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Surface-capped copper nanoadditive for improvement of base oil properties

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Abstract

Copper nanoparticles surface-capped by alkanethiol with long carbon chain length was prepared successfully by chemical reduction method. 1-dodecanethiol was used as the coating material for the desired smooth and protected surface. Various reaction parameters, like effect of pH, molar ratio of the reactants etc. had been tested experimentally to explore the most suitable and economical way of using the chemical reduction method. Uniform, smooth surface and spherical shaped copper nanoparticles, with particle size of about 40-60 nm had been produced successfully. Copper nanoparticles surface-capped by alkanethiol (C_{12} S-Cu) was characterized by means of x-ray diffraction, scanning electron microscopy, Fourier transform infrared spectrometry and ultraviolet-visible spectroscopy. Uniform dispersion of copper nanoadditive in base oil using ultrasonic method was investigated. The tribological behavior of C_{12} S-Cu as an additive for base oil was evaluated. Viscosity, pour point, and flash point of nano lubricants at different concentrations of nanoadditive (0.2, and 0.5 wt %) were evaluated.

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Introduction

A number of studies have been conducted in relation to the synthesis and characterization of various inorganic nanoparticles as well as the effect of nano-sized lubricant additives on wear and friction with the development of nano technology (Zhou et al., 2001; Sun et al., 2004; Liu and Chen, 2000). It has been generally recognized that the mechanisms for nanoparticle lubricating additives to reduce friction and wear are mainly linked with three aspects (Zhang et al., 2011). First, spherical nanoparticles behave as ball-bearings between rubbing surfaces to reduce friction and wear by way of polishing surface and increasing surface hardness (Xu et al., 1996). Second, nanoparticles in lubricating oil can fill wear scars and grooves and form physico-chemical adsorption film resulting in reduced friction and wear (Choi et al., 2009). Finally, colloid nanoparticle additives, in particular, soft metal nanoparticles and their alloys can penetrate the elastohydrodynamic contacts mainly by a mechanism of mechanical entrapment in thin film contacts, or they can form boundary lubricating films in rolling contacts at slow speeds, both resulting in improved load carrying capacity, antiwear and friction

reduction properties (Chinas-Castillo and Spikes, 2003, 2004; Zhang *et al.*, 2010).

In addition to the distinctive catalytic, optical, thermal, magnetic, antimicrobial, electronic and electrical conducting properties, copper nanoparticles (Cu-NPs) present a wide range of potential applications in nanotechnology including catalysts (Judai et al., 2011), additives for lubricants (Shi et al., 2013), heat transfer nanofluids (Garg et al., 2008), manufacture of electronic and optical devices (Pacioni et al., 2010), conductive inks (Park et al., 2007), materials for solar energy conversion (Musa et al., 1998), biosensors (Kumar et al., 2010), antibiofouling agents (Kumari and Majewski, 2013) and cancer cell treatments (Mamun et al., 2009). Moreover, due to the remarkable tribological properties of Cu nanoparticles, together with good self-repair functions the worn surface, and excellent to an environmental-friendly property, they have been desired for an excellent candidate to replace expensive noble metal nanoparticles such as silverand gold (Khanna et al., 2007; Luo et al., 2012; Seo et al., 2013).

There are diverse approaches to the preparation of the nanoscale materials that have been reported in the literature. Some of these methods include chemical reduction (Huang et al., 1997; Lisiecki et al., 1996), radiation method (Joshi et al., 1998), microemulsion technique (Lisiecki and Pileni 1993, Pileni et al., 1999; Qi et al., 1997), supercritical technique (Ziegler et al., 2001), thermal reduction (Dhas et al., 1998), sonochemical reduction (Kumar et al., 2001), and laser ablation (Yeh et al., 1999). We can focus on the chemical reduction method over other nanoparticle preparation techniques because of its ease of application, cost-effectiveness, variation in particle characteristics and different experimental parameters such as concentration, temperature and pH (Grouchko et al., 2009).

Nanoparticles are likely to agglomerate in liquid medium because of large specific surface and high surface energy, which greatly restrict the application of nanoparticles as lubricating additives (Cushing *et al.*, 2004). To overcome this obstruction, researchers usually adopt polyelectrolytes (Radtchenko *et al.*, 2001; Li *et al.*, 2006) and surfactants (Shen *et al.*, 2009; Puntes *et al.*, 2001; Zhang *et al.*, 2003) as modifiers to control the growth of particles and to coat nanoparticles, thereby preventing them from surface oxidation or aggregation (Hou *et al.*, 2005, Sun and Xia, 2002).

In the case of copper NPs some surfactants were usually added as dispersant or surface modifier such as sodium dodecyl sulfate (SDS) (Lisiecki et al., 1996), poly(vinylpyrrolidone) (PVP) (Park al., 2007a), et dialkyldithiophospate (Zhang et al., 2009). alkyl al., aryl-sulfonate (AAS) (Lee et 2009), cetyltrimethylammonium bromide (CTAB) (Chen et al., 2006), and polyelectrolytes such as poly (ethyleneimine), polyethylene glycols, and poly (ethylether ketone) (Dung et al., 2011). Among them CTAB plays a critical role in controlling the size and improve the disperse ability of copper nanoparticles (Chen et al., 2006).

The aim of capping ligands in synthesis of copper nanoparticles is to bind with the particle surfaces. They provide a steric barrier to aggregation and are also effective in preventing inorganic nanoparticles from oxidation, setting up ground for them to be used as lubricating additives. But most of the currently used surfaces modifying agents have phosphorus and sulphur which are harmful to environment and human body (Zhou *et al.*, 2001; Zhang *et al.*, 2010). Therefore it is important to seek for novel P- and S-free surface modifying agents for Cu nanoparticle so as to make an environmentally acceptable nano-Cu lubricant additive (Zhu *et al.*, 2009). In particular, alkanethiol-capped

nanoparticles (monolayer protected clusters, MPCs) are stable in air, soluble in nonpolar organic solvents, and capable of facile modification with other thiols through exchange reactions. In addition longer chains of octanethiol, decanethiol and dodecanethiol (C_8-C_{12} alkanethiols) were suggested for a good barrier layer that can protect the copper cores from oxidation (Ang *et al.*, 2004).MPCs are generally stabilized with thiolated ligands that are known to covalently bond to metal surfaces, with their properties primarily determined by the terminal functional groups. Among thiol-capped metal nanoparticles, Au and Ag probably have been studied extensively due to their simplicity of preparation and relative stability (Lisiecki *et al.*, 2000; Henglein, 1998).

We addressed а successful preparation on of copper-nanoadditive surface capped by 1-dodecanethiol by chemical reduction method. A complete characterization of the nanoadditive was performed by various techniques such as Fourier transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), ultraviolet-visible (UV-vis) spectroscopy, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX).Particle size distribution of the nanoparticles was between 60-80 nm. Uniform dispersion of copper nanoadditive in base oil using ultrasonic method was investigated. The tribological behavior of C₁₂S-Cu as an additive in base oil was investigated. Viscosity, pour point and flash point of nano lubricants at different concentrations (0.2, and 0.5 wt %) were evaluated.

Materials and methods





Fig. 1. X-ray powder diffraction patterns of synthesized copper nanoparticles

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Copper sulfate pentahydrate (CuSO₄·5H₂O, AR grade) and toluene (C₆H₆) were obtained from Merck Specialties Private Ltd. Mumbai, India. 1-dodecanethiol (CH₃ (CH₂)₁₁ SH), cetyltrimethylammonium bromide (CTAB, 99% grade) and hydrazine hydrate (N₂H₅OH) used were the products of Loba Chemie Pvt. Ltd. Mumbai, India. Ethanol (C₂H₅OH) was obtained from Merck KGaA, Germany. Dichloromethane (CH₂Cl₂) was purchased from Riedel-de Haen, Germany and base oil SN-150 was collected from Renish Petrochem FZE (Trading *company* of *virgin base oil* based in Dubai), United Arab Emirates. Water is purified by distillation process and maintains the water quality of 0.1 μ S/cm throughout the work.

Instruments

Absorption spectra of reaction solutions were measured by UV-vis spectrophotometer (UV-1800), CPS-240A model, Shimadzu Corporation, JAPAN. The XRD pattern of the synthesized copper nanoparticles was recorded by a Diffractometer, Ultima-IV model, Shimadzu Corporation. JAPAN, operating at 40 KV and 40 mA over a diffraction angle from 30° to 90° under a scan rate of 0.02° per step at a speed of 3.0 deg/ min. The Scanning Electron Microscopy (SEM) analysis coupled with EDX analysis of synthesized copper nanoparticles was performed by JEOL Field Emission Scanning Electron Microscope, JSM-7600F model, JAPAN, operating at 5.0 KV, with a width of 8.5 mm and magnification was X 15,000; 30,000; 50,000 and 1,00,000. The Attenuated Total Reflectance (ATR) and FT-IR spectroscopy of synthesized copper nanoparticles and the capping agent 1-dodecanethiol were carried out by FT-IR Spectrophotometer, IRPrestige-21 model, Shimadzu Corporation, JAPAN, equipped with an ATR device in the wavenumber range 500-4000 cm⁻¹ with 20 scanning rate with resolution of 4 cm⁻¹. The FT-IR spectra were taken in a transmittance mode.

Preparation of surface-capped Cu –nanoparticles

The details about the preparation of surface-modified Cu nanoparticles are as follows: 2.497 g (10 mmol) copper sulfate was dissolved completely in 50 mL of distilled water. 0.456 g (1.25 mmol) CTAB was first dispersed into the distilled water using the sonicator and then into the copper sulfate solution, CTAB was added under vigorous stirring. Then approximately 12 mL of hydrazine hydrate was added drop-wise into the mixed solution to rapidly change the solution color into dark brown. The mixture was stirred for 10 min at 30°C, followed by the addition of 2.4mL1-dodecanethiol in 50 mL toluene under additional 3 h vigorous stirring at 30°C. After stirring for a long time, it was assumed that all reactions were completed and then the organic layer was collected using separating funnel. Then toluene was removed with a rotary evaporator under reduced pressure, yielding crude nanosized copper surface-capped with alkanethiol. The crude product was fully washed with ethanol for several times to remove residual ligands and other impurities, affording purified surface-capped copper nanoparticles as a black powder. As-obtained black powder C_{12} S-Cu was centrifuged and washed with ethanol and dried in the vacuum dryer at 120°C before characterization and tribological investigation.

Preparation of nano lubricants

Ultrasonic method was used to disperse nanoparticles inside the base oil bath. To achieve the best and the most stable state, 0.2wt% and 0.5 wt% sample of oil/Cu- have been made by dispersing at 40°C for 30 min and at 100°C for 60 min respectively. All of the samples were kept in the transparent glass containers in a completely stagnant condition for about 72 h for evaluating their stability conditions. During this period, the stable conditions of all the samples were periodically and visually inspected. The same procedure was followed to synthesize uncapped copper nanoparticles except that no capping agent was used.

Results and discussion

X-ray diffraction

Typical XRD patterns of synthesized copper nanoparticles are shown in the Fig. 1.

As shown in Fig. 1. four main characteristic diffraction peaks at $2\theta = 43.36$, 50.48, 74.14 and 90° correspond to the [111], [200], [220] and [311] crystal planes of metallic Cu, confirming the formation of pure face-centered-cubic (fcc) Cu nanoparticles without significant oxides or other impurity phases such as CuO, Cu₂O, or Cu(OH)₂. These are in close agreement to the JCPDS File No. 04–0836. This indicated that the prepared Cu material was highly pure, crystalline and well arranged in specific orientation. The sample stored for 30 days in ambient condition shows the same XRD peaks, corresponding to good stability of synthesized Cu nanoparticles. From the Debye–Scherrer equation (Langford and Wilson 1978, Monshi *et al.*, 2012), we estimated the particlesize. The crystal size of products as calculated by Scherrerformula is 48.6 nm.

Surface morphology

Cu nano particles are spherical in shape with a smooth surface morphology. The diameter of the nano particles is found to be ranging from 40 nm to 60 nm. SEM image also



Fig. 2. SEM images of synthesized copper nanoparticles

shows that the produced nanoparticles are more or less uniform in size and shape. The agglomeration of the particles is almost clear (Fig.2). As the nanocopper particle is encapsulated by 1-dodecanethiol, there is no surface oxidation and hence prevents the oxidation of the nanocopper particle. During chemical reduction, the reducing agent donates electrons to the copper ions (Cu^{2+}), causing copper to convert to its metallic form (Cu^{0}). In case of using CTAB as protecting agent, the stabilization of Cu^{2+} was highly effective. Cu Nanoparticles (NPs) have a high surface area to volume ratio along with high fraction of surface atoms that elicits elevated lubrication activity compared to the copper metal as a whole. C_{12} S-Cu nanoparticles were prepared under different reaction conditions and SEM images obtained are shown in the Fig 3. It can be shown that when the pH value of copper sulfate solution was adjusted to alkaline (pH=10), without CTAB introduced into the reactant solution, large aggregates with severe agglomeration were obtained (Fig. 3 a). When the pH value of copper sulfate solution was not adjusted, and no CTAB stabilizer was introduced into the reactant solution, aggregates with moderate agglomeration were produced (Fig. 3 b).However, when 1.25 mmol CTAB was added into the solution, fine spherical Cu nanoparticles with a size of about 60-80 nm were harvested even when the pH value of the reactant solution was not adjusted to alkaline condition (Fig. 3 c). This is closely related to the strong reduction ability of hydrazine hydrate in alkaline conditions and to the stabilizing actions of CTAB. Namely, Cu2+ is instantly reduced into uncapped Cu nanoparticles by hydrazine hydrate in alkaline solution and uncapped Cu nanoparticles tend to agglomerate in the absence of stabilizer CTAB generating aggregates before being surface-capped by C12SH. Lowering the pH value of copper sulfate solution slows the reduction of Cu²⁺by hydrazine hydrate affording better dispersed uncapped Cu nanoparticles but not aggregates. After CTAB is added into the CuSO₄ solution, CTAB may surround nascent Cu particles to prevent them from agglomeration and keep them off O₂ in the aqueous solution yielding fine C₁₂S-Cu nanoparticles with a narrow size distribution. The role of CTAB is to control the growth of the Cu nucleus to some extent and facilitate final surface-capping of Cu nanoparticles by C₁₂SH possessing good oxidation resistance and dispersibility. This can be rationally understood because CTAB as a ligand is weaker than thiol, Cu nanocrystals coated by CTAB can be easily replaced by thiol via ligand exchange. Since stabilizer CTAB plays an important role in



Fig. 3. SEM images of C₁₂S-Cu nanoparticles prepared when (a) the pH of CuSO₄ solution was adjusted to 10 in the absence of CTAB, (b) the pH of CuSO₄ solution was not adjusted and no CTAB was added, and (c) 1.25 mmol CTAB was added but the pH of aqueous CuSO₄ was not adjusted

preparing well-dispersed Cu nanoparticles, and we investigated the influence of molar ratio of CTAB to $CuSO_4$ on the size and morphology of as-synthesized $C_{12}S$ -Cu nanoparticles.

detected. The result indicates that the as- synthesized product is composed of high purity Cu nanoparticles. The similar EDX spectrum was obtained for each sample analyzed.



Fig. 4. SEM images of C₁₂S-Cu nanoparticles prepared at different cetyltrimethyl ammonium bromide to CuSO₄ molar ratio: (a) 1:4, (b) 1:8, (c) 1:12

Fig. 4 shows the SEM images of samples obtained at various molar ratio of CTAB to CuSO_4 .Cu nanoparticles obtained at a CTAB to CuSO_4 molar ratio of 1:4 have a spherical shape and a particle diameter of about 60-80 nm (Fig 4a). At increased molar ratios of CTAB to CuSO_4 an oily organic layer which can be hardly separated and removed is formed around as-synthesized Cu nanoparticles (Fig 4 c).Because decreasing molar ratio of CTAB to CuSO_4 (at CTAB to CuSO_4 molar ratio of 1:8 and 1:12) leads to an increased particle size and agglomeration of Cu nanoparticles (Figs 4 b and 4 c) proper CTAB to CuSO_4 molar ratio at 1:4 for synthesizing desired C_{12} S-Cu nanoparticles can be suggested.

Energy dispersive X-ray analysis (EDX)

The elemental analysis of the copper nanoparticles was performed using the EDX on the SEM. Fig. 5. Shows the EDX spectrum of the spherical nanoparticles prepared with hydrazine hydrate as a reducing agent. The peaks around 0.930 keV, 2.307 keV, 0.277 keV and 0.525 keV correspond to the binding energies of Cu L, S K, C K, and O K, respectively. The carbon and the copper peaks correspond to the SEM holding grid. Throughout the scanning range of binding energies, no obvious peak belonging to impurity is



Fig. 5. Energy dispersive X-ray analysis of Cu nanoparticles

FTIR spectroscopy

Fig. 6 depicts the FT-IR spectra of modifier 1-dodecanethiol, C_{12} S-Cu nanoparticles, base oil and produced nanolubricants by dispersing copper nanoparticle in the base oil



Fig. 6. Overlay FT-IR spectra of the modifier 1-dodecanethiol, synthesized copper nanoparticle, base oil and produced nanolubricants by dispersing copper nanoparticle in the base oil

The absorption band at 2849-2919 cm⁻¹ is attributed to the C-H stretch vibration of $-CH_3$ and $-CH_2$ -, and the strong absorption at 1468 cm⁻¹ corresponds to the bending vibration of C-H ($-CH_3$ and $-CH_2$ -). Besides, the absorption at 719 cm⁻¹ is assigned to long alkyl chain and the absorption band of C_{12} S-Cu nanoparticles and dodecanethiol at 880-960 cm⁻¹ is assigned to stretching vibration of C-S. Moreover, C_{12} S-Cu nanoparticles or other spectra except the 1-dodecanethiol do not show the S-H stretching vibration at 2590 cm⁻¹, which implies that S-H is destroyed and S atom is anchored on the surface of Cu nanoparticles via strong interaction. The absorption at 1700 cm⁻¹ corresponds to the bending vibration of aromatic C=C groups.

UV-vis spectroscopy

UV-vis absorption spectrum of as-synthesized Cu nanoparticles modified by 1-dodecanethiol is shown in the Fig.7. The absorption maximum for C_{12} S-Cu nanoparticle emerges at about 490 nm.

No characteristic absorption band for copper oxide is observed around 800 nm, which provides an evidence for generation of metallic Cu nanoparticles. The nanoparticles suspension is stable for long time when there are negative surface charges and prevents two particles from aggregating due to strong columbic repulsion leading to a metastable solution of single particles.



Fig. 7. UV-vis absorption spectra of Cu nanoparticles surfacecapped by alkanethiol

Effect of Cu-nanoparticle loading on viscosity

Viscosity of the base oils, lubricating oils containing capped and uncapped copper nanoparticles at two different concentrations (0.2 and 0.5 wt %) and temperatures (40°C and 100°C) were measured. The results are shown in the Table I.

Table I Experimental data of viscosity using capped and uncapped copper nanoadditive

The viscosity of nanolubricants at each temperatures increased with increasing concentration of nanoparticles, although the changes in viscosity at lower concentrations is much smaller than that at higher concentrations. The highest amount of increase in viscosity with respect to the base fluid is 18.07%, which is related to the nanolubricants with 0.5 wt% concentration and at 40°C temperature by the sample which was prepared by dispersing Cu nanoparticles in base oil for 40°C- 30 min.

Kinematic viscosities of samples with 0.2 and 0.5 wt% concentrations (100°C-60 min) decrease compared to the base oils because of the very fine dispersion of Cu nanoadditive in the base oil at increased temperature and 60 min of dispersion. The interesting point related to the viscosity of nanolubricants with 0.2 wt% concentration for the kinematic viscosity at 100°C, is that in each of the two mentioned temperatures (40°C and 100°C) of the produced samples , the viscosity of the oil which did not contain Cu nanoparticles had a very slight decrease. When nanoparticles

	Surface capped Cu-nanoadditive		Uncapped Cu-nanoadditive		
	Viscosity at 40°C (cSt)	Viscosity at 100°C (cSt)	Viscosity at 40°C (cSt)	Viscosity at 100°C (cSt)	
Base oil	284.875	38.471	284.875	38.471	
0.2 wt%	338.625	31.9083	305.71	27.35	
(40°C-30min)					
0.5 wt%	341.744	37.1132	312.744	32.73	
(40°C-30min)					
0.2 wt%	227.9	33.945	220.5	28.05	
(100°C-60min)					
0.5 wt%	223.6	40.734	217.6	38.98	
(100°C-60min)					

Table I. Experimental data of viscosity using capped and uncapped copper nanoadditive

are added to the oil, they are placed between the oil layers and lead to ease of fluid layer movement on each other. As a result, viscosity slightly decreases. As concentration increases, nanoparticles agglomerate and create larger and asymmetric particles, which prevent movement of oil layers on each other, so viscosity increases. Therefore, the sample at 0.5 wt% concentration exhibited increase in the viscosity than the base fluid.

It can be concluded that the viscosity of SN 150 base oil which contains Cu nanoparticles is a function of concentration of nanoparticles and at lower concentrations it has minor change with respect to the viscosity of the base oil. Similar results were obtained when uncapped copper nanoparticles were dispersed in the base oil. But the only difference is that, the improvement of the viscosity of base fluid was very little compared to surface-capped copper nanoadditive due to the absence of desired protecting layer as there was no capping agent used in the synthesis process. As a result, particle agglomeration occurred. It is obvious that the rate of improvement of the viscosity change is very much similar to the results obtained by using surface-capped copper nanoparticles but the average percentage of improvement is poor compared to the surface-capped copper nanoparticles due to the agglomeration of the uncapped copper nanoparticles.

Effect of Cu-nanoparticle loading on flash point and pour point

Table II shows that addition of Cu nanoparticles to the base oil causes an increase in flash point and pour point of the base oil. Increase in thermal conductivity through addition of nanoparticles is attributed to the increase of oil resistance against ignition. Also, flash point has a direct relation with concentration of nanoparticles, although this relation is not linear and the intensity changes in lower concentrations are more than the changes at higher concentrations. The increase in flash point of the nanofluid at 0.2 wt% concentration with respect to the base fluid is 11%, and the highest amount of increase is related to the 0.5 wt% sample, which is 26%. It can also be observed that in 0.5 wt% concentrations (both the samples made in 40°C and 100°C) the pour point decreased due to the presence of excess nanoadditive which create particle agglomeration, but in the 0.2 wt% concentration, there was 9.7% improvement with respect to the base oil.

Conclusion

Copper nanoparticles could be prepared in a two-phase system in the presence of stabilizer CTAB and reductant hydrazine hydrate. Particle size and its distribution can be controlled by adjusting the synthesis parameters such as concentration of $CuSO_4$, pH and ratio of CTAB to $CuSO_4$

		Nanolubricants				
	Base oil	0.2 wt% (40 °C - 30min)	0.5 wt% (40 °C - 30min)	0.2 wt% (100 °C-60min)	0.5 wt% (100 °C-60min)	
Flash point	49 °C	53 °C	54 °C	72 °C	80 °C	
Pour point	-13 °C	-17.5 °C	-11.5 °C	-18 °C	-12 °C	

Table II. Experimental data of flash point and pour point

CTAB plays an important role in terms of dispersibility of copper nanoparticles, and it inhibits the agglomeration of Cu particles before being surface-capped by modifier dodecanethiol. Alkanethiol-capped Cu nanoparticles can be harvested through ligand exchange, since CTAB as a ligand is weaker than thiols. Ultrasonic method for dispersing copper nanoparticles inside the base fluid is the most suitable method because it supplies high energy preventing their agglomeration and precipitation. Nanolubricants with 0.2 wt% concentration have been found to be the best samples for Cu/oil with improved pour point and flash point and insignificant change in viscosity. It can be concluded that the methods of preparation and dispersion can produce about 40-60 nm of spherical copper nanoadditive with good dispersion property in the base oil.

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