Electronic Supplementary Information

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

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1. The sketch of the experimental setup of preparing the copper nanoparticles through photoreduction

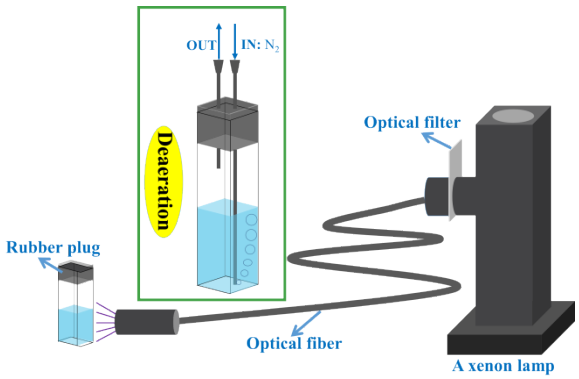
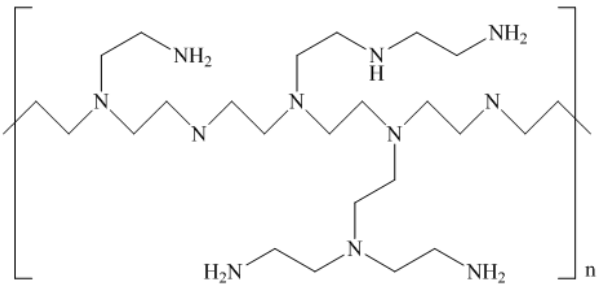


Figure S1. The sketch of the experimental setup of preparing the copper nanoparticles through photoreduction

2. Calculation of the quality of PEI which was added in the solution

The structure unit of PEI is as follows. And the molecular weight of PEI used in this article is 1800.



The structure unit of PEI

According to this structure, the molecular weight of this structure unit is 543 and every structure unit of PEI has 11 amine groups. Let us suppose that every amine group could be coordinated with copper ion. So, if the molar ratio of amine to copper ion is 8:1, and the copper ion is 0.01 M, the mass of PEI in 10 milliliter ethanol solution is calculated as follows:
$((0.01\ M \times 10\ mL \times 10^{-3} \times 8)/11) \times 543 = 0.0395\ g$

The density of ethanol is 0.79 g/mL. The content of the PEI in the ethanol solution is 0.0395/(0.79×10)×100%=0.5%

Therefore, if the molar ratio of amine to copper ion is 16:1, the content of the PEI in the ethanol solution is 1%.

3. TEM images of copper particles prepared from the ethanol solution with different concentration of copper-diethanol amine coordination compound

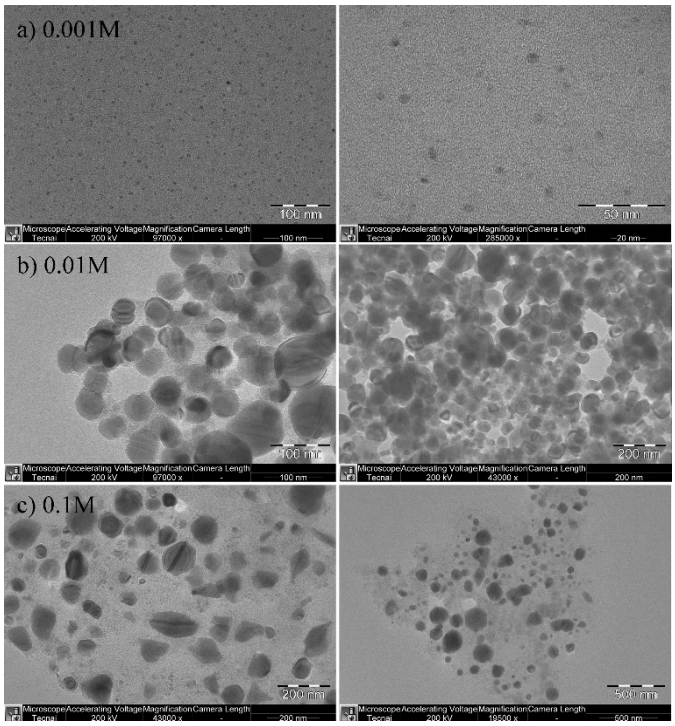


Figure S2. TEM images of copper particles prepared from the ethanol solution with different concentration of copper-diethanol amine coordination compound

With the increase of the ethanol solution of copper-diethanol amine, the size of copper particles increases greatly. The concentration increases from 0.001M to 0.1 M, the size of copper particles increases from 10 nm to 200 nm.

4. The change of UV-vis spectra of 0.01 M ethanol solution of copper chloride and PVP without diethanol amine

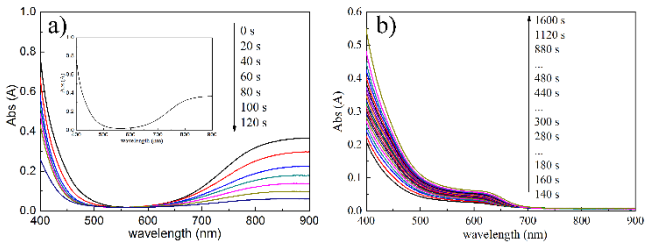


Figure S3. UV-vis spectra of 0.01 M ethanol solution of copper chloride, photoinitiator 184 and PVP without diethanol amine. a) the decrease of absorption of the wavelength range from 600 nm to 900 nm, the inside is the UV-vis spectrum of the 0.01 M ethanol solution of $CuCl_2$; b) the increase of absorption of the wavelength range from 400 nm to 700 nm.

Compared with the UV-vis spectrum of the 0.01 M ethanol solution of $CuCl_2$, the UV-vis spectrum of the 0.01 M ethanol solution of $CuCl_2$ and PVP has no obviously change, which indicates that PVP maybe has

no coordination with copper ion. Under irradiation, the absorption peak of copper ion disappeared, but there was no appearance of absorption peak of copper nanoparticles.

5. The color of the solution with the copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with different amine.

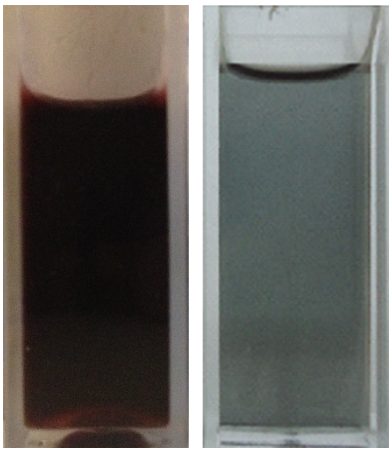


Figure S4. The color of the solution with the copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with different amine, left is with PEI, right is with diethanol amine.

The solution with the copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with PEI is bright red(left), and with the diethanol amine is black(right). That's totally different.

6. The XRD spectra of copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with PEI and $CuCl_2$

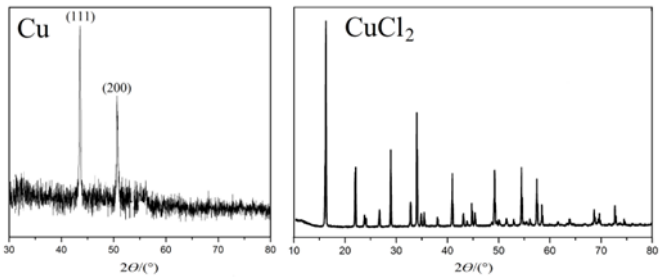


Figure S5. XRD spectra of copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with PEI and $CuCl_2$.

According to the PDF 00-001-1242 standard XRD database, the peak positions are consistent with those of metallic copper. The peak at 2Θ =43.55° is the crystal face of Cu(111), whereas that at 2Θ =50.66° is the crystal face of Cu(200). The intensity of peak (111) is stronger than that of peak (200), which also agrees with the XRD database. The XRD analyses confirm that the nanoparticle is a copper particle.

7. The EDS analysis of the the copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with PEI.

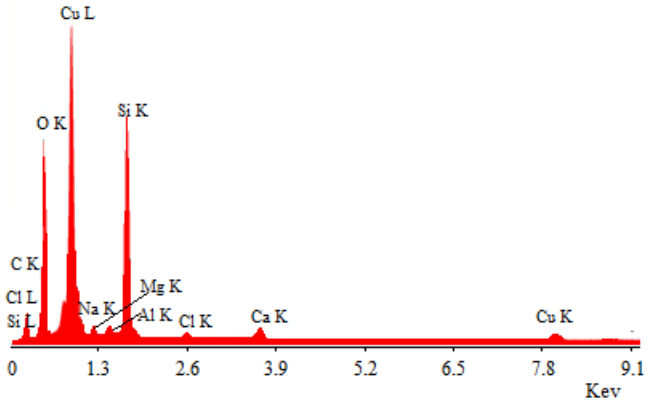


Figure S6 EDS analysis of copper nanoparticles on the glass.

Figure S6 is the EDS spectrum of the copper nanoparticles prepared from 0.01 M ethanol solution of copper chloride with PEI(the molar ratio of PEI to copper ion is 24:1). The substrate which supported copper nanoparticles was glass. So, except the strong spectrum line of the element of copper, the other elements' spectrum lines, such as Si, Mg, Al, Ca et al were caused by the glass. The presence of small amount of chlorine may come from the precursor copper chloride.

8. 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

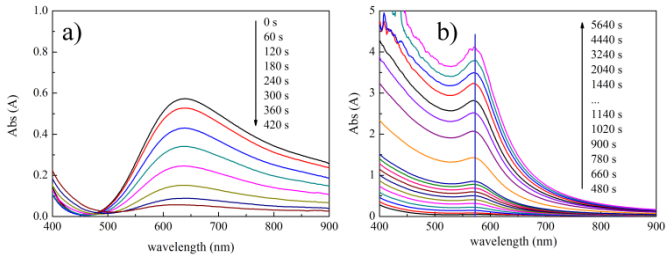


Figure S7. UV-vis spectra of 0.01 M ethanol solution of copper chloride with PEI and the molar ratio of amine group to copper ion was 24:1. a) the decrease of absorption of the wavelength range from 500 nm to 900 nm; b) the increase of absorption of the wavelength range from 400 nm to 900 nm.

9. 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 is 24:1)

Figure S8. 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 is 24:1)

The color of the solution with the copper nanoparticles prepared from 0.1 M ethanol solution of copper chloride with PEI is black red.

10. The change of UV absorption spectra of the copper dispersion prepared from 0.1 M ethanol solution of copper chloride and PEI(the molar ratio of amine to copper ion was 24:1).

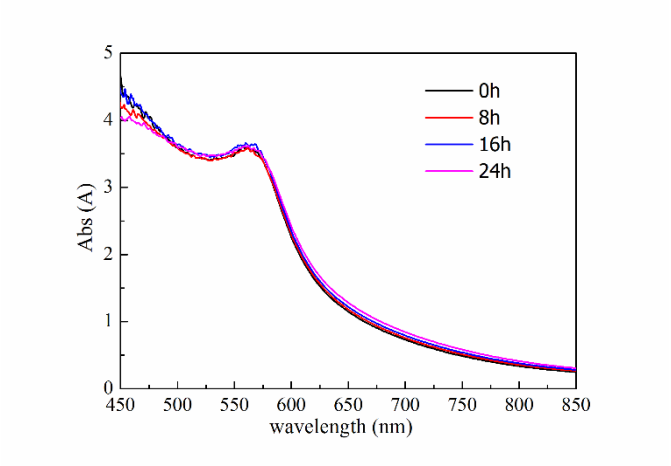


Figure S9. The change of UV absorption spectra of the copper dispersion prepared from 0.1 M ethanol solution of copper chloride and PEI (the molar ratio of amine to copper ion was 24:1)

After 24 h, the UV absorption spectra of the copper dispersion prepared from 0.1 M ethanol solution of copper chloride and PEI (the molar ratio of amine to copper ion was 24:1) has no obvious change which demonstrated that the dispersion of copper nanoparticles was very stable. It was due to superfine copper nanoparticles and the action of polymer capping agent.