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ARTICLE TYPE

## Effective oxidation protection of polymer micelles for copper nanoparticles in water

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Copper nanoparticles are often susceptible to rapid oxidation in water. We report a water-dispersible and long-term stable copper nanoparticle protected by a block copolymer micelle that can effectively inhibit the access of oxygen to the copper inside its hydrophobic core, providing a sufficient diffusion barrier against oxidation in water.

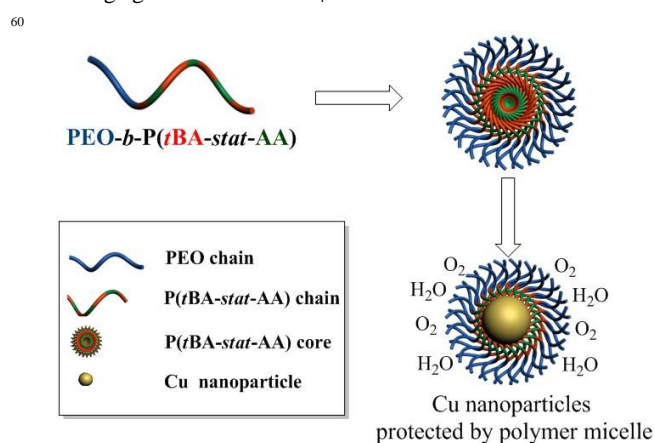
Copper nanoparticles have been widely used in catalysis, sensors, microelectronics, and nanotechnology.<sup>1-6</sup> They play an important role in modern electronics circuits and future nanodevices due to their low cost, excellent electrical conductivity and surface enhanced Raman scattering activity.<sup>7</sup> Traditionally, organic solvents were used in an inert atmosphere during their preparation to prevent them from oxidation and aggregation.<sup>8</sup> However, synthesis of copper nanoparticles with long-term stability in aqueous media is still a technical challenge due to the propensity of easy oxidation on their surfaces.<sup>1, 2, 9-12</sup>

It is well known that chlorophyll is stable in leaves because the membrane of chloroplast provides a good barrier to the oxygen and water. In addition, the amphiphilic chlorophyll molecule containing a hydrophobic paraffin chain (the green chain in Scheme S1† in ESI) prefers to insert into the membrane of chloroplast and tylakoidy, leading to a further blocking to oxygen and water. Similarly, micelles prepared from amphiphilic polymers usually have a hydrophobic core and hydrophilic coronas. They have offered great potential in drug delivery, nanoreactors and biomineralization,<sup>13-18</sup> and may block oxygen and water in a nano-sized domain just like the chlorophyll molecule inserting in the membrane of chloroplast and tylakoidy.

Inspired by the protection mechanism of chlorophyll by the chloroplast in leaves and the corona-core structure of amphiphilic polymer micelles, herein we propose to use polymer micelle as a novel capping agent to prepare copper nanoparticles in water (Scheme 1). The polymer micelle serves as the template and the surface stabilization agent (Scheme 1), providing a good barrier to water and oxygen (fast oxidation in water occurs without the micelle protection). Moreover, the polymer micelle core provides a good location for the growth of copper nanoparticles.

The poly(ethylene oxide)-block-poly(*tert*-butyl acrylate-*stat*-acrylic acid) [PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>)] block copolymer can self-assemble into polymer micelles in THF/water by a solvent switch method.<sup>19</sup> The hydrophilic PEO coronas are expressed on the surface of the micelle core composed of P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) segments to stabilize the micelle. The hydrophobic P*t*BA

segments provide the driving force for self-assembly by the hydrophobic effect.<sup>13, 16</sup> Also, they can be hydrolyzed to negatively charged PAA chains, which can absorb positively charged Cu<sup>2+</sup> ion in aqueous solution by electrostatic interactions. It is noteworthy that small amount of hydrophilic PAA chains are constrained within the hydrophobic P*t*BA core due to their molecular structure, rather than forming micelle coronas. Upon addition of CuCl<sub>2</sub>, the Cu<sup>2+</sup> ions are enriched in the micelle core as a result of interactions between Cu<sup>2+</sup> ion and PAA. The copper nanoparticles can be formed immediately after the addition of reducing agent such as NaBH<sub>4</sub>.

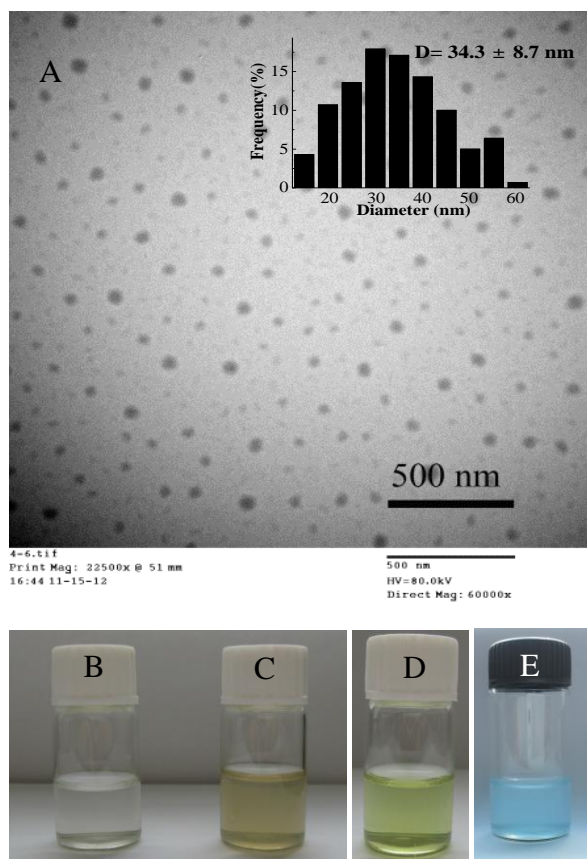


Scheme 1. Synthetic route to copper nanoparticles stabilized by polymer micelles in water. Copper nanoparticles are formed *in situ* among the micelle core after introduction of CuCl<sub>2</sub> and subsequent reduction by NaBH<sub>4</sub>.

The PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) block copolymer was synthesized according to our recent procedure (Scheme S2†),<sup>16, 17, 19</sup> but with a different degree of polymerization. Firstly, the atom transfer radical polymerization (ATRP) macroinitiator, PEO<sub>43</sub>-Br, was synthesized by the reaction of 2-bromoisobutyl bromide with MeO-PEO-OH (*M<sub>n</sub>* = 1900) in the presence of triethylamine in anhydrous toluene.<sup>16</sup> Secondly, PEO<sub>43</sub>-*b*-P*t*BA<sub>20</sub> was synthesized by ATRP of *t*BA monomer in methanol at 60 °C for 24 h. Finally, to obtain PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) copolymer, the precursor PEO<sub>43</sub>-*b*-P*t*BA<sub>20</sub> block copolymer was partially hydrolyzed in dichloromethane in the presence of trifluoroacetic acid (TFA; 2.0 equiv to the *tert*-butyl ester). DMF GPC in Fig. S1† shows an *M<sub>n</sub>* of 6500 with an *M<sub>w</sub>*/*M<sub>n</sub>* of 1.07, clearly

indicating the growth of polymer chain. The compositions of PEO<sub>43</sub>-*b*-P*t*BA<sub>20</sub> and PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) copolymers are evaluated by <sup>1</sup>H NMR spectra in Fig. S2†.

The PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) copolymer can easily form micelles in THF/water mixture, with a critical micellization concentration (CMC) of 39.8 μg mL<sup>-1</sup> (Fig. S3†). THF was then removed by dialysis against water. The digital photo of the micelle solution is shown in Fig. 1B. The micellar structure was confirmed by transmission electron microscopy (TEM) analysis in Fig. 1A, with a number-averaged mean diameter of 34.3 ± 8.7 nm. Dynamic light scattering (DLS) study indicates an intensity-averaged bimodal distribution of particle size (Fig. S4A†), giving a hydrodynamic diameter (*D*<sub>h</sub>) of 23.4 nm with a polydispersity of 0.366. However, the corresponding number-averaged size distribution shows a unimodal peak (Fig. S4B†), suggesting the majority particles are small polymer micelles.



nanoparticles formation.<sup>16, 17, 20</sup> The micelle solution was treated with CuCl<sub>2</sub> solution for 30 min. Copper nanoparticles were obtained by addition of excess NaBH<sub>4</sub>. The solution immediately turned light brown when the NaBH<sub>4</sub> was added, indicating the formation of copper nanoparticles. The aqueous copper nanoparticles solution is purified by dialysis to remove excess Cu<sup>2+</sup> ions and is colloidally stable for more than one year without precipitation or any change in colour, indicating the excellent protection for Cu nanoparticles provided by polymer micelles. In a control experiment where no polymer micelle solution was added into the CuCl<sub>2</sub> solution, the solution immediately turned black after addition of NaBH<sub>4</sub>. Furthermore, some black sediment was observed within 10 minutes, indicating very poor stability of copper particles without polymer micelles. Finally, the copper particles were oxidized to a blue solution (Fig.1 E).

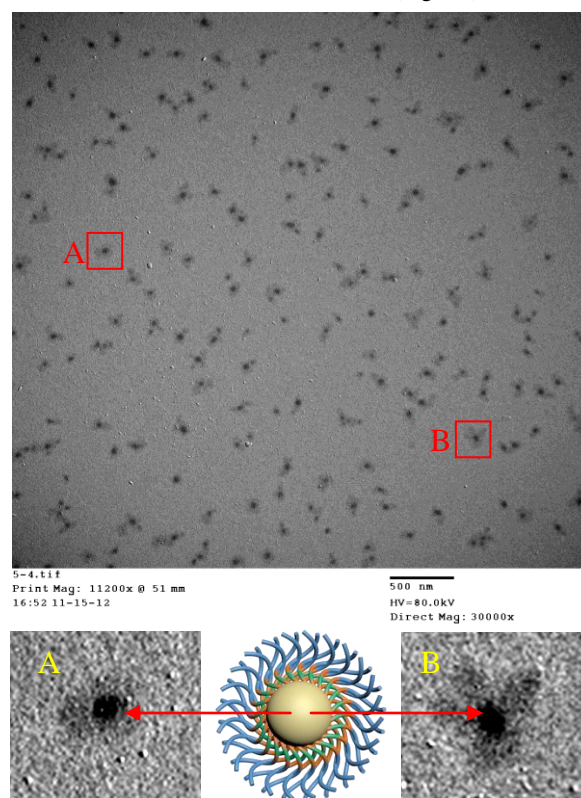


Fig. 2 TEM images of copper nanoparticles protected by PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) micelles. (A) and (B) are the magnified structure of copper nanoparticles.

Fig. 1 (A) TEM image of PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) block copolymer micelles stained by phosphotungstic acid, with the insert showing their diameter distribution. (B) A digital photo of polymer micelle solution. (C-D) Digital photos of copper nanoparticles stabilized by the micelles (1.0 mg mL<sup>-1</sup>) for one year with initial the copper concentrations of 45 and 76 μg mL<sup>-1</sup>, respectively. (E) Copper particles without the micelle stabilization in water were easily oxidized, showing a blue solution in one day.

The Cu<sup>2+</sup> ions have a strong electrostatic interaction with the –COO<sup>-</sup> groups in the P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) core of the micelles. Therefore, it is possible to *in situ* deposit copper nanoparticles in the micelle core according to a similar mechanism to sliver

The coronas around the copper nanoparticles provide an excellent capping layer to protect the inner copper nanoparticles against oxidation in water. TEM images in Fig. 2 clearly demonstrated the core-corona nanostructure of polymer micelle-stabilized copper nanoparticles (45 μg mL<sup>-1</sup> of copper). The nanoparticle is very clear by TEM without staining because they are located in the micelle core. The average diameter of the copper nanoparticles is around 36.6 ± 7.4 nm while the size of the whole nanoparticle with a corona is 97.1 ± 22.8 nm. DLS analysis in Fig. S4† revealed an intensity-averaged *D*<sub>h</sub> of ca. 270 nm with a low PDI of 0.072. This value is twice larger than that by TEM, probably due to the hydration of the micelle-protected copper nanoparticles in water.

The size of the micelle-protected copper nanoparticles is much bigger than that of pure polymer micelles without copper in the core, indicating that the self-assembly behaviour of PEO<sub>43</sub>-*b*-P(*t*BA<sub>18</sub>-*stat*-AA<sub>2</sub>) copolymer is strongly dependent on the concentration of Cu<sup>2+</sup> ions. For example, when the concentration of copper increased from 45 to 76 μg mL<sup>-1</sup>, the colour of the solution changed from light brown to green, suggesting less protection from oxidation by polymer micelles at higher copper concentration (Fig. 1 C and D). TEM study further revealed that bigger nanoparticles without a clear corona can be observed with a mean diameter of 163.9 ± 26.8 nm (Fig. S6†).

To further confirm the effective protection of polymer micelles against oxidation for copper nanoparticles, X-ray photoelectron spectroscopy (XPS) studies were performed as there was usually one characteristic peak at around 930 ~ 933 mV for Cu(0) nanoparticles while Cu(I) or Cu(II) has more than one peak.<sup>9, 21, 22</sup> Fig. 3 shows that the XPS spectrum of copper nanoparticles (0.45 μg mL<sup>-1</sup>) protected by polymer micelles for more than one year in water. The sharp peak at 932 mV indicates the existence of Cu(0) nanoparticles, suggesting sufficient protection of polymer micelle for metallic copper nanoparticles. This is because both water and oxygen are inhibited by the polymer micelle, similar to the protection mechanism of chlorophyll by the chloroplast in leaves.

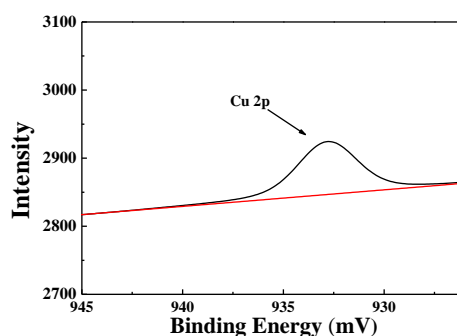


Fig. 3 XPS spectrum of copper nanoparticles stabilized by polymer micelles at 45 μg mL<sup>-1</sup> of copper (as displayed in Fig. 2).

The copper nanoparticles may offer good catalytic activity for some chemical reactions. Classical Michael type reactions are important but usually need quite severe reaction conditions and thereby causing limitations in their use in practice.<sup>23</sup> Copper nanoparticles are particularly attractive because they are cheap, high yielding, recyclable and can catalyze the reaction under mild conditions.<sup>2</sup> A typical Michael addition reaction between thiazolidine-2,4-dione and styrene in THF is performed at 25 °C to evaluate their catalytic activity of Cu nanoparticles shown Fig. 2. As expected, those copper nanoparticles displayed better catalytic activity for Michael addition reaction than bulk copper powders (Scheme S3† and Fig. S8†).

In summary, we have successfully developed a novel method for preparing long-term stable copper nanoparticles in water based on polymer micelles. Such micelles offer effective protection against oxidation for copper nanoparticles in water. Those copper nanoparticles are water-dispersible and stable for a long time (more than one year). Also, they showed good catalytic activity in Michael addition reaction. They may have potential applications in biosensors, catalysis, etc. in the future. As far as

we know, this is for the first time that polymer micelles are applied to effectively protect copper nanoparticles against oxidation. Moreover, our strategy may be extended to facilitate prepare and effectively protect other metal nanoparticles with a long-term stability in water.

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## Notes and references

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