Supplementary Information for

A general strategy for metallic nanocrystals synthesis in organic medium

Peng Huang,[a] Jing Lin,[b] Zhiming Li,[a] Hengyao Hu,[a]Kan Wang,[a] Guo Gao,[a] Rong He[a] and Daxiang Cui*[a]

Experimental section

1. Method

1.1 Phase transfer of metal ions from water to toluene.

In a typical experiment, 20 ml of 0.4 M aqueous metal salt solution (Ag(i), Cu(ii), Ni(ii), Fe(iii), Fe(ii), and Co(ii)) was mixed with 50 ml of toluene. After 5 ml of 0.2 M aqueous sodium oleate solution was added and stirring was continued for 3 min. Phase transfer of metal ions from water to toluene would then occur quickly and completely, as evident by the complete colour bleaching of the aqueous phase.

1.2 Preparation of metallic nanocrystals

After phase transfer of metal ions from water to toluene, 10 ml of aqueous hydrazine hydrate was rapidly added to the above two-phase system, and the mixture was vigorously stirred for 5 minutes to ensure that the reduction reaction is completely finished.

1.3 Heat treament of metallic nanocrystals

The organic phase (including the formed metallic nanocrystals) was taked out in an autoclave, which was heated up at ~150 ℃ for 2, 4, 10 or more hours. The time of extraction is adjustable for accurately controlling the size of the as-prepared nanocrystals. The metallic colloids thus obtained were highly stable, with no sign of agglomeration even after weeks of storage.

2. Characterization

TEM: Transmission Electron Microscopy (TEM) images (including high resolution images) and selected area electron diffraction (SAED) patterns were acquired using a JEM-2010 transmission electron microscope (JEOL Ltd., Japan) operated at 200 kV. The specimens of TEM were prepared by dropping the sample onto a copper mesh coated with an amorphous carbon film. This mesh was then dried in a vacuum desiccator.

UV-vis spectra: Absorption spectra were recorded on a UV-2550 UV-vis spectrometer (SHIMADZU, Japan). The toluene suspensions of metallic nanocrystals were used as the UV-vis samples, and the pure toluene was used as reference.

X-Ray powder diffraction（XRD）: The X-ray powder diffraction patterns were recorded on a BRUKER-AXS diffractometer (Bruker, Germany) using Cu Kα radiation ($\lambda = 0.154$ nm).

FT-IR spectra: The FT-IR spectra were obtained on a Fourier Transform Infrared spectrometer (EQUINOX 55, Bruker, Germany). The samples for FT-IR measurement were prepared by grinding the dried powder of metallic nanocrystals with KBr together, and then compressed into thin pellets.

Part Results and Discussions

TEM images of alloy, semiconducting, and magnetic nanocrystals

Based on the synthesis of metallic nanocrystals, we also successfully prepared alloy, semiconducting, and magnetic nanocrystals in supplementary data Fig. 7. Alloy nanoparticles of Cu-Fe, Ni-Fe, and Co-Fe, were synthesized by co-reduction of the metal precursors with hydrazine hydrate. Semiconductor nanocrystal of CdSe was prepared by using Na_2SeSO_3 as Se source, which was added in the two-phase system after Cd^{2+} was tranfered into organic phase. Magnetic nanoparticle of Fe_3O_4 was synthesized by co-precipitating Fe^{2+} and Fe^{3+} in organic medium using ammonia($NH_3•H_2O$). Na_2SeSO_3 and $NH_3•H_2O$ are water-solubility in aqueous phase, so reaction of molecular precursors were spatially separated in the organic and aqueous phase. Subsequently, the nucleation stage of nanocrystals overlapped with the growth stage only occurring at the liquid–liquid interface.

EDS result

The obtained metallic nanocrystals were also determined by energy dispersive X-ray spectrometry (EDS), which was performed using the TEM equipped with energy dispersive spectrum and the spot size is about 10 nm. The EDS results of the chemical composition analysis, presented in Supplementary Fig. 9, confirm that these nanoparticles are apparently silver, copper, nickel and iron by the elemental mapping. It is clear that the peaks of Ag, Cu, Ni and Fe in nanocrystals are higher than Cu in the copper mesh. The copper nanocrystals include 9.26 wt % oxygen element, which can be attributed to oxidation of the part sample of the copper nanoparticles.

Reaction Mechanism (Formation of metallic nanocrystals)

Regarding the liquid-liquid system used for synthesis of colloidal nanocrystals, the original method may date back to 1857, in which Faraday firstly fabricated the dispersed gold particles by an aqueous gold salt reduction with phosphorus in carbon disulfide[8]. Then, Brust combined the two-phase approach with some elaborate ion extraction techniques and the method of self-assembly based on alkane thiols, established a novel method and synthesized one kind of new thoil-derived gold nanoparticles[9]. Since then, the liquid-liquid systems have been frequently employed to fabricate various nanocrystals[2a, 4, 10, 11]. Among the reported liquid-liquid systems, toluene-water was mainly adopted. Other organic/water systems such as chloroform-water[12],cyclohexane-water[13],and benzene-water[14], were also often used. Besides above-mentioned methods, there are two important reagents in the route of the two-phase approach, that is, phase transfer reagents and surfactants. The phase transfer reagents can be classified into cation-transfer reagent and anion-transfer reagent. Tetraoctylammonium bromide ($N(C_8H_{17})_4Br$) was used to transfer $AuCl_4^-$[9, 15] and $PtCl_4^-$[16]. O,O'-dialkyl dithiophosphoric acid[17], trioctylphosphine oxide (TOPO)[18] and tetra n-octylammonium bromide (TOABr)[19] were used to transfer Cu^{2+}, Cd^{2+}, and Pd^{2+} respectively. However, these phase transfer reagents were toxic and costly, so they can not be used broadly. In this study, we firstly report oleate salts as the phase transfer reagent because of low toxicity and cost.

During the synthesis and applications of nanoparticles, the appropriate surfactant is crucially important to control the nucleation and growth of the nanocrystals, and plays a key role to disperse and stabilize the nanocrystals in solvents. Sodium oleate (SO)[20] is one kind of the most widely employed anionic surfactants to stabilize and disperse the nanoparticles in the practical applications of nanoparticles. The presence of a carboxylic group and a nonpolar tail group for sterical hindering is the basis for the excellent stabilizing function of this ligand. Meanwhile, the presence of C=C bond of sodium oleate makes the final products easily react with polymer matrix, which is very important for potential industrial application.

The precipitation of metallic nanocrystals from aqueous or non-aqueous solutions typically requires the chemical reduction of a metal cation[3a]. Reducing agents have many forms, of which the most common are gaseous H_2, solvated ABH_4 (A=alkali metal), hydrazine hydrate ($N_2H_4•H_2O$), hydrazine dihydrochloride($N_2H_4•2HCl$), and hypophosphite[5]. A typical reduction reaction of a transition metal cation is
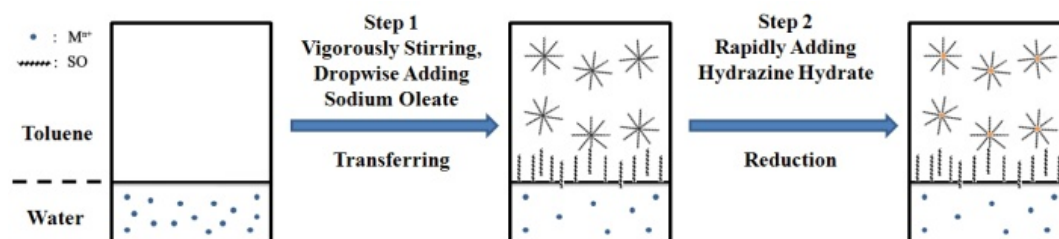
as follow: $M^{n+} + ne^- \rightarrow M^0$. Hydrazine hydrate is freely soluble in water, but since N_2H_4 is basic, the chemically active free-ion is normally represented as $N_2H_5^+$, the hydrazinium ion. In comparison to the reduction process with solvated ABH_4 (A=alkali metal) or hypophosphite, the reduction with hydrazine hydrate produces harmless byproducts such as nitrogen gas and water.

In theory, the reduction of any metal with an $E°$ more positive than -0.481 V or -0.23 V, respectively, should be possible at room temperature, given a sufficient excess of reducing agent and proper control of pH. Regarding the metals precipitating from solution, this obviously includes many first-row transition metal ions, such as Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, but also many second- and third-row transition metals, as well as most post-transition elements and a few non-metals. Hence, we selected hydrazine hydrate to reduce various metals and alloy at room temperature. Our results have confirmed its feasibility.
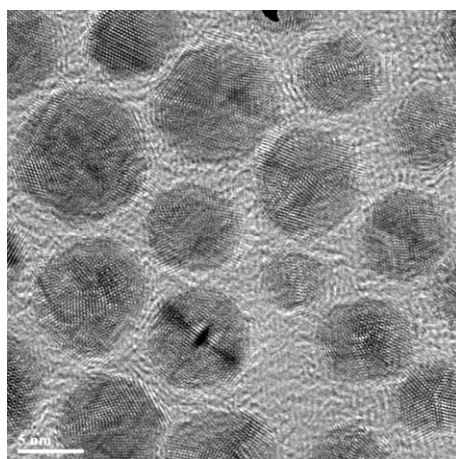
A possible mechanism for the formation of monodisperse nanocrystal is discussed as follows. The modified two-phase approach consists of two stages: first stage is that a burst nucleation overlapped with the ephemeral growth in the liquid-liquid system; the second stage is post-treatment of obtained nanocrystals in the organic phase. In the first stage, although the nucleation rate was quite fast, which favors the formation of monodisperse nanoparticles according to the LaMer mechanism[21], the growth rate was also fast. Therefore, there was no time to focus the size distribution of nanoparticles due to the fast growth rate. In addition, the surface of the formed nuclei and nanocrystals is capped by long-chain ligands (SO), so the nuclei and nanocrystals are hydrophobic, and can be well dispersed in the organic phase (see supplementary data Fig. 8). Once the nuclei and nanocrystals form, they will go into the organic phase. This process can stop the growth of nanocrystals. In the second stage, the growth process was aroused, with that smaller particles were essentially consumed by larger particles. The time plays an important role in the size control of the nanocrystals. With the increase of post-treatment time, the size of the nanocrystals is also accordingly increased. Finally, monodisperse nanocrystals have a narrow size distribution and dissolve in a nonpolar solvent with excellent stability (at least a few months).

In the whole process, the pH value of water phase can regulate the transfer efficiency of Metal ions. The polarity of the organic medium and the reaction temperature could change the solubility of complexes (surfactants and metal ion) in the organic medium. Other appropriate surfactants should be developed to improve the transfer efficiency of Metal ions. In addition, the temperature and the reaction time of post-treatment can control the size of the products. The parameters mentioned above may improve our process. We also are investigating.
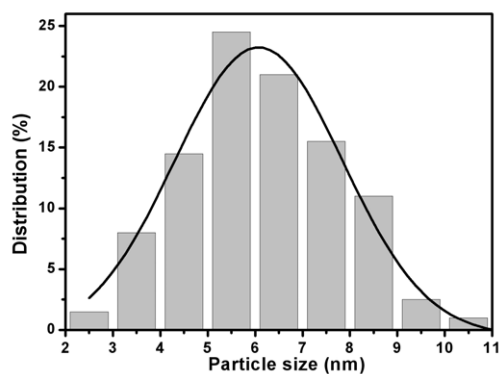
Supplementary data

Supplementary scheme 1. Diagram showing, step 1: hydrophobization and phase transfer of metal cations from an aqueous to a toluene phase by vigorously stirring after dropwise adding sodium oleate; step 2: reduction of metal cations (entrapped in SO reverse micelle) by hydrazine hydrate and formation of monodisperse hydrophobic nanocrystals capped and stabilized by SO.
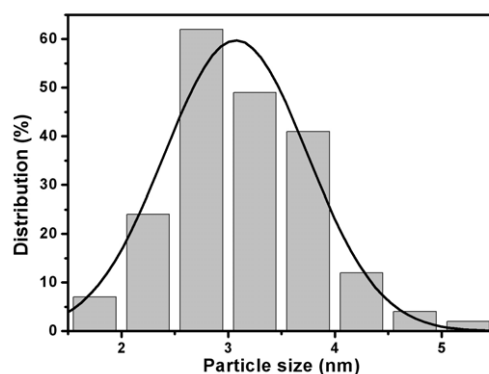

Supplementary Fig. 1 High resolution transmission electron microscopy of Ag nanocrystals

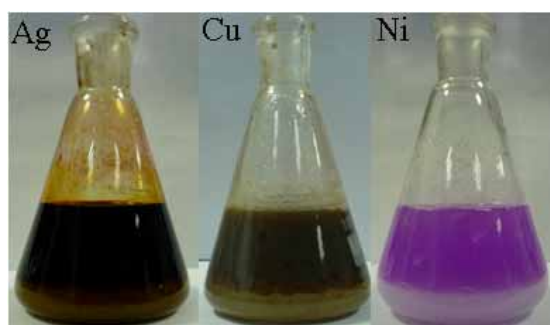**Supplementary Fig. 2** High resolution transmission electron microscopy of Cu nanocrystals.

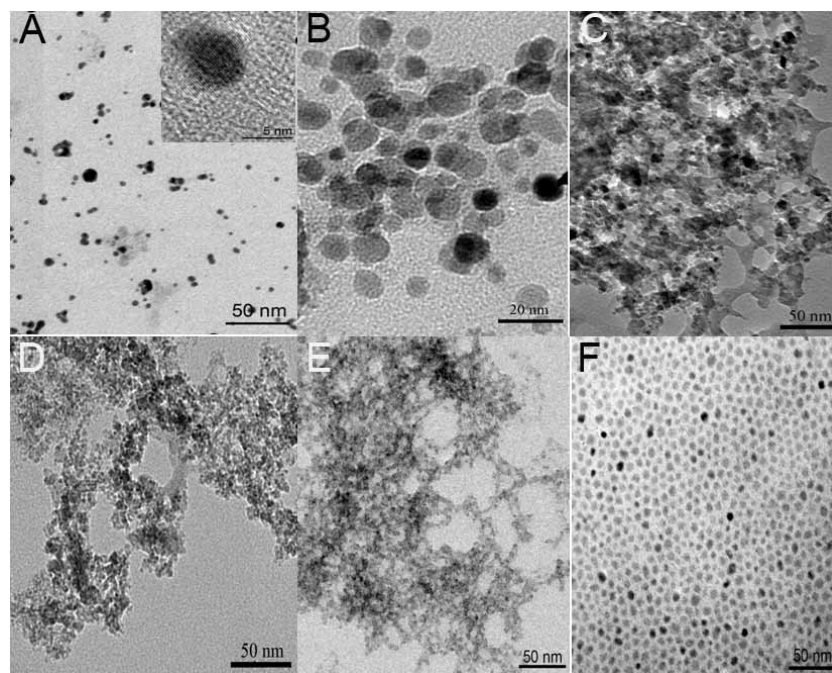**Supplementary Fig. 3** The histogram of Ag nanocrystals.

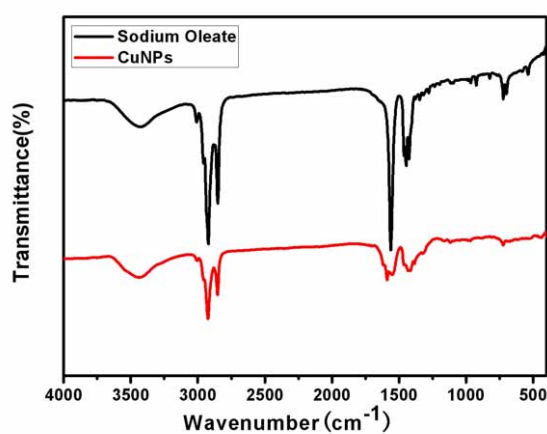**Supplementary Fig. 4** The histogram of Cu nanocrystals.

Supplementary Fig. 5 Photographs of large-scale syntheses of hydrophobic Cu nanocrystals in toluene-water system.
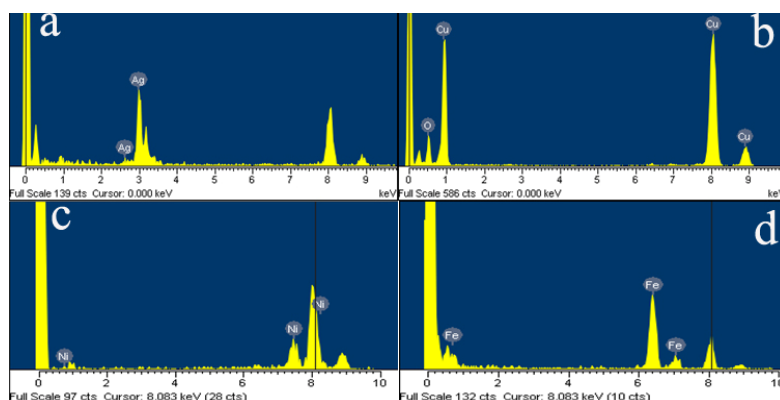

Supplementary Fig. 6 Photographs of large-scale syntheses of hydrophobic Ag, Cu, Ni nanocrystal in toluene-water system.

Supplementary Fig. 7 TEM images of (A) Co, (B) Cu-Fe, (C) Ni-Fe, (D) Co-Fe alloy nanocrystals, (E) CdSe, (F) Fe_3O_4; Inset: HRTEM image of Co nanocrystals.

Supplementary Fig. 8 The FT-IR spectra of pure sodium oleate (black line) and Cu nanocrystals (red line).

Supplementary Fig. 9 EDS spectra of metallic nanocrystals (a.Ag; b.Cu; c.Ni; d.Fe).