

Research Article

New Thiophene Monolayer-Protected Copper Nanoparticles: Synthesis and Chemical-Physical Characterization

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For the first time copper 3-(6-mercaptohexyl)thiophene-protected nanoparticles (Cu T6SH) have been synthesized by a one-phase system, utilizing an NaBH₄/LiCl mixture in diglyme as the reducing reagent and avoiding water medium dissolving copper salts. The prepared nanoclusters, characterized by transmission electron microscopy (TEM), have shown a constant spherical morphology with a size dimension of 5-6 nm in diameter. After their synthesis, no morphological evolution and irreversible aggregation process has been observed after a storage in CH₂Cl₂ at low temperature for a period up to six months long. Cu T6SH nanoparticles have been investigated by UV-Visible (UV-Vis) and Fourier transmission infrared (FTIR) spectroscopes to characterize the alkylthiophenes monolayer conformations and the particles optoelectronic properties. The UV-Vis reveals the lack of the surface plasmonic band, previously observed in Cu-nanosized clusters at about 556–570 nm, and shows a wide-band centered at 293 nm, probably due to the high-conformational surface ordering of thiophene rings on the Cu core. The results highlight the importance of the modifications ported to the well-known one-phase synthetic reactions to obtain a clear lack, even after a storage of six months, of any irreversible aggregation that has always characterized chain thiophene-protected metallic nanoparticles.

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1. INTRODUCTION

The properties of materials, which can be tailored by controlling their size and morphology, recently have been engineered by nanotechnology [1]. Nanostructured and nanosized materials have allowed recently innovated technological applications in catalysis [2, 3], biomedical [4], optic, photoresponsive, and electronic devices [5]. Nanoparticles are very interesting for the quantum effect by which their properties are tunable by the particle nanosize and surface chemical-physical characteristics [6]. Nanoparticle science and technology have received an important advancement by Schmid et al., they formerly synthesized ligand-stabilized gold nanoparticles [7] opening the right way to Brust et al. [8] to prepare monolayer-protected gold nanoparticles [8]. The organic monolayers on the surface of metal nanoparticles prevent aggregation and oxidation [9]. Many organic compounds with reactive head groups, such as thiol

[10], sulphide [11], thiosulfate [12], xanthate [13], amine [14], selenide [15], and isocyanide [16], have been utilized to protect by self-assembly different metal nanoparticles including Au [10–16], Ag [13], Cu [13, 17], Pt [18], Pd [19], Ni [20], and bimetallics [21]. The synthesis of metal nanoparticles protected with various monolayers containing different reactive head and functional tail groups is of high significance to improve their chemical and biochemical technological applications. Because of the expected marked electronic and optical properties of copper nanoparticles, there has been an increased interest in the preparation of stable monolayer-protected copper nanoparticles. Alkyl xanthates [13], alkylamines [22], tetraalkyl ammonium complexes [23], and alkanethiols [17, 24] ligands have been utilized to protect copper nanoparticles. However, a limited progress has been obtained because of the high instability of copper nanoparticles. In order to contrast copper nanoparticles, irreversible aggregation and oxidation, Chen and

Sommers [17] have prepared copper nanoparticles protected by alkanethiolate in one-phase system. Their prepared spherical (1–2 nm in diameter) Cu particle bound hexanethiolate monolayers undergo to the oxidation of copper core, morphological evolution, and irreversible aggregation process. Long-chain alkanethiols, which have been found to self-assemble into compact monolayers (i.e., three-dimensional self-assembled monolayers) on metallic nanoparticles [25, 26], cannot only induce metallic nanoparticles to be readily isolated, but also reduce their conductivity. The aim of this study is to synthesize 3-(6-mercaptohexyl)thiophene-protected copper nanoparticles which, in absence of long-chain alkanethiols and in absence of irreversible aggregation, could represent new high-conductive metallic nanoparticles with improved potentialities of tuning their optical and electronic properties.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Copper chloride (CuCl_2 , Sigma Aldrich, Milano, Italy), 1-butanethiol ($\text{C}_4\text{H}_9\text{SH}$, 97,0%, Fluka), sodium borohydride (NaBH_4 , 99%, Aldrich), lithium chloride (LiCl , 98%, Fluka) were used as received. The solvents were purchased from Fluka (diethyl ether), Riedel de Haen (tetrahydrofuran, THF), and Acros (2-methoxyethyl ether 99%, diglyme) and used as received.

Water was supplied by a Millipore A 10 system (18.50 M Ω).

2.2. Synthesis of 3-(6-mercaptohexyl)thiophene

The preparation of the monomer 3-(6-mercaptohexyl)thiophene has been performed according to the guidelines described by Ahn et al. [27]. 1.65 g (6.67 mmol) of 3-(6-bromohexyl)thiophene were added to a solution of 0.61 g (8.00 mmol) of thiourea dissolved in 36 mL of anhydrous ethanol. The reaction was refluxed for 3 hours under stirring and in inert atmosphere. 0.46 g (11.10 mmol) of NaOH dissolved in 15 mL of distilled water were then added and, after refluxing for 1 hour, the reaction mixture was poured into 150 mL of an aqueous solution of HCl (pH = 4) and extracted several times with diethyl ether. The collected organic phases were washed with distilled water, dried over MgSO_4 , and after evaporation of the solvent at reduced pressure 1.25 g (6.24 mmol) of crude monomer were obtained (94% yield). The latter was then purified by column chromatography (silica gel; *n*-heptane/ CHCl_3 8:2) giving 1.09 g (5.45 mmol) of pure monomer (82% yield). ^1H and ^{13}C -NMR were run on a Varian Gemini 300 FT-NMR spectrometer (300 MHz) using TMS as reference. Mass spectrometry (MS) was carried out on a VG7070E spectrometer at 70 eV.

^1H -NMR (CDCl_3 , ppm): δ 7.22 (m, 1H), 6.98 (m, 2H), 2.62 (t, 2H), 2.50 (t, 2H), 1.60 (m, 4H), 1.40 (m, 4H).

^{13}C -NMR (CDCl_3 , ppm): δ 143.71, 128.92, 125.78, 120.52, 32.83, 31.09, 30.87, 30.30, 29.57, 29.40.

FT-IR-ATR (Ge crystal): 3102, 3050, 2928, 2855, 2673 (-SH), 1537, 1462, 1439, 1410, 1293, 1279, 1264, 1238, 1152, 1079, 939, 856, 833, 771, 684, 661, 633, 595, 577 cm^{-1} .

Mass (m/z, relative intensity): 200 (11.4, M^+), 98 (100.0, $\text{C}_5\text{H}_6\text{S}^+$).

2.3. Synthesis of 3-(6-mercaptohexyl)thiophene monolayer-coated copper nanoparticles

The particles were synthesized according to a modification of the one-phase system method of Chen and Sommers [17], avoiding any aqueous solvent during the nanoparticles formation.

In a round-bottomed flask 0.24 mmol (41 mg) of CuCl_2 dissolved in 20 mL of tetrahydrofuran (THF) were dropped in 0.71 mmol (143 mg) of 3-(6-mercaptohexyl)thiophene (T6SH) under stirring until the solution remained transparent becoming yellowish. In this solution, 247 mg of $\text{NaBH}_4/\text{LiCl}$ mixture (2/3 molar ratio—92 mg $\text{NaBH}_4/155$ mg LiCl) suspended in 40 mL of diglyme ($\text{CH}_3\text{OCH}_2\text{CH}_2$) $_2\text{O}$ were dropped under stirring. The rapid turn of solution to dark brown reveals the 3-(6-mercaptohexyl)thiophene-coated Cu nanoparticles formation. Diethyl ether (150 mL) was added to the reaction mixture before the coated nanoparticles extraction with an NaCl saturated solution. The extraction was performed using 300 mL of saline solution and was repeated three times. The diethyl ether solvent was removed under reduced pressure. The dark brownish precipitate was washed twice with cooled methanol and was then separated by centrifugation at 3000 rpm.

2.4. Morphological characterization

Transmission electron microscopy (TEM) investigations were carried out using a Philips CM 100 electron microscope at an accelerating voltage of 100 kV. The powdered samples were ultrasonically dispersed in ultrapure water and then deposited by dropcasting on conventional Formvar/Carbon 200 mesh copper microgrids.

2.5. Spectroscopic characterization

FTIR spectra were collected with a Thermo Nicolet FTIR 380 spectrometer equipped with ATR accessory and the spectra resolution was 4 cm^{-1} . The spectrum of the capping agent 3-(6-mercaptohexyl)thiophene was obtained by dropcasting the monomer thiophene onto germanium crystal and the spectrum of the Cu thiophene-capped nanoparticles was acquired by placing an aliquot of 5–10 mg onto germanium crystal without any additional sample preparation. The spectra were the result of 32 scans.

UV-Vis spectroscopy has been carried out using a Varian Cary 300 Bio spectrophotometer with a 1 cm quartz cuvette. Solutions of Cu T6SH nanoparticles were prepared at concentration of 0.1 mg/mL in dichloromethane (CH_2Cl_2).

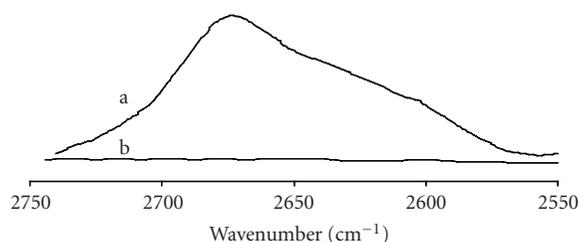


FIGURE 1: Comparison of the infrared spectra in the range from 2750 to 2550 cm^{-1} of the free thiophene (a) and Cu T6SH-protected nanoparticles (b).

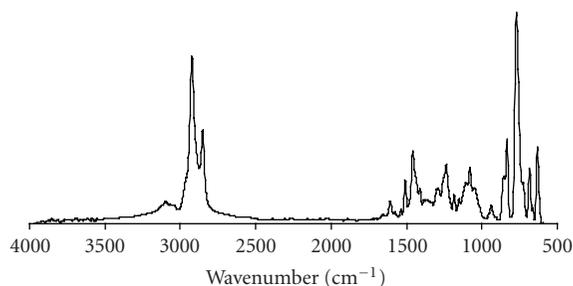


FIGURE 2: Infrared spectrum of Cu T6SH-protected nanoparticles.

3. RESULTS AND DISCUSSION

3-(6-bromohexyl)thiophene was first synthesized as previously described [28] and reacted with thiourea giving 3-(6-mercaptohexyl)thiophene (MDT) with a good yield. Monolayer-protected Cu nanoparticles were prepared in one-phase system by modified Brust reaction [8] using as reducing reagent a mixture of finely grounded LiCl and NaBH_4 (3/2 molar ratio) suspended in diglyme ($(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}$, instead of LiBH_4 (super hydride) dissolved in tetrahydrofuran (THF) according to Chen and Sommers (2001) [17]. These authors have dissolved $\text{Cu}(\text{NO}_3)_2$ in water-THF mixture, while we have used pure THF to suspend $\text{CuCl}_2 \cdot 2 \cdot \text{H}_2\text{O}$, in order to avoid any oxidation process and enhance the LiBH_4 reducing capacity. Furthermore, diglyme acts not only as chelating agent of the Li cations, but also as dissolvent. The MDT/ $\text{CuCl}_2 \cdot 2 \cdot \text{H}_2\text{O}$ reactants ratio was 3:1.

3.1. Spectroscopic studies

The conformational structure of the Cu particle-organic surfactant monolayer has been examined by FTIR spectroscopy. In Figure 1, infrared spectra in the range of 2750 cm^{-1} and 2550 cm^{-1} of the free thiophene (a) and Cu thiophene on protected nanoparticles (b) are compared. The lack of the SH stretching of the free ligand at about 2580 cm^{-1} is due to the chemisorptions on the Cu nanoparticles. The CH_2 antisymmetric (d^-) and symmetric (d^+) stretching recorded for thiophene ligand have been repeatedly used as a sensitive diagnostic indicator for the conformational ordering of the metal-linked alkyl chains [29–31]. In fact, these two characteristic vibrational stretching modes for the

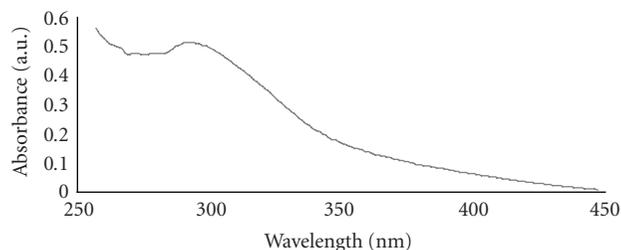


FIGURE 3: UV-Vis spectrum of the Cu T6SH-protected nanoparticles dissolved in CH_2Cl_2 .

3-(6-mercaptohexyl)thiophene have been found at 2928 and 2856 cm^{-1} in solution [17, 32, 33], while in crystalline state, for all zigzag trans ordered conformations the $\nu_{\text{as}}(d^-)$ and $\nu_{\text{s}}(d^+)$ are usually found at 2920 and 2850 cm^{-1} , respectively [20]. The lyophilized Cu thiophene-protected nanoparticles FTIR spectrum reported in Figure 2 shows the characteristic $\nu_{\text{as}}(d^-)$ and $\nu_{\text{s}}(d^+)$ vibrational stretching modes of CH_2 at 2924 cm^{-1} and at 2852 cm^{-1} , respectively, revealing a marked shift toward lower wave numbers than those recorded for the free thiophene ligand. This finding highlights that the capping agent for synthesized Cu T6SH has an enhanced ordered structure close to the Cu cluster surface [32]. The FTIR spectrum reported in Figure [2] has been obtained for Cu T6SH particles immediately after synthesis, but it does not differ appreciably from the FTIR spectra recorded for the same Cu thiophene-protected nanoparticles after a long period of storage at low temperature ($+4^\circ\text{C}$), suspended in CH_2Cl_2 up to six months long.

Usually, the optical properties of alkanethiolate-capped transition-metal nanoparticles analyzed by UV-Vis characterization display the presence of a remarkable surface plasmon band (SP) having an intensity and an energy that are strongly dependent on the size and the chemical composition of the system we are studying. The typical absorption peak of the characteristic surface plasmon Cu-nanosized cluster is expected at about 556 nm [21], 566 nm [17], and 570 nm [33, 34]. On the contrary, a UV-Vis absorption profiles exhibiting an exponential decay Mie scattering [35] with decreasing photon energy, without the surface-plasmon band, is a characteristic of nanosized particles and has been observed for a copper very small core size diameter of the particles (<2 nm) [17, 36]. The spectrum of the Cu T6SH particles, reported in Figure 3, does not reveal any evidence of the surface plasmonic band at about 556–570 nm, but shows only a wideband centered at 293 nm due according to Mie's theory is the summation of all electronic and magnetic multipole oscillations, contributing to the absorption and scattering of the interacting electromagnetic field [37]. A comparable adsorption band at about 340 nm has been observed for dodecanethiol-protected Cu nanoclusters of about 3 nm in diameter [21]. The lowest position of the band at 293 nm, never observed before also for <2 nm sized nanoparticles, could be attributed to the shorter (C6) alkyl chain of thiophene ring surface ordered on the Cu core. Furthermore, a possible interaction between the thiophene

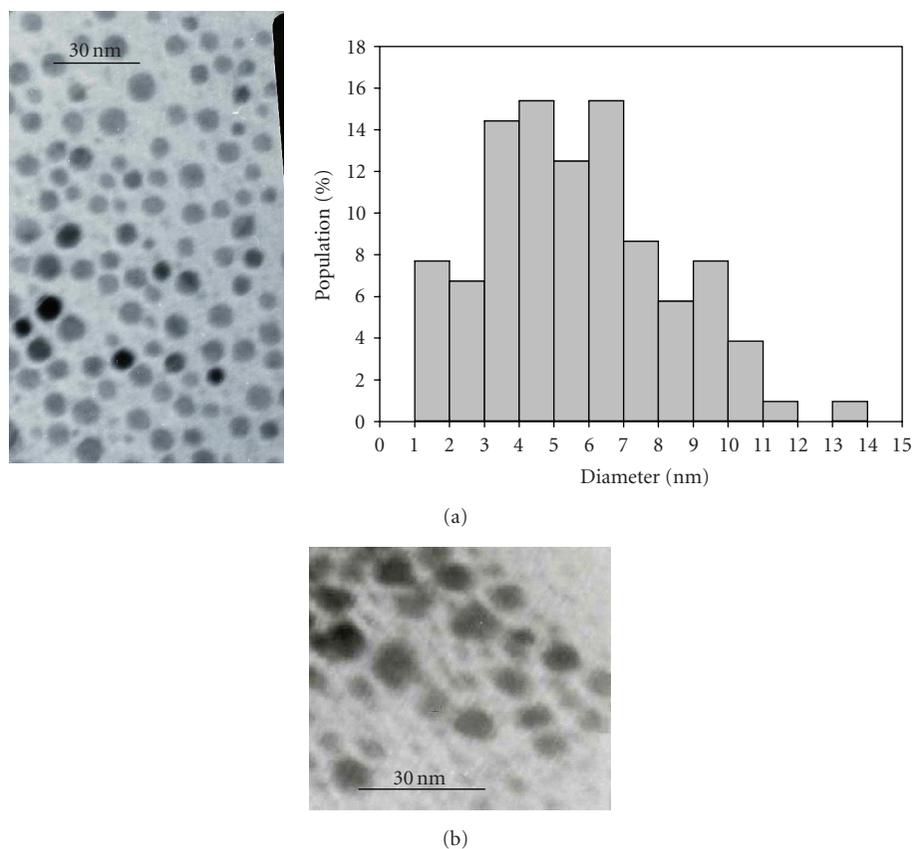


FIGURE 4: TEM image (a) of the fresh Cu T6SH nanoparticles synthesized by (Li diglyme)BH₄ as a reducing agent and the depict of the nanoparticle size histogram is reported. (b) TEM image of the Cu T6SH nanoparticles synthesized by (Li diglyme)BH₄ as a reducing agent after a period of six months long of storage at low temperature (+4°C) were suspended in CH₂Cl₂ after their synthesis.

rings and the metallic core cannot be left out considering the short alkyl chain length.

After a storing period of six months long, the same Cu T6SH particles exhibit a UV-Vis absorption profile very close to that previously recorded for fresh nanoparticles, but reveal a slight decrease to 291 nm of the adsorption band. This data support s the lack of irreversible aggregation previously observed for metallic thiophene-protected nanoparticles [17].

3.2. Transmission electron microscopic investigation

TEM has been utilized in investigating the Cu T6SH particles dimension. Figure 4(a) shows a TEM image of the Cu T6SH nanoparticles recorded after a period up to six months long of storage at low temperature (+4°C) suspended in CH₂Cl₂ after their synthesis. Nanoparticles exhibit spherical shape while particle size histogram inserted in Figure 4(a) puts in evidence that the median size is 5.65 nm in diameter. The Cu T6SH nanoparticles shape is homogenously spherical without exhibiting the irregular shapes and the well-defined faceted morphologies observed for other polythiophene-coated transition-metal nanoparticles [38] and especially for copper nanoparticles dodecanethiol protected [17, 21]. The Cu T6SH nanoparticles morphology and dimensions

observed immediately after synthesis (Figure 4(b)) were appreciably unchanged after six months of storage at low temperature (+4°C) and suspended in CH₂Cl₂ after their synthesis. This finding reveals the absence of irreversible nanoparticles aggregation reported for long-chain alkanethiols capped metallic nanoparticles [17].

This result is due to the modifications produced to the one-phase synthetic process of alkanethiolate-protected copper nanoparticles [17] which undergo to the oxidation of copper core, morphological evolution, and irreversible aggregation process.

4. CONCLUSIONS

Copper 3-(6-mercaptohexyl)thiophene-protected nanoparticles have been synthesized in a one-phase system by a modified Brust reaction [8] utilizing an NaBH₄/LiCl mixture in diglyme as the reducing reagent and avoiding water medium in dissolving copper salts. TEM investigation carried out on the Cu T6SH nanoparticles immediately after synthesis and after different periods up to six months long of storage at low temperature has put in evidence that their spherical shape of about 5-6 nm in diameter does not vary appreciably. The same invariability related to the storage period has been observed for the Cu T6SH nanoparticles by FTIR and UV-

Vis spectroscopic characterizations. The characteristic FTIR adsorption bands related to $\nu_{\text{as}}(\text{d}^-)$ and $\nu_{\text{s}}(\text{d}^+)$ vibrational stretching modes of CH_2 have been recorded for synthesized Cu T6SH at lower wave numbers than those recorded for the free thiophene ligand, revealing an enhanced ordered structure for the capping agent.

The UV-Vis spectrum of the Cu T6SH nanoparticles does not reveal any evidence of the surface plasmonic band previously observed in Cu-nanosized clusters at about 556–570 nm, but shows only a wideband centered at 293 nm probably due to the shorter (C6) alkyl chain of thiophene ring surface ordered on the Cu core.

TEM, FTIR, and UV-Vis results have pointed out the lack of irreversible aggregation previously observed for long-chain thiophene-protected metallic nanoparticles [17] revealing the importance of the modifications ported to the well-known one-phase synthetic Brust reaction [8]. The presence of short-chain alkanethiols around the metallic core and the observed absence of irreversible aggregation could improve their conductivity and potentialities of tuning their optical and electronic properties which are under investigation.

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