Synthesis of Dialkyl Dithiophosphate Surface-Capped Copper Nanoclusters

Xiaobo Wang, Weimin Liu,* Fengyuan Yan, Zhijun Zhang,[†] and Binshi Xu[††]
State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou 730000, P. R. China
[†]*Key Laboratory of Functional Materials, Henan University, Kaifeng 475001, P. R. China*
[††]*State Key Laboratory for Remanufacturing, Beijing 100072, P. R. China*

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Dialkyl dithiophosphate-capped lyophobic copper nanoclusters of a mean size of 4.0 ± 1.1 nm were synthesized by a novel method. The method was characterized by the generation of small copper clusters through aqueous reduction and the extraction of the clusters into organic solvent using dialkyldithiophosphate.

The creation of perfect nanometer-scale crystallites is an ultimate challenge of modern materials research with outstanding fundamental and potential technological consequences.[1] In this respect, two-phase method first reported by Schiffrin is of great success and has been extensively utilized.[2] This relatively simple preparative method based on ion extraction and the formation of self-assembled alkyl thiolate monolayer on metal surface, results in monolayer-encapsulated Au nanocrystal materials. The analogous methods have also been used to prepare silver nanoparticles.[3] The resulting so-called thiol-capped, monolayer-encapsulated, or lyophobic[4] Au and Ag nanoparticles possess common promising features,[1] including high intrinsic stability, sufficient solubility, monodispersed size distribution, etc., and have been widely used in many fields, especially as entirely new building blocks for the construction of nanostructure supperlattice.[1,2,5] However, those methods to prepare Au and Ag nanoparticles are not suitable for the preparation of chemically unstable Cu nanoparticles. This is because that no proper surface passivating agent has been found to be chemisorbed as strongly on such a metal surface as the sulfur-hydryl on the gold surface.

Dialkyl dithiophosphates (abbreviated as DTPs), which are collectors in mineral flotation,[6] have been successfully used as capping agents in the preparation of several metal sulphides nanoparticles in our laboratory.[7] DTP has strong interaction with the surfaces of many materials including Cu,[8] thus we expect that DTPs might be proper capping agents for Cu nanoparticles.

With respect to the preparation of metallic nanoparticles by the traditional two-phase method, it is imperative that the corresponding metal ions be transferred into an organic phase by ion extraction. However, this method is unsuitable for the preparation of DTP-capped Cu nanoparticles, because Cu ions react with DTP to form a stable complex and not to be reduced. Therefore, we modified the traditional two-phase method, so as to obtain DTP-capped Cu nanoparticles by the extraction of the Cu nanoclusters grown from an aqueous solution into the organic phase containing the surface passivating agent. The modified process is somewhat similar to the traditional ion extraction process provided that the extraction units are colloid particles. It is worth pointing out that this method is characterized by a simultaneous phase transfer and surface passivating of the colloid particles, which could be extended to the isolation and surface modification of all kinds of colloid particles prepared from and dispersed in an aqueous solution. Accordingly,[9] copper ions were reduced by hydrazine (excess) in aqueous medium. When the copper colloid was generated, DTP dissolved in benzene was added to the colloid. Subsequently the copper cluster was surface-passivated and extracted into the organic layer through a two-phase reaction. The size and size distribution depended on the preparation conditions such as the length of alkyl chains, the ratio of DTP to copper, the reduction time, and so on.

Similar to thiol-derivated gold nanoparticles, DTP-capped copper nanoparticles could be handled and characterized as a simple macromolecular material. The dry powder is dark brown and well dissolved in nonpolar solvents, soluble in slightly polar solvents, but insoluble in short-chain alcohols, acetone or water. The capped Cu nanoparticles are stable in atmosphere, with the thermal decomposition temperature in air determined by thermogravimetric analysis to be above 170.1 °C. Their colloidal solution is much stable and does not show signs of decomposition or aggregation over a period of several years.

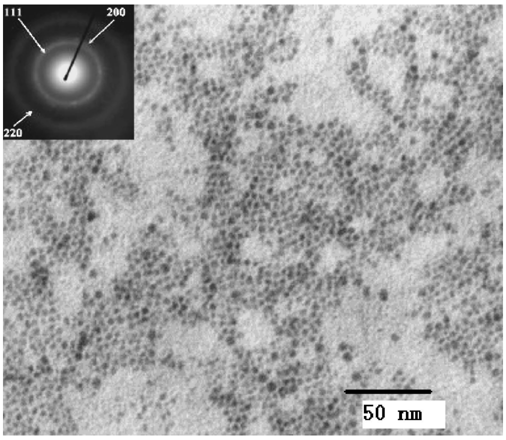

Figure 1. TEM picture and ED pattern of the C_8DTP surface-passivated copper nanoclusters.

Figure 1 shows the TEM photograph of the nanoparticles and the relevant electron diffraction (ED) pattern. It is seen that the as-prepared nanoparticles are monodispersed and have a relatively narrow size distribution. They have a mean diameter of 4.0 ± 1.1 nm, based on the measurement of at least 200 particles. The two ED rings assigned to the lattice planes (111), (200) and (220) of copper indicate that Cu exists as face-centered cubic phase in the capped nanoparticles.

The IR spectra of the di-*n*-octyl dithiophosphate surface-passivated copper nanoparticles (abbreviated as Cu-DTP) are similar to that of di-*n*-octyl dithiophosphoric acid (abbreviated as C_8DTP), indicating that DTP is chemically bonded to Cu in the composite. The absorptions at 1629, 628, and 558 cm^{-1} and the disappearance of the absorption within 2400–2600 cm^{-1} for the Cu-DTP are attributed to the conjugate structure between the (SPS) group of DDP and Cu atom.[7,8,10]

The composition of the capped Cu nanoparticles is determined as 4.79% H, 26.12% C, 4.35% O, 4.21% P, 8.71% S, and 51% Cu, by elemental analysis. The ratios of C:H:S:O:P from the elemental analysis conform to that of the theoretical value of C_8DTP, indicating that DTP remains unchanged after capping the Cu nanoparticles. The ^{1}H NMR spectrum of the present Cu nanoparticles shows the signals of CH_3 and CH_2 of long alkyl chains, while the ^{31}PNMR spectrum of the nanoparticles gives multiplets at 105.8 and 99.5 ppm,[11] which confirms the bonding between the P nuclei and the Cu atoms on the surfaces of the nanoparticles.

Table 1. Binding energies of the elements in ammonium *O*,*O*′-di-*n*-octyl dithiophosphate, *O*,*O*′-di-*n*-octyl dithiophosphate-capped Cu nanoparticles, Cu, and Cu_2O

Samples	Binding Energy/eV				
	C_{1s}	O_{1s}	S_{2p}	P_{2p}	$Cu_{2p3/2}$
NH_4DTP	284.7	532.3	162.1	133.2	
Cu-DTP	284.7	532.2	162.3	133.0	932.6
Metallic Cu					932.7
Cu_2O		530.3			932.5

The chemical states of the elements in our product, determined by X-ray photoelectron spectroscopic analysis, are listed in Table 1. The binding energies of C_{1s}, O_{1s}, S_{2p}, and P_{2p} in DTP-capped Cu nanoparticles and in ammonium *O*,*O*′-di-*n*-octyl dithiophosphate are similar, indicating that they are in similar chemical states. The binding energy of $Cu_{2p3/2}$ at 932.6 eV is different from that of Cu^{2+} compounds and resembles in a way to that of Cu^+ and metallic Cu. In combination with the O_{1s} peak at 532.3 eV which differs from that in Cu_2O (at 530.3 eV) and CuO (at 529.6 eV), it is inferred that Cu exists as elemental Cu and remains stable in the product. Therefore, it is supposed that DTP-capped metallic Cu nanoparticles are prepared in the present work and DTP as a modifying agent acts to prevent the metallic Cu nanoparticles from oxidation.

In conclusion, the following interesting findings can be stated: Compared to the traditional two-phase method, the colloid-extraction method is a handy method for the synthesis of lyophobic nanoparticles. DTP is proven to be a suitable surface passivating agent for copper nanoparticles and possibly for other nanoparticles as well. A new kind of surface-passivated lyophobic copper nanoparticles possessing the features of thiol-derivated noble metal nanoparticles was successfully prepared, which can be used as a novel building units for the construction of nanostructured supperlattice. Further work on synthesis process optimization and properties of the copper nanoclusters is under way. It was anticipated that the facile manipulation and the low cost of copper would stimulate wide industrial applications.

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9 Typical synthesis procedure was as follows (the entire process took place at ambient temperature and in air). Firstly, a freshly prepared aqueous solution of $N_2H_4 \cdot H_2O$ (500 mL, 0.1 mol/L) was mixed with the solution of $Cu(acac)_2 \cdot 2H_2O$ (500 mL, 10 mmol/L) under vigorous stirring in ambient condition; a brown Cu sol was formed in several minutes. Second, 4 mmol *O*,*O*′-di-*n*-octyl dithiophosphoric acid dissolved in 500-mL benzene was added to the sol and further stirred for 3 h, with the gradual transformation of the organic phase into dark red colour. Third, the organic phase was separated and evaporated at 80 °C in a rotary evaporator to remove the solvent; then the organic layer was mixed with 100-mL acetone to allow the generation of brown precipitate. The precipitate was filtered after storing for several hours and washed with acetone for three times. Finally, the crude product was dissolved in 10-mL ether and precipitated with acetone again, to allow the generation of the target compound at a yield of copper 81%. Further purification of the product could be achieved by the chromatographic separation of the crude product in a silica gel column using petroleum ether/acetone (4:1) as the eluent. In this case a dark brown solid was obtained at a yield of 40%.

10 Infrared spectra were recorded as pressed KBr disks on a Nicolet FTIR 10 DX spectrometer. C_8HDTP: 2960(s), (CH_3), 2926(s), (CH_2), 2856(s), (CH_2), 2400–2600 (ν S–H), 1466(s), (CH_3), 1378(s), (CH_3), 995(s), (OPO), 660(s), (ν P=S), 532(w), (ν P-S) cm^{-1}; Cu-DTP: 2926(s), 2856(s), 1620, 1466(s), 1378(s), 996(s), 628(s), 558(w), cm^{-1}.

11 ^{1}H NMR and ^{31}P NMR spectra were recorded on a Bruker AM-400 MHz spectrometer in $CDCl_3$ vent at ambient temperature. Chemical shifts are given in relative to $SiMe_4$ and phosphoric acid. ^{1}H NMR (400 MHz $CDCl_3$, δ): for Cu-DTP, 0.88 (br d, CH_3), 1.28 (br, CH_2); for C_8HDTP, 0.88 (br d, CH_3) 1.28 (br, CH_2). ^{31}P NMR (400 MHz $CDCl_3$, δ): for Cu-DTP, 105.8 (m), 99.5 (m); for C_8HDTP, 82.3.

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