many amine groups on the main and side polymer chains. These amine groups could coordinate with copper ion. The copper ions or copper nanoparticles could be fixed on the chain through the coordination bond, reducing the possibility of copper nanoparticle aggregation. The results of the photoreaction and the size of the copper nanoparticles show that PEI inhibited the growth of copper particles and significantly reduced the effect of the concentration of copper salt on the size of copper nanoparticles. Even with high concentration of copper salt (0.1 M), the size of the copper nanoparticles was less than 20 nm.

2 Experimental Section

2.1 Materials and Equipment

Copper chloride, diethanol amine, and ethanol were purchased from China National Medicines Corporation, Ltd. (Beijing, China). PEI ($M_w = 1800$) was purchased from Aladdin Reagent, Inc. PVP ($M_w = 40,000$) was purchased from Sigma-Aldrich Co., LLC (USA). Photoinitiator 184 (1-hydroxycyclohexyl phenyl ketone) was supplied by Changzhou Tronly New Electronic Materials Co., Ltd. (Changzhou, Jiangsu, China). All reagents were used as received. UV cuvettes (Germany, Brand 759150) with 5 mm optical path length were made of polymethyl methacrylate.

A xenon lamp (Minebea Co., Ltd., Beijing, China) was used as light source. In order to exclude the irradiation from the Xe lamp to heat the solution, two measures were taken. The first measure was that only the range of irradiation wavelength from 320 nm to 390 nm was used by an optical filter and the other wavelength was filtered out. This range of irradiation not only was in line with the UV absorption spectrum of the photoinitiator 1173, but also had no heat to the solution. Besides, an optical fiber with length of 1.5 meter was used to increase the distance between the lamp and the reactor to avoid heat conduction. These measures confirmed that reactor was not heated by the irradiation. The radiation intensity was 45 mW/cm². The light intensity was measured using a ferric oxalate actinometer, which was constructed by the Photoelectric Instrument Factory of Beijing Normal University. The vacuum glove box (ZKX-1) was obtained from the Nanjing NanDa Instrument Plant (China).

UV-vis spectra of the solution were obtained using a Hitachi U-3010 UV-vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). Transmission electron microscopy (TEM) was conducted at 200 kV by using an FEI TecNai G2 20S Twin TEM. TEM specimens were prepared by placing microdrops of colloidal solutions on a carbon film supported by copper grids in a vacuum glove box filled with nitrogen. The EDX was measured using a Bruker AXS Quantax 4010 Energy dispersive X-ray spectrometer that was attached to a scanning electron microscope (S-4700 FE-SEM, Hitachi).

2.2. Preparation of Copper Nanoparticles from Copper–Diethanol Amine Coordination Compound with PVP

An ethanol solution of the copper–amine coordination compound was prepared by mixing CuCl₂ (13.5mg), diethanol amine (42 mg), photoinitiator 184 (41 mg), PVP (40 mg), and ethanol (10 mL). The constituent concentrations in the as-prepared solution were as follows: [CuCl₂] = 0.01 M, [diethanol amine] = 0.04 M, and [photoinitiator 184] = 0.02 M. PVP was 0.5% of the mass of the solution. Prior to irradiation, 1.5 mL of the solution was sealed in a UV cuvette with a rubber plug and deaerated by bubbling nitrogen for 15 min. The sketch of the experimental setup could be reference to supporting materials 1. The details of deaeration process were described as below: three syringe needles were used. One needle which was inlet of N₂ was inserted to the bottom of the cuvette, the other two needles that were outlet were on the top of the solution. The air in the solution could be flushed out from the solution by deaeration for 15 minutes. At ambient temperature, the solution was irradiated from the transparent side of the UV cuvette by the xenon lamp at a radiation intensity of 45 mW/cm². The photoreaction process was monitored using UV-vis spectroscopy. The procedure for UV measurements is described as follows: the solution which was in the UV cuvette was irradiated for some time, then the cuvette was transferred into the UV-vis spectroscopy and the UV-vis spectra were recorded. This process was repeated for lots of times.

2.3. Preparation of Superfine Copper Nanoparticles from the Ethanol Solution of Copper Chloride and PEI

An ethanol solution of copper chloride and PEI was prepared by mixing CuCl₂, photoinitiator 184, PEI, and ethanol. The constituent concentrations in the as-prepared solution were as follows: [CuCl₂] = 0.01 M and [photoinitiator 184] = 0.02 M. The content of PEI is presented in the Supporting Materials 2. The procedure for the preparation of copper nanoparticles was the same as that discussed in Section 2.2.

All the solutions were preserved in a dark environment away from sunlight. The prepared solution was unstable in the presence of oxygen, so it was prepared in an oxygen-free environment.

3. Results and Discussion

In our previous work, copper chloride was rapidly photoreduced by radical produced from the photolysis of photoinitiator under irradiation after adding diethanol amine⁴⁶. Acting as coordination agent, diethanol amine coordinating with copper ion could avoid producing cuprous chloride, which is insoluble and would prevent further photoreduction reaction of cuprous ion. The results show that the copper particles were about 100 nm in size, with 0.01 M ethanol solution of copper–amine coordination compound. When the concentration of copper–amine coordination compound ethanol solution increased from 0.001 M to 0.1 M, the size of the copper particles increased from approximately 10 nm to more than 200 nm (Supporting Materials 3, Figure S2). These results indicate that the concentration of copper–amine coordination compound exerted tremendous effect on the size of the particles, and

superfine copper particles from high concentration of copper salt could not be prepared through this photoreduction method under the provided conditions.

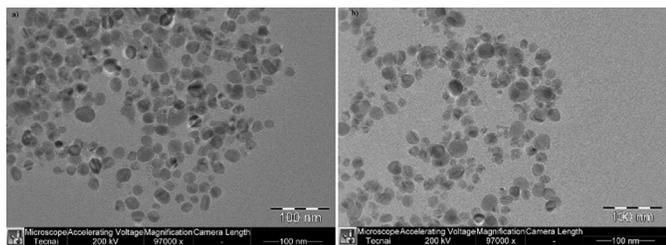


Figure 1. TEM images of copper particles prepared from 0.01 M ethanol solution of copper–amine coordination compound with PVP of a) 0.5% (w/w) and b) 1% (w/w)

Numerous methods can be used to improve the size distribution of copper nanoparticles. The most commonly used method involves the chemical reduction of copper ions in aqueous solution by adding various capping agents, such as cetyltrimethylammonium bromide (CTAB)^{47–48}, ethylenediamine (EDA)⁴⁹, polyvinylpyrrolidone (PVP)¹⁸, poly(allylamine) (PAAm)⁵⁰ and sodium dodecylbenzene sulfonate (DBS)^{51–52}. PVP is most commonly used as a capping agent to improve the size and distribution of copper nanoparticles. Figure 1 shows the TEM images of the copper particles prepared from the 0.01 M ethanol solution of copper–diethanol amine coordination compound with different contents of PVP (0.5% (w/w) and 1% (w/w)). As shown in Figure 1, under the same concentration of ethanol solution of copper–diethanol amine, the sizes of most of the copper nanoparticles with PVP ranged from 20 nm to 40 nm, and were significantly smaller than the 100 nm particles prepared without PVP (Supporting Materials 3, Figure S2). Therefore, PVP was an effective capping agent for preparing small copper nanoparticles in this photoreduction system. In this photoreduction system, diethanol amine and PVP acted as coordination and capping agents, respectively. Diethanol amine was a coordination agent that prevented cuprous chloride formation and PVP was an effective capping agent that controlled the size of the copper particles. According to the TEM images, the content of PVP increased from 0.5% (w/w) to 1% (w/w) and the size of the copper nanoparticles slightly decreased, but the size distribution of copper nanoparticles became more non-uniform. These results indicate that the addition of more PVP did not help control the size and distribution of the copper nanoparticles.

Before discussing the photoreduction of the 0.01 M ethanol solution of copper–diethanol amine coordination compound with PVP, it should be compared first with the same solution without diethanol amine. A control experiment of photoreduction of CuCl₂ and PVP without diethanol amine was conducted (Supporting Materials 4, Figure S3). UV–vis absorption of the 0.01 M ethanol solution of CuCl₂ and PVP without diethanol amine was 900 nm, which was the same as that of the 0.01 M ethanol solution of CuCl₂⁴⁶, demonstrating that the Cu²⁺ electronic structure did not change with the

presence of PVP or that the PVP may have no coordination with Cu²⁺. No absorption peak of copper nanoparticles was observed under irradiation. Thus, without diethanol amine, CuCl₂ could not be photoreduced to copper with PVP.

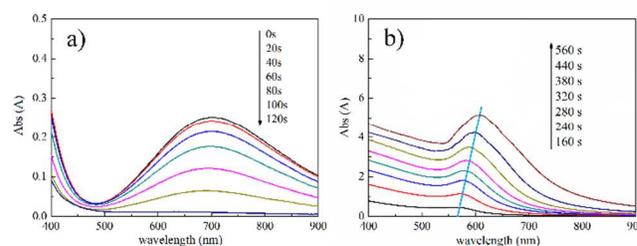


Figure 2. UV–vis spectra change of the 0.01 M ethanol solution of copper–diethanol amine coordination compound with PVP under UV irradiation: (a) decline in the absorption with increase in irradiation time; (b) increase in the absorption with increase in irradiation time.

Change in the UV–vis spectrum was monitored using a UV–vis spectrophotometer to determine the process of photoreduction of the copper–amine coordination compound ethanol solution with PVP under UV irradiation (Figure 2). The UV–vis spectrum of the ethanol solution of the copper–amine coordination compound with 0.5% (w/w) PVP was similar to that of the ethanol solution of the copper–amine coordination compound. Both solutions exhibited an absorption peak at 700 nm, which is the absorption peak of copper–diethanol amine^{46,53}, indicating that copper ion had no coordination with PVP. Under irradiation, the absorbance of the solution from 522 nm to 900 nm decreased (Figure 2a), and the absorption peak at 700 nm completely disappeared after irradiation for 120 s, indicating that all Cu²⁺ had been reduced to Cu⁺. A peak at approximately 570 nm, which was the absorption peak of Cu nanoparticles, was observed with further irradiation to 160 s (Figure 2b)^{46,53}. This phenomenon is similar to the process of UV–vis spectra of 0.01 M ethanol solution of copper–amine coordination compound without PVP that we previously reported⁴⁶. The copper nanoparticles distributed very well in the solution and did not precipitate because of the stabilization of PVP and the small size of the copper nanoparticles. As shown in Figure 2(b), the absorption peak of copper nanoparticles increased with increase in irradiation time, indicating that the copper ion was gradually reduced to copper under irradiation. Moreover, the absorption peak of the copper nanoparticles exhibited an obvious red shift with increase in irradiation time. According to the literature^{46,54}, this red shift can be attributed to the aggregation and growth of the copper nanoparticles, indicating that the foregoing still existed in the photoreaction although the copper particles with PVP were smaller than those without PVP. PVP could not completely prevent copper, which was constantly being produced in the solution, from growing.

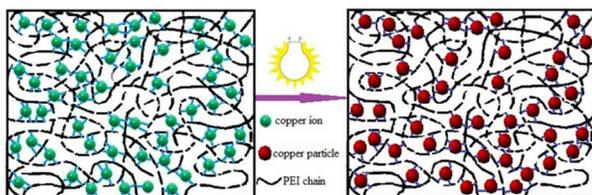


Figure 3. The scheme of copper–diethanol amine coordination compound photoreduction in the ethanol solution with PVP

When PVP was used as capping agent in the photoreduction, one of its functions was to entangle polymer chains and form separated spaces like “cages” (Figure 3), which will trap copper–diethanol amine ions. The produced copper particles inside the same cages could aggregate, but those inside different cages could not aggregate easily. Thus, the size of copper could be controlled by using PVP as capping agent. The size of the copper nanoparticles slightly decreased with increasing PVP. However, the entangled polymer chain was unstable, and thermal movement could cause the re-entanglement of the polymer chain. The copper ion and copper coordinated with the amine group because of the existence of diethanol amine, so the PVP chain and the copper ion and copper particles did not interact with each other. Moreover, the copper ion, copper particles, and PVP chain were able to move randomly and separately, so copper was able to re-aggregate, increasing the size of the copper nanoparticles (red shift in the UV spectrum). The increase in PVP did not help much in controlling the size of the copper nanoparticles because of the random and separate movements of these substances. Therefore, as basis for these analyses, we conjectured that if a polymer could serve as a coordination agent, then the copper ions could bind on polymer chains. The produced copper could link with the polymer chain, which in turn confines the polymer chain movement and couples with the polymer cage effect. Consequently, the aggregation of copper nanoparticles could be reduced, and significantly smaller copper particles can be prepared.

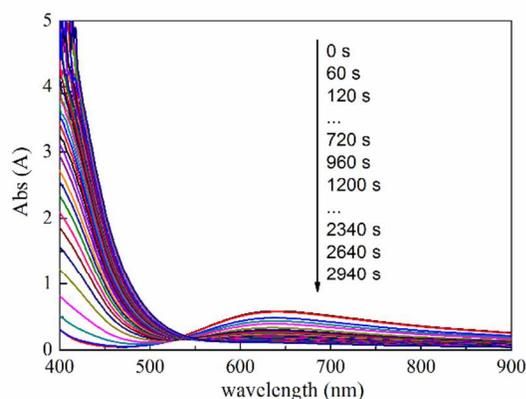


Figure 4. UV–vis spectra of 0.01M ethanol solution of copper chloride with PEI when the molar ratio of amine to copper ion was 8:1 under UV irradiation.

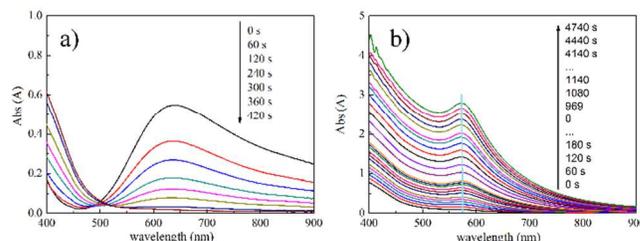


Figure 5. UV–vis spectra of 0.01M ethanol solution of copper chloride with PEI when the molar ratio of amine to copper ion was 16:1 under UV irradiation: (a) decrease in copper ion absorption; (b) increase in copper nanoparticle absorption.

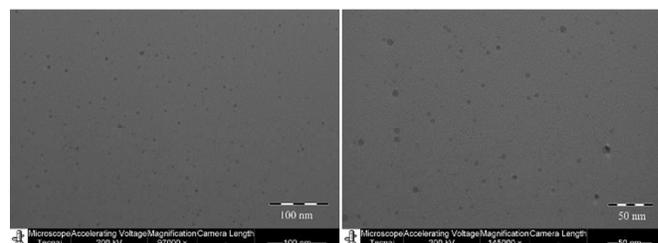


Figure 6. TEM images of the copper nanoparticles prepared from 0.01 M ethanol solution of copper–PEI when the molar ratio of amine to copper ion was 16:1 under UV irradiation

According to the hypothesis and the specificity of the proposed photoreduction system, the polymer containing numerous amine groups may satisfy all of the aforementioned criteria. PEI, which has many imine groups on the chain and side chain of the polymer (Supporting Materials 2), could serve as a coordination agent to form chemical bonds with copper ion and exhibit the same function as diethanol amine. Moreover, PEI could form separated cages through entanglement of the polymer chain. Copper ion or copper could coordinate with four amine groups, which can be inside the same or different polymer chains. Therefore, the polymer could be interlinked in the solution by the coordination, preventing the polymer chain from moving randomly and separately. To verify our hypothesis, PEI was investigated instead of both diethanol amine and PVP. The quality of PEI that was added in the solution was calculated as shown in Part 1 of ESI. Figure 4 shows the UV–vis spectra results of 0.01 M ethanol solution of copper chloride using PEI, wherein the molar ratio of amine to copper ion was 8:1 (or 0.5% w/w), replacing diethanol amine. Compared with the absorption peak of copper–diethanol amine, the absorption peak of copper–amine with PEI had a 70 nm blue shift that shifted to approximately 630 nm. The change in the UV–vis spectrum was induced by the change in the Cu^{2+} electronic structure. Under irradiation, the absorption peak of copper–amine declined and disappeared ultimately, whereas no absorption peak of copper nanoparticles was observed. These results indicate that the 8:1 molar ratio of amine to copper ion was insufficient for the proposed photoreduction system. This insufficiency can be attributed to the steric hindrance or spatial conformation of polymer chain in the solution. Thus, some amine groups on the PEI could not be coordinated with copper

ion. When the molar ratio of amine to copper ion was increased to 16:1, the absorption peak of copper–amine decreased and disappeared (Figure 5a) and the absorption peak of the copper nanoparticles appeared (Figure 5b). The absorption peak of the copper nanoparticles was broad, but the peak turned narrow and no red shift of the absorption peak of copper nanoparticles was observed with increase in irradiation time. These results demonstrate that growth of copper nanoparticles existed in the initial period but was not obvious in the latter stage of the photoreduction process. Moreover, the color of the solution after reaction was completely different from that of the solution with diethanol amine with the same concentration of copper ion (Supporting Materials 5, Figure S4). After photoreduction, the solution with diethanol amine was black and the copper nanoparticles precipitated, whereas with PEI, the solution was bright red and the copper nanoparticles were suspended in the solution. The nanoparticles were investigated by XRD and EDS (Supporting Materials 6, Figure S5 and Supporting Materials 7, Figure S6) and the result demonstrated the nanoparticles were copper nanoparticles. Nanoparticles have size-dependent properties, and their colors vary with their size. This property can be confirmed by the TEM images of the copper nanoparticles (Figure 6). The copper nanoparticles were approximately 10 nm in size, which was half of the copper nanoparticles prepared from the same concentration of solution of copper ion with diethanol amine and PVP.

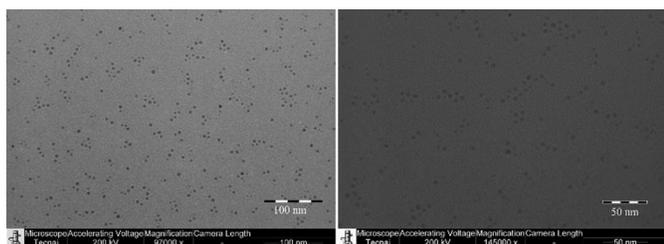


Figure 7. TEM images of copper nanoparticles prepared from 0.01M ethanol solution of copper–PEI when the molar ratio of amine to copper ion was 24:1 under UV irradiation

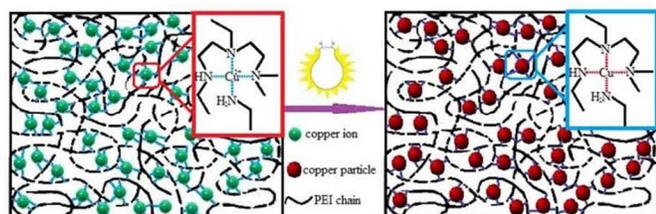


Figure 8. Schematic illustration of the photoreduction of copper chloride with PEI.

In summary, no copper particles were observed when the molar ratio of amine to copper ion was 8:1. Copper nanoparticles were prepared when the molar ratio of amine to copper ion was 16:1. The UV–vis spectra of the 16:1 ratio were not significantly different from those of the 24:1 ratio, except for the increase in reaction time and the value of absorption peaks, which indicated the formation of more copper–amine ion and

copper nanoparticles (Supporting Materials 8, Figure S7). This result demonstrates that the quantity of amine groups affected the quantity of copper ion coordinated, consequently affecting the quantity of copper nanoparticles. Due to this photoreduction system, only the copper ion coordinated by amine could be reduced to copper⁴⁶. The copper particles prepared from 0.01 M ethanol solution of copper ion with PEI were only 10 nm in size, which was only one-tenth that of the copper particles prepared from the same concentration of solution with diethanol amine and approximately half of the copper nanoparticles prepared from the solution of copper ion with diethanol amine and PVP. Figure 7 shows the TEM images of the copper nanoparticles with 24:1 molar ratio of amine to copper ion. The particles with 24:1 molar ratio were smaller compared with those with 16:1 molar ratio, proving our hypothesis that the curled polymer chain could serve as the cages that reduced the chance of the copper particles to a certain extent. Aside from acting as polymer cages, PEI contains amine groups that serve as coordination agents in the reaction. The copper ion and the produced copper atom with empty orbitals could coordinate with the amine groups on the PEI chain, reducing the chance of further copper growth. The copper ion could coordinate with amine groups. Thus, the copper ion coordinates with amine groups in different polymer chains, which could confine the activity of polymer chain in the solution. Given these synergistic effects, superfine copper nanoparticles could be prepared from the solution of copper ion with PEI, as shown in Figure 8.

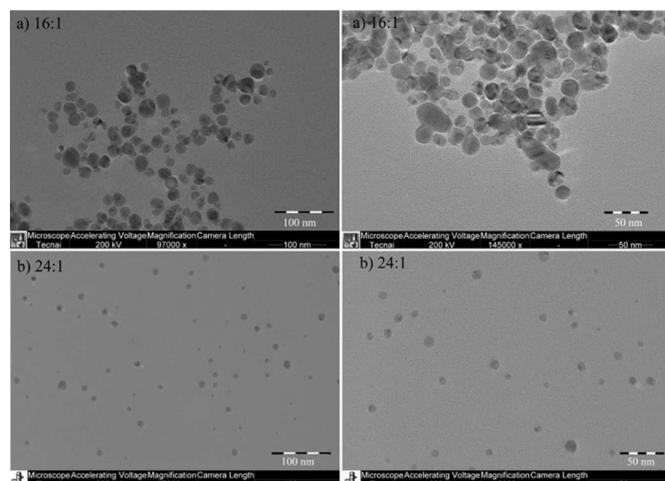


Figure 9. TEM images of copper nanoparticles prepared from 0.1 M ethanol solution of copper–PEI with different molar ratios of amine to copper ion under UV irradiation.

The size of the copper particles significantly increased with increase in the amount of copper ion per unit volume and in the concentration of copper ion. Thus, the molar ratios of amine to copper ion were 16:1 and 24:1 when the concentration of the ethanol solution of copper–PEI was set to 0.1 M. The morphologies of the copper nanoparticles were observed using TEM (Figure 9). The color of the solution of copper nanoparticles was dark red, the copper nanoparticles were

suspended in the solution (Supporting Materials 9, Figure S8), and no precipitation occurred. The stability of the dispersion was monitored by UV spectroscopy and the results were shown in the Supporting Materials 7, Figure S6. After 24 h, the UV absorption spectrum of the solution has no obviously change which demonstrated that the dispersion was very stable (Supporting Materials 10, Figure S9). The copper nanoparticles were less than 30 nm when the molar ratio of amine to copper ion was 16:1, and the copper nanoparticles were below 20 nm when the molar ratio of amine to copper ion was increased to 24:1. This phenomenon occurred because the content of the polymer increased, so the quantity of the cages increased and the quantity of copper ions in the cages decreased. Consequently, the size of the copper particles decreased, indicating that the polymer served as cages. The size of the copper particles prepared from 0.1 M ethanol solution of copper–diethanol amine was 200 nm. The former was only one-tenth the size of the latter. PEI significantly reduced the effect of concentration of copper ion on the size of the copper particles. Superfine copper nanoparticles could be prepared even with high concentration of copper ion.

4. Conclusions

Superfine copper nanoparticles with size less than 20 nm were achieved through photoreduction at high concentration of copper chloride and PEI. In the present case, PEI acted as capping agent and coordination agent simultaneously. This method used to prepare superfine copper nanoparticles was controlled by UV irradiation, so heat was not required, making it convenient for use in the production of copper nanoparticles in situ. Combining the convenient in situ photoreduction method with photopolymerization, possible application of the proposed strategy in various aspects, such as metal–organic composite materials, print ink and printing circuit board, can be reasonably anticipated.

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Notes and references

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China.

^b Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, P.R. China.

*Corresponding author. Tel.: +86 1064421310.

E-mail: zhuxq@mail.buct.edu.cn

Supporting Information Available

Information concerning the sketch of the experimental setup of preparing the copper nanoparticles through photoreduction, Calculation of the quality of PEI which was added in the solution, TEM images of copper particles prepared from the ethanol solution with different concentration of copper-diethanol amine coordination compound, the change of UV-vis spectra of 0.01 M ethanol solution of copper chloride and PVP without diethanol amine, the color of the solution with the copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with different amine, the XRD and EDS analysis of the copper nanoparticles prepared by 0.01 M ethanol solution of copper chloride with PEI, the change of UV-vis spectra of 0.01 M ethanol solution of copper chloride with PEI and the molar ratio of amine group to copper ion was 24:1, the color of the solution with the copper nanoparticles prepared from 0.1 M ethanol solution of copper chloride with PEI (the molar ratio of amine to copper ion was 24:1), the change of UV absorption spectra of the copper dispersion prepared from 0.01 M ethanol solution of copper chloride and PEI (the molar ratio of amine to copper ion was 24:1).

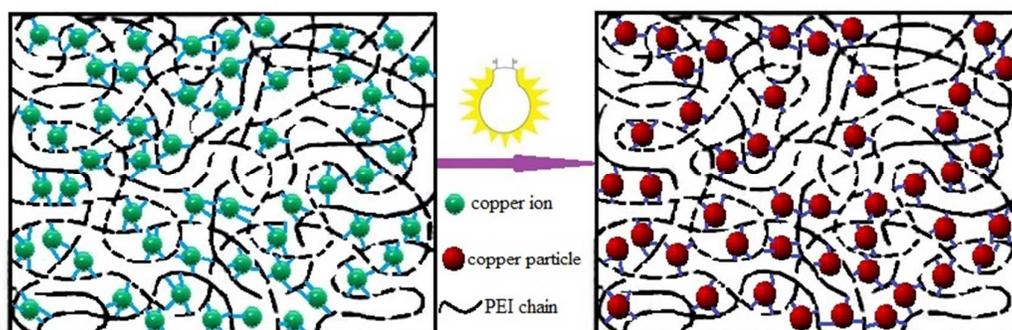
The authors declare no competing financial interest.

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Through photoreduction, superfine copper nanoparticles were prepared from high concentration of copper chloride at room temperature in the presence of capping agent of PEI.