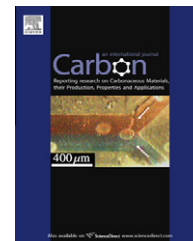


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Functionalization of C₆₀ with gold nanoparticles

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ABSTRACT

Gold nanoparticles (GNPs) with attached C₆₀ molecules (C₆₀-GNPs) were prepared through the amination reaction of fullerene C₆₀ with peripheral amino groups located on the surface of gold. Molecules of 4-aminobenzenethiol/1-hexanethiol containing amino groups were introduced onto the surface of gold by the reduction of a gold salt (HAuCl₄) with sodium borohydride (NaBH₄) in a one-pot way, which was accompanied by anchoring of the targeted thiol mixture on the gold cluster by Au–S bonds. This simple system avoids many difficult reactions and purification processes and does not involve a complicated chemical modification of C₆₀ and exchange reactions of GNPs.

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1. Introduction

Since the discovery of a method for producing fullerene (C₆₀) in 1985 by Kroto et al. [1,2], fullerenes (such as C₆₀, C₇₀, C₇₆, C₈₄, and others) have attracted extensive attention for technological applications in chemistry, biology, and nanoscience [3]. The C₆₀ fullerene has been used extensively to deposit films on many kinds of sensitizers and adsorbents [4]. In 2005, it was found that metallofullerenes (Gd@C₈₂) possessed a very high antineoplastic efficiency in mice, and that finding encouraged many researchers to probe their anti-tumor activity [5]. Also, for many years, researchers have investigated the functionalization of fullerenes with metal particles using both covalent and non-covalent methods, because nanometer-sized metal particles possess novel size-dependent and shape-dependent optoelectronic and catalytic properties [6–12]. Due to combination effects, these composite nanomaterials show promise for application in various areas, such as electronic nanodevices [13], optics [7,14], photo-electrochemical conversion [15], and electrochemical technology [16].

Because of the good thermal stability, alkanethiolate gold nanoparticles can be isolated repeatedly, redissolved, or functionalized without irreversible aggregation or decomposition,

just like molecular compounds in organic solvents [17]. Changeable ligand-alkanethiol chains provide another important study field, such as of C₆₀ with amination, C₆₀-metal hybrid composites [14,18], and C₆₀ thin films [19]. Amino groups can attack fullerenes and couple onto their surfaces has been firmly established and is well understood [20–22]. The incorporation of metals into fullerene matrices has been accomplished by the reaction of gold nanoparticles with mercapto derivatives of C₆₀ and by coupling reactions between C₆₀ and monolayer-protected gold nanoparticles with amine moieties on the surface [6,7,13–16]. Shih et al. described the use of propyl 2-aminoethyl disulfide as medium molecules for fabricating two-dimensional arrays of gold nanoparticles that may have potential applications as nanoelectronic materials [13]. In Ref. [14] and [16], researchers reported the preparations of C₆₀-gold nanoparticle hybrid films based on monolayer-protected gold nanoparticles and explored their electrochemical, spectroscopic, and optical properties. However, the modification of C₆₀ or metal nanoparticles was a complex and time-consuming procedure before they were linked together.

In this paper, we prepared gold nanoparticles with attached C₆₀ molecules (C₆₀-GNPs) and found that 4-aminobenzenethiol/1-hexanethiolate (containing amino groups)-

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protected gold nanoparticles (GNPs) could be prepared in one step in ethanol, which is much simpler and more convenient for fabricating the final product. From the aspect of potential applications, it is essential to develop synthetic methodologies for making carbon-based composites more readily available because of their unique physicochemical properties.

2. Experimental

2.1. Chemicals

All analytical, reagent-grade chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC), PR China, except for 4-aminobenzenethiol and 1-hexanethiol (>96.0%, TCI, Japan). These chemicals were used as received. Milli-Q water (18.20 M Ω cm resistivity) was used in the process of dialyzing the GNPs.

2.2. Preparation of 4-aminobenzenethiol/1-hexanethiolate protected gold nanoparticles

GNPs were prepared by reduction of auric chloride acid with sodium borohydride (NaBH₄) in absolute ethanol solution [23,24]. In detail, 0.09 mmol of gold salt was dissolved in 200 mL of absolute alcohol and 0.09 mmol of the desired thiol mixture was then added while stirring vigorously for approximately 10 min before the next step. Subsequently, 30 mL of freshly-prepared NaBH₄ ethanol solution (0.40 mol/L) was slowly dropped into the solution within a 2 h period of time. Soon after the gold nanoparticles formed, the color of the solution changed from yellow to dark brown. The dark brown solution was stirred for 3 h, and the mixture was kept at -18 °C overnight. Finally, the mixture was evaporated to approximately 10 mL by a rotary evaporator at < 40 °C. The dark brown precipitate was collected by centrifugation. The crude product was washed with ethanol and acetone. In order to remove the free thiols completely, the GNPs were dialyzed in dialysis membrane tubes (MWCO 8000–15,000) with fresh Milli-Q pure water for at least three days. The black precipi-

tates were dried under vacuum by a Martin Christ Freeze Dryer alpha 2–4 (Germany). The resulting GNPs were found to be soluble in a variety of organic solvents, including toluene, *n*-hexane, dichloromethane, ethanol, and dimethyl sulfoxide.

2.3. Linkage of fullerene C₆₀ and gold nanoparticles

C₆₀-GNPs were fabricated as described below. Generally, 20 μ mol of C₆₀ and 5 μ mol of dried GNPs were suspended in 100 mL of toluene and sonicated in a sonic pool for at least 10 min before they were stirred vigorously for three days at room temperature. The C₆₀-metal complex solution was concentrated by rotary evaporation. Then, methanol (3/1 v/v) was added to the toluene solution, and the mixture was purified by centrifugation (10,000 rpm, 10 min). The supernatant was removed carefully, and the sediment was dissolved in an organic solvent, such as toluene, dichloromethane, or ethanol, and subsequently placed in a sonic bath for 30 min. This process was repeated several times until the C₆₀ absorption peak disappeared in the supernatant, and thereby, the solution of C₆₀-GNPs was obtained.

2.4. Characterization

UV/Vis spectra were obtained by using a Hitachi U-3010 spectrometer. Fourier transform infrared (FTIR) spectra were obtained by using a Thermo Nicolet Avatar 370 FT-IR spectrometer in absorption mode. Transmission electron microscopy (TEM) experiments were performed using a JEOL 2010 transmission electron microscope with an acceleration voltage of 200 kV. Samples were dissolved completely by sonication, and a drop of the sample was placed on a carbon-coated Cu grid and air dried. X-ray photoelectron spectroscopy (XPS) data were obtained on a Multitechnique Electron Spectrometer (Kratos Axis Ultra DLD, UK) equipped with a monochromated Al K α , 15 kV, 10 mA excitation source. Raman spectra were recorded on a LabRAM-1B micro spectrometer (France) with 632.8 nm laser excitation.

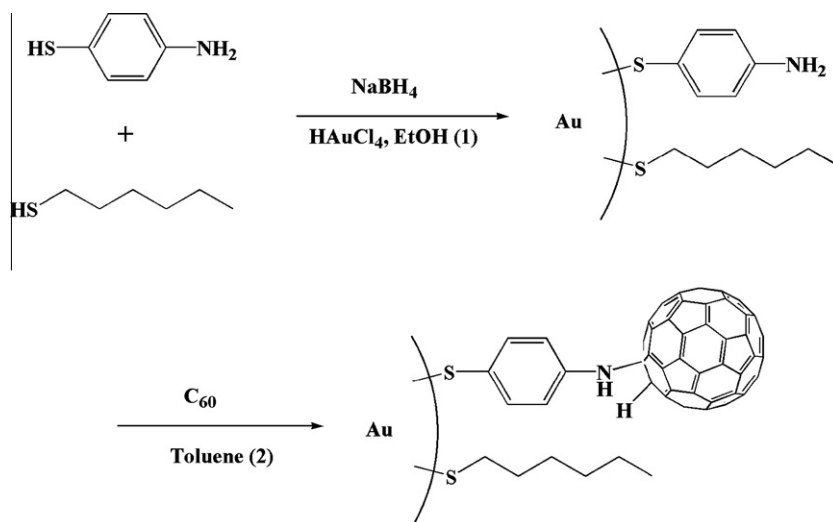


Fig. 1 – Experimental procedure for anchoring C₆₀ onto GNPs – (1) synthesis of GNPs and (2) fabrication of C₆₀-GNPs.

3. Results and discussion

The general method used for the synthesis of C_{60} -GNPs is shown in Fig. 1. In our design, 4-aminobenzenethiol and 1-hexanethiol with alkyl groups were chosen as the surface modified molecules for two reasons. First, chain alkanes would undoubtedly result in the nanoparticles having a pronounced solubility in organic solvents. Second, the density of the amino groups attached to the gold surface can be regulated.

Fig. 2 shows XPS analysis of the indicated GNPs. The binding energies of the doublet for Au $4f_{7/2}$ (84.3 eV) and Au $4f_{5/2}$ (88.0 eV) shown here are characteristic of Au^0 . The absence of a band at 84.9 eV as found for Au^I in thiolate gold nanoparticles indicates that the gold element must be present mainly as Au^0 . As expected, weak sulfur bands were observed in the XPS spectra. From the elemental analysis data, we were able to determine that the molar ratio of Au to S is 6.5:1.

Raman spectroscopy is a powerful and non-destructive technique for characterizing molecules on surfaces. Fig. 3

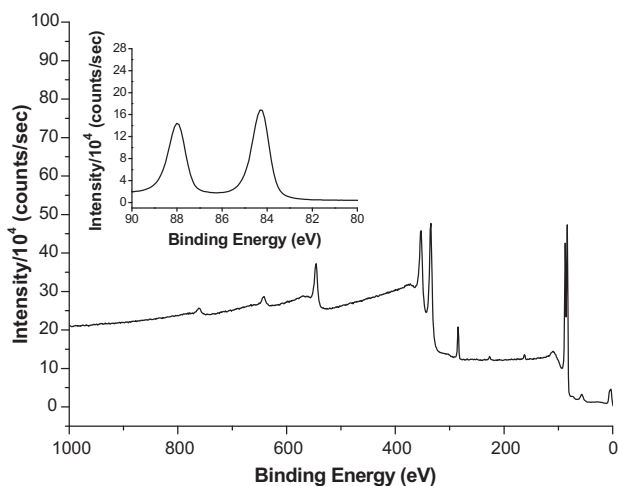


Fig. 2 – High-resolution XPS survey spectra showing wide scan of GNPs; XPS region spectra of Au $4f_{7/2}$ and Au $4f_{5/2}$ (inset).

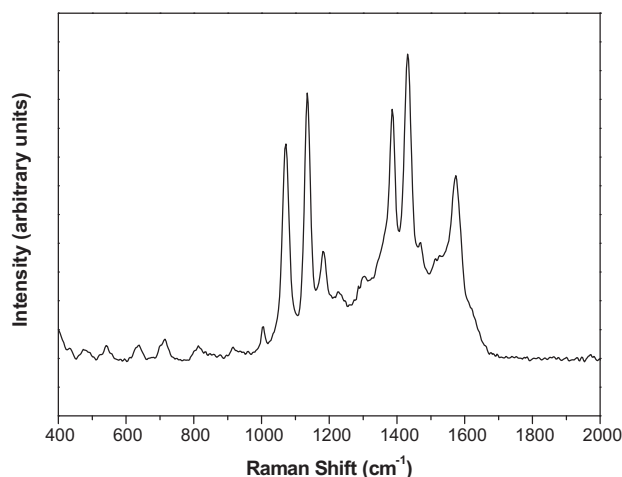


Fig. 3 – Raman spectrum of GNPs.

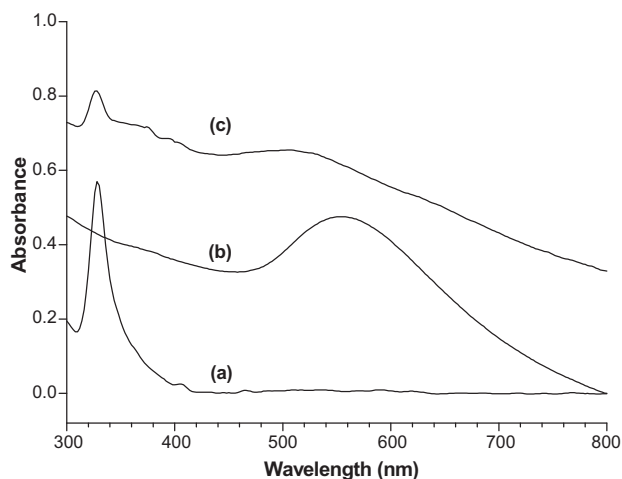


Fig. 4 – UV/Vis spectra of (a) C_{60} , (b) GNPs, and (c) C_{60} -GNPs.

shows the specific Raman spectrum of organic molecules (4-aminobenzenethiol and 1-hexanethiol) on the surface of gold. The peaks at 916, 1006, 1135, and 1185 cm^{-1} were C–C stretching vibrations that result from the carbon backbone of the molecules on gold. The peaks at 715 and 1072 cm^{-1} were assigned to the C–S stretch of the monolayer. In addition, the peaks at 1469 (CH), 1522 (CH), 1574 (CH) cm^{-1} were responses to 4-aminobenzenethiol because of the existence of phenyl group [25–27].

Fig. 4 shows the UV/Vis absorption profiles of GNPs, C_{60} , and C_{60} -GNPs. The absorption at 554 nm corresponds to the surface plasmon absorption of alkanethiolate GNPs. According to Mie theory, the surface plasmon band of naked gold nanoparticles is around 520 nm, however, the ligand shell alters the refractive index and causes either a red or blue shift. This shift is especially obvious with thiolate ligands, which causes a strong ligand field that interacts with the electron cloud on the surface of the Au [8]. For the GNPs used in the present study (about 3 nm diameter), the surface plasmon band is shifted to the higher wavelengths as the spacing between the particles is reduced.

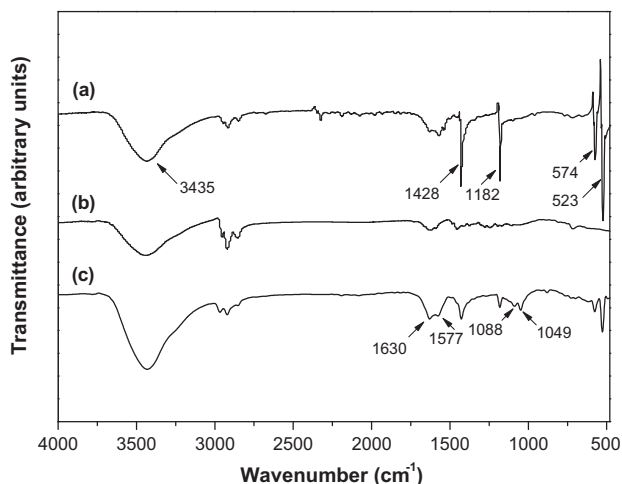


Fig. 5 – FTIR spectra of (a) C_{60} , (b) GNPs, and (c) C_{60} -GNPs.

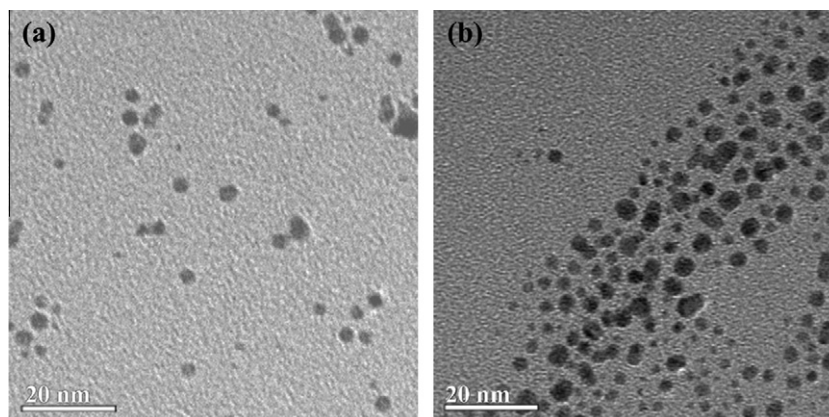


Fig. 6 – Representative TEM images of (a) GNPs and (b) C₆₀-GNPs.

A characteristic UV absorption band of a C₆₀ control can be observed at 328 nm, along with a much weaker peak at 406 nm. The main absorption peak also appeared at 328 nm when the C₆₀ monomers were placed on the surface of the gold. However, one may note that the intensity became smaller and that the shoulder peak generated a slight blue shift. It is very likely that the shift resulted from the saturation of one of the double bonds of C₆₀ due to the amination reaction [28].

As compared with GNPs and C₆₀, the absorption spectra of C₆₀-GNPs exhibit absorption extending into the near-IR region, and the plasmon absorption band becomes broader. Further, a blue shift was found when C₆₀ was placed on the surface of the gold.

FTIR spectroscopy is a useful tool for obtaining structural and conformational knowledge regarding small organic molecules on the surface of the gold. FTIR spectra of the GNPs, pristine C₆₀, and C₆₀-GNPs are shown in Fig. 5. Compared with the absorption location of pure C₆₀, in addition to the four characteristic peaks of C₆₀ at 523, 574, 1182, and 1428 cm⁻¹ [29], two new bands are observed in the absorption spectra of C₆₀-GNPs at 1088 and 1049 cm⁻¹. The former one is similar to the spectrum of C₆₀ monoanion [30], which further indicates the transfer of electrons from gold to C₆₀ in C₆₀-GNPs because of the amination reaction. The latter corresponds to the peaks of the slight oxidation of C₆₀ because of the oxidation–reduction reaction of the C₆₀ monoanion [31]. Also, multiple bands became more visible near 1600 cm⁻¹ in the C₆₀-GNPs, which provides additional evidence of the C=C bonds in C₆₀ and monolayer molecules formed on the surface of the gold; this result is consistent with the results of previous works [16]. The intense peak at 3435 cm⁻¹ was attributed to stretching of the O–H bond either from H₂O (KBr films) or ethanol.

Fig. 6 shows the transmission electron micrographs of alkanethiol-stabilized GNPs and C₆₀-GNPs. These kinds of GNPs dispersed in toluene are 3 nm in diameter. However, the images of C₆₀-GNPs exhibit aggregation with the addition of C₆₀ [6,11].

4. Conclusions

We reported the mild synthesis of C₆₀-GNPs by the amination reaction. The synthesis does not relate to a complicated

chemical modification of C₆₀ prior to the attachment on the surface of the gold particles, and it does not involve exchange reactions of GNPs. This system avoids many difficult reactions and purification processes. We believe that the simple preparation method of C₆₀-GNPs is particularly promising for the design of novel composites. In this increasingly active field, new breakthroughs are expected to occur periodically. In fact, the outstanding chemical structure and electronic properties of C₆₀-GNPs are unequalled, so they should be extensively tested to determine applications in which their unique properties can be exploited in the fields of nanoscience and nanotechnology. These carbon-based nanomaterials will probably provide significant opportunities for productive and beneficial applications in the fields of optics, nanoelectronics, and nanobiotechnology in the near future.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.carbon.2010.05.055](https://doi.org/10.1016/j.carbon.2010.05.055).

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