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Research of nonlinear optical properties of copper nanoparticles

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Abstract. This research reports the preparation and characterization of copper nanoparticles modified by didecyl benzene sulfonate (DBS). The Cu nanoparticles' size was determined to be 4.0 nm by transmission electron microscope (TEM). The X-ray photoelectron spectrometry (XPS) results show that there are interactions between the copper nanoparticles and DBS function group. The nonlinear optical properties were studied by the four-wave mixing method. The value of $\chi^{(3)}/\alpha_0$ was found to be 6.9×10^{-11} esu cm.

PACS. 73.61.Tm Nanocrystalline materials – 83.70 Surfactants – 42.65.R Nonlinear optics

1 Introduction

Colloidal-size metal and semiconductor particles with diameters of 1–20 nm have been an interesting area of advanced materials research because they mark a materials transition range between molecular and bulk properties [1]. In this area, many remarkable characteristics, which result from the quantum-size effect and which cannot be observed in the bulk materials, appear and can be utilized in new electronic and photonic devices [2–4]. The potential applications of small metal or semiconductor particles as functional units in innovative microelectronics and photonic devices, as well as new types of catalysts, have inspired much recent research on the synthesis and properties of these metals and particles [5–9].

Copper is one of the most widely used materials in the world. It has great significance in all industries, particularly in the electrical one. Copper nanoparticles have been synthesized and characterized with different methods [10–12].

Stability and reactivity are the main two important factors that impede the use and development of the metal cluster as a new generation of nanoelectronic device [7]. Most of the clusters known so far lack the stability required for a realistic application in electronic devices and other applications. Thus, synthesizing the stable metal nanoparticles is a challenging project.

Theory and experiments have demonstrated that small particle size and narrow distribution can improve the nonlinear optical response of nanoparticles [13]. Previous research claims that placing polar groups onto the surface is very helpful for improving nonlinear optical applications, particularly electrooptical and $\chi^{(3)}$ effects, and for controlling sphere–sphere interactions [14]. Thus it is of importance to synthesize and control the particle size and size distribution as well as surface chemical environment of nanoparticles.

Here, copper nanoparticles modified by didecyl benzene sulfonate (DBS) organosol were prepared by using a microemulsion method in the system of water/toluene. The copper nanoparticles show extremely stable properties. The nonlinear optical properties were determined with the four-wave mixing method. A great response of third order nonlinear optics was found.

2 Synthesis and characterization

2.1 Synthesis of copper nanoparticle organosol

20 ml of 0.01 mol/l aqueous $(CH_3COO)_2Cu$ and 100 ml of toluene were poured into a beaker, and 22 ml of 0.1 mol/l DBS was added as a surfactant. The mixing solution was stirred for 0.5 h, then while the stirring speed was kept constant, 32.5 ml of 10% N_2H_2 aqueous solution were dropped into the mixture with a dropping bottle. After this process, the reaction system was at a standstill for 12 h. The mixture automatically separated into two layers. The upper layer was a reddish brown, transparent, organic layer, and the lower layer was a water phase with a little light brown precipitation. The transparent solution of the upper layer was put into a flask and then refluxed for 1 h under the protection of high purity N_2. As a result, the copper organosol was obtained. This organosol shows long-term stability.

2.2 Characterization of copper nanoparticles

The copper nanoparticles' size and shape were characterized by transmission electron microscope (TEM) (JSM-2000x, Japan).

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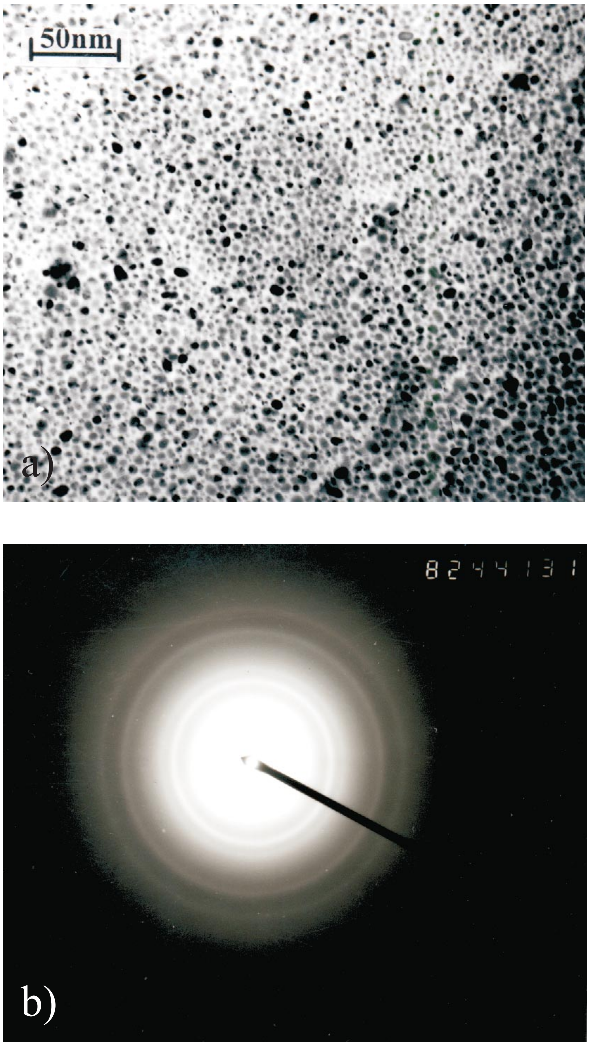

Fig. 1. TEM micrograph of copper nanoparticles (a, upper panel) and corresponding polycrystalline electron diffraction pattern (b, lower panel).

X-ray photoelectron spectrometry (XPS) measurements were made for this sample and the pure DBS one at the XPS station of Beijing Synchrotron Radiation Facility. The former was prepared as follows: One drop of copper organosol was placed onto a clean Pt substrate, and the solvent was allowed to evaporate. The latter was prepared by the moulding of DBS powder into a pill (AR, Beijing Chemical Agent Factory). UV-Vis 3100 (SHIMAOZU, Japan) were used to determine the UV-Vis absorption spectra.

2.3 Measurement of the nonlinear optical properties

The three-order nonlinear optical properties of the copper colloids were measured using degenerate four-wave mixing (DFWM). The laser pulses were generated from a frequency-doubled Nd:YAG laser at a wavelength of 532 nm, repetition rate of 10 Hz, and pulse width of 10 ns.

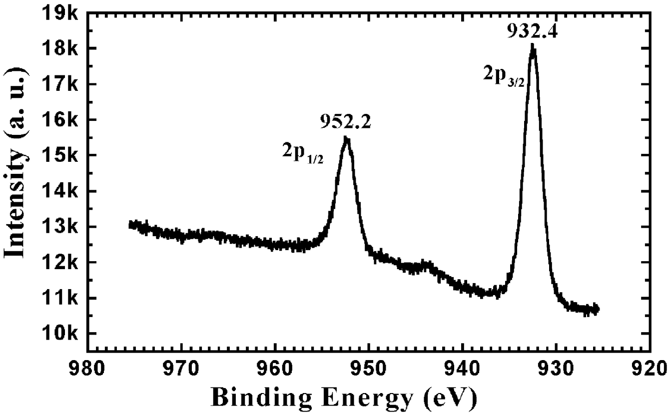

Fig. 2. XPS spectra of copper $2p_{3/2}$ and $2p_{1/2}$ regions, for the copper nanoparticles modified by DBS.

3 Results and discussion

The TEM bright field image of copper nanoparticles (operating at 20 kV) and the corresponding selected area diffraction pattern are shown in Figs. 1a and 1b, respectively.

The diffraction rings can index to (111), (200), (220), (311), and (400). It investigated that the sample's structure is face center cubic (FCC) Cu. The diffuse nature of the rings is a simple manifestation of the crystal shape effect caused by the nanoscale size of the particles [6]. The TEM result shows that the copper nanoparticles modified by DBS take the shape of a sphere with a mean diameter of 4.0 nm.

A series of XPS spectra, with Mg $K\alpha$ at 1253.6 eV, were measured for characteristic core levels of C, O, S, and Cu elements in pure coating reagent DBS and in Cu nanoparticles modified by DBS. The XPS spectrum, within the range of 10–1005 eV for the copper nanoparticles, showed the presence of the Cu, C, O, S, and Pt elements. Elemental analysis demonstrated that there is no evidence of the starting materials.

Figure 2 shows the spectrum of the Cu $2p$ region. Two copper bands, $2p_{3/2}$ and $2p_{1/2}$, occur at 932.4 eV and 952.2 eV, respectively. These results certify that almost all the copper atoms in the nanoparticles are in the Cu^0 state.

An obvious and interesting phenomenon manifested in the XPS spectra for all three elements (C, O, and S) in the DBS is that their main peak positions have ~ 2 eV shift towards binding-energy sides in the DBS-coated Cu nanoparticles that are lower, relative to those in the free DBS molecules; this is shown in Fig. 3 for carbon element. The binding-energy change of the elements seems to be related to the interaction between the surfactant function group and the Cu nanoparticle. A tentative interpretation for this equal-amount shift of the binding energies is that they are due to final-state effects [15]. This means that, if we follow the emission of one electron from core level, we see that the emitted photoelectron has left a positively charged core hole behind it, and because of the lack of screening effect in the free DBS molecule, it gives higher binding energy, e.g., 286.3 eV for C $1s$. While in the DBS-modified Cu nanoparticle, the

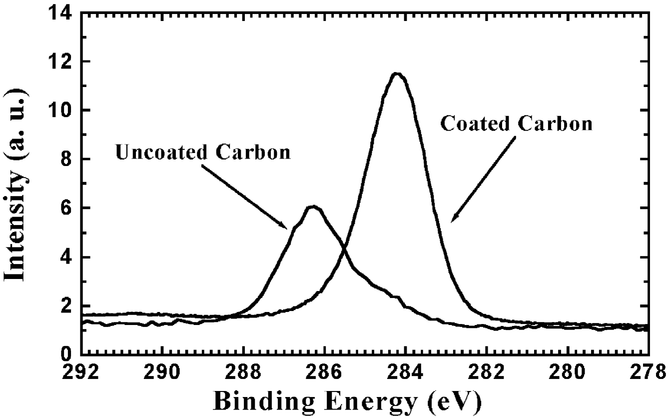

Fig. 3. XPS spectra of carbon 1*s* region, for pure DBS and for Cu nanoparticles modified by DBS.

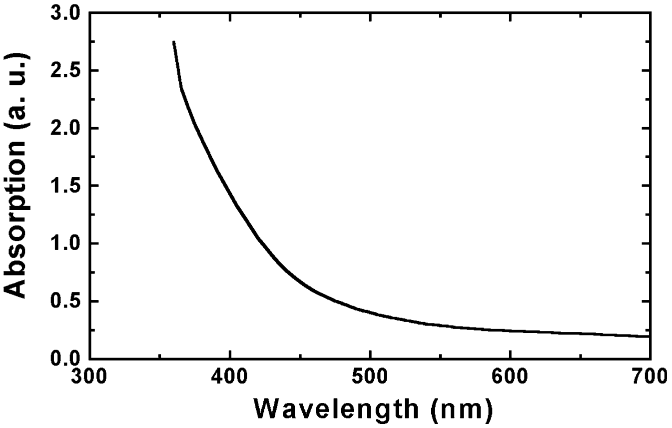

Fig. 4. The UV-Vis absorption spectrum of the copper nanoparticles in toluene.

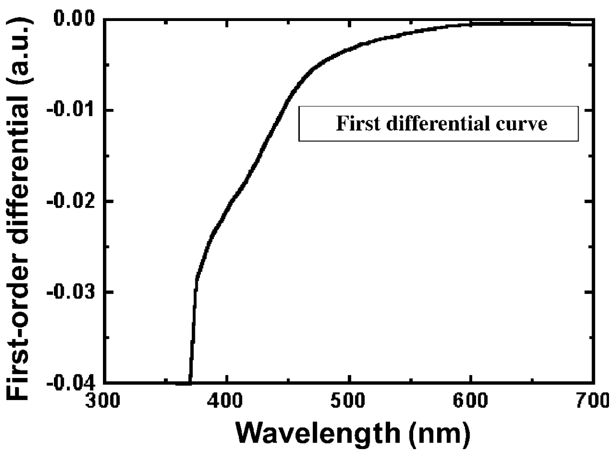

Fig. 5. The first-order differential curve of the UV-Vis absorption spectrum for copper nanoparticles in toluene.

binding energy of C 1*s* appears at 284.3 eV, this is because the same core hole is well screened by the electron transferred from the Cu nanoparticle. In other words, this binding-energy shift is not due to initial effects. According to the above considerations, and taking into account the Cu 2*p* core level band structure, the interaction between the surfactant function group and the Cu particles is very possible, thanks to inductive attraction, but does not form explicit chemical bonds. This result is very similar to that reported for the Au nanoparticles modified by thiol [9].

The UV spectrum of copper nanoparticle organosol is shown in Fig. 4; there are no obvious plasma peaks that can be observed; this contradicts what is reported in [16, 17]. However, after doing the first- order differential for the UV curve, as shown in Fig. 5, obviously, one finds a weak and broading peak located at about 420 nm. The decreasing of the plasma peaks of the Cu nanoparticles can be attributed to the interaction between the surfactant function group and the Cu nanoparticles.

The value of $\chi^{(3)}/\alpha_0$ for copper colloids was calculated as 6.9×10^{-11} esu cm. It is better than the reported values (10^{-12}–10^{-11} esu cm) for the copper nanoparticles embedded in glass [18] and for those prepared by reduction of copper (II) acetate in water and 2–ethoxyethanol by the use of hydrazine under reflux [19]. The increasing of $\chi^{(3)}/\alpha_0$ probably results from the difference among surface chemical environments. Conversely, this further demonstrates that there are interactions between the surfactant function group and the copper nanoparticles. This new kind of copper nanoparticle has many potential applications, for example, optical switches.

4 Summary

Colloidal copper nanoparticles modified by DBS have been successfully synthesized with microemulsion methods, and the copper organosol shows that they have long-term stability. Our results demonstrate that there are interactions between the surfactant function group and copper nanoparticles, thanks to the inductive attraction, but no explicit chemical bonds. The value of $\chi^{(3)}/\alpha_0$ of copper nanoparticle organosol was obtained to be 6.9×10^{-11} esu cm. The increase in this value is attributed to the difference of surface chemical environments.

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