

## COMMUNICATION

# Facile synthesis of gold nanoparticle (AuNP)–carbon nanotube (CNT) hybrids through an interfacial Michael addition reaction†

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**A CNT–AuNP hybrid has been synthesized through the Michael addition reaction between thiol-functionalized single-wall CNT and small water-soluble Maleimide–AuNP. The resilience and stability of this hybrid nanosystem is ensured by a covalent bond linking the nanoparticle to the CNT and by the fact that the functionalization reaction involves the organic shell of the AuNP and not its metallic core.**

Since their discovery in 1991 carbon nanotubes (CNT) have been extensively studied for uses in emitting devices, energy storage, sensor field, and for biological and biomedical applications.<sup>1–5</sup> CNT combined with gold nanoparticles (AuNP) resulting in AuNP–CNT hybrid materials bring together the high conductivity of the CNT and combine it with the size-dependent optothermal properties of the AuNP with potential direct application as gas sensors, catalysts, and especially as structural components of electrochemical sensors.<sup>6–11</sup>

Different synthetic strategies have been explored to decorate CNT with AuNP. Generally all of these require the introduction of functionalities onto the CNT sidewalls that enable them to bind the nanoparticles. For this purpose electrostatic<sup>12,13</sup> or hydrophobic<sup>14,15</sup> interactions between the functionalized CNT and the AuNP, or the affinity of amines and thiols for gold<sup>6,16–18</sup> have been exploited. However, these methodologies generally lead to a non-robust nanohybrid material where the AuNP can be easily detached because of the lack of a covalent bond that links them to the CNT, or can rapidly coalesce, especially when solvent is removed, thereby destroying their size dependent properties.<sup>14</sup> Because of the high cost of these nanomaterials, it is desirable that the final product has a long life and is stable, and that the functionalization reaction works quickly and efficiently. To address these requirements we developed

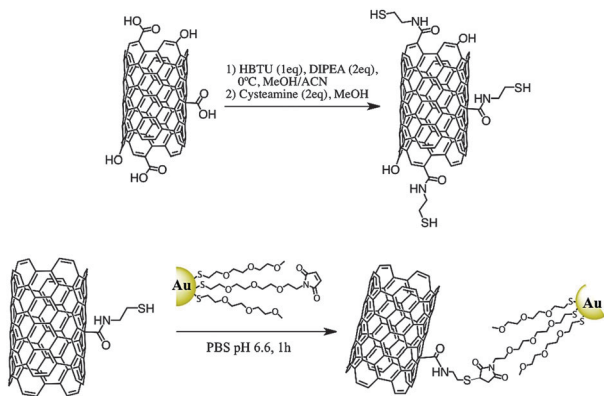
photochemical routes towards the synthesis of covalent AuNP–CNT hybrids exploiting interfacial carbene and nitrene reactions that involve the organic shell of the AuNP and not its gold core.<sup>19,20</sup> However, these systems utilize organic soluble AuNP and because CNT generally form stable dispersions in water and very polar organic solvents,<sup>21,22</sup> it is desirable that in these media the partner nanoparticles are soluble and stable, and that the functionalization reaction works efficiently. We synthesized small Maleimide–AuNP that addresses these two requirements. These AuNP can undergo a Michael addition reaction with thiols and amines, thanks to Maleimide functionalities present at their interface.<sup>23</sup> The Michael addition is one of the most used reactions for creating AuNP–bioconjugates and, as such, it is meant to be very fast and efficient, and to take place in water and at room temperature.<sup>24,25</sup> Here we show for the first time the use of an interfacial Michael addition reaction towards a facile, convenient and efficient way for creating AuNP–CNT hybrids. These small water-soluble Maleimide–AuNP react readily with thiol-modified single-wall CNT (SWCNT-SH) under very mild conditions, leading to a robust AuNP-decorated SWCNT (SWCNT–AuNP).

Scheme 1 shows the synthetic strategy leading to the formation of gold nanoparticles-decorated single-wall carbon nanotubes (SWCNT–AuNP). The first step involves the introduction of thiol functionalities onto the CNT sidewalls through a coupling reaction between cysteamine and the carboxylic groups already present on the native SWCNT (see Scheme 1). This procedure is similar to the one reported by Z. Liu *et al.*<sup>21</sup> However, it is noteworthy that it is not necessary to chemically oxidize the CNT before the coupling reaction. The protocol is simple. Briefly, 10 mg of SWCNT were dispersed in 5 ml of dry MeOH in a round bottom flask. The system was cooled down to 0 °C, and the solution was purged with argon for 10 minutes. 20 mg of HBTU (53 μmol) and 19 μl of DIPEA (106 μmol) were dissolved in a separate round bottom flask with 5 ml of a MeOH–Acetonitrile (2 : 1) mixture and they were purged with argon for 10 min. Once the two solutions were purged, HBTU and DIPEA were transferred using a glass syringe into the ice-cold solution of CNT. The reaction was left for 15 min at 0 °C.

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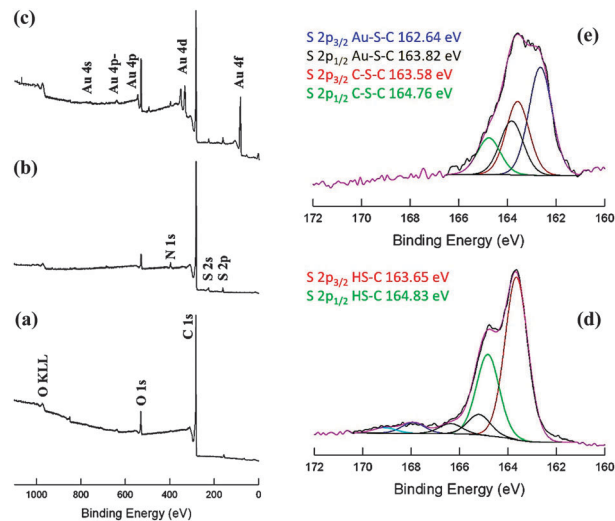


**Scheme 1** Synthetic approach to the preparation of SWCNT-AuNP through Michael addition reaction at the Maleimide-AuNP interface.

In a clean round bottom flask a solution of cysteamine (8.2 mg, 106  $\mu\text{mol}$ ) in 2 ml of dry methanol was purged with argon. After 15 minutes the solution of cysteamine was injected into the ice-cold solution of CNT, HBTU and DIPEA, the ice-bath was removed and the reaction mixture was left overnight under vigorous stirring. The solution was then centrifuged (10 min, 6000 rpm) and the supernatant removed. The resulting thiol functionalized CNT (SWCNT-SH) were re-dispersed in acetonitrile, sonicated for 10 min, centrifuged again, and the solvent was decanted. This washing procedure was repeated once more, then acetonitrile was substituted with water and SWCNT-SH were washed and centrifuged twice. Finally, the solvent was evaporated and the SWCNT-SH was dispersed in a phosphate buffer solution (PBS) pH 6.6 to obtain a concentration of 2 mg ml<sup>-1</sup>. This mother solution was stored in the freezer.

SWCNT-SH was characterized by X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy. The XPS survey of SWCNT-SH (Fig. 1b) compared to that one of the starting material (Fig. 1a) clearly shows the appearance of the peaks related to the sulphur at 160 eV (2p) and at 228 eV (2s) and to the nitrogen at 396 eV (1s). High-resolution scans of these regions indicate a successful coupling reaction. The N 1s core line (Fig. S2, ESI<sup>†</sup>) shows a single peak at 399.78 eV related to the amide nitrogens, while the S 2p core line clearly shows that the majority of the sulphur is present as thiol (S 2p<sub>3/2</sub> at 163.65 eV, S 2p<sub>1/2</sub> at 164.83 eV) (Fig. 1d). It is noteworthy that XPS measurements carried out on samples two months old (Fig. 1d) show that SWCNT-SH have a good stability to oxidation with only ~15% of the sulphur oxidized. The IR spectrum of SWCNT-SH also confirms this result showing the peaks related to the C-H stretching of the cysteamine at 2949, 2919, and 2848 cm<sup>-1</sup>, and a band at 1580 cm<sup>-1</sup> related to the stretching mode of the amide C=O (Fig. S1, ESI<sup>†</sup>).

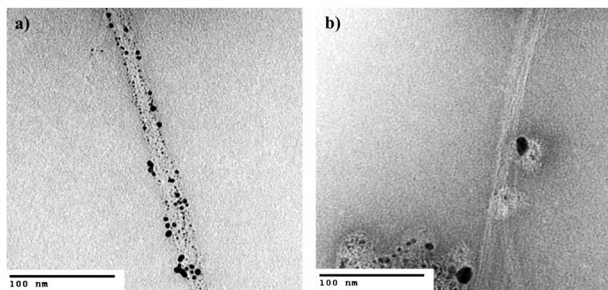
In order to obtain the AuNP-decorated CNT, SWCNT-SH were reacted with the water-soluble Maleimide-AuNP through the Michael addition reaction in PBS pH 6.6. Maleimide-AuNP was synthesized accordingly to our previously established procedure.<sup>23</sup> Briefly, Maleimide-AuNP was obtained through a retro Diels-Alder strategy because of the (desired) reactivity of the Maleimide functionality towards nucleophiles. The basic triethylene glycol monomethyl ether AuNP (Me-EG<sub>3</sub>-AuNP) underwent a place



**Fig. 1** On the left XPS survey of (a) SWCNT starting material; (b) SWCNT-SH; (c) SWCNT-MaleimideAuNP. On the right high resolution S 2p spectra of (d) SWCNT-SH; (e) SWCNT-MaleimideAuNP.

exchange reaction with furan-protected-Maleimide tetraethylene glycol-thiols ligands (PtMaleimide-EG<sub>4</sub>-SH). The resulting PtMaleimide-AuNP was deprotected from the furan using an improved methodology: the PtMaleimide-AuNP were dissolved in a toluene-acetonitrile (10:1) mixture and heated at 110 °C overnight under vigorous stirring. The new mixture of solvents was found to readily redissolve all the PtMaleimide-AuNP (while before just the toluene-soluble fraction of PtMaleimide-AuNP could be deprotected) and still being suitable for the retro Diels-Alder reaction without forming any hydrolysis by-product<sup>23</sup> and leads to small water-soluble Maleimide-AuNP with a gold core diameter ranging from 2 to 4 nm.

The Michael addition reaction was carried out adding 4 mg of Maleimide-AuNP dissolved in 1 ml of PBS pH 6.6 to a 1 ml of SWCNT-SH mother solution (see Scheme 1). The reaction was stirred for 1 hour at room temperature, and then the SWCNT-AuNP was centrifuged in a Pyrex centrifuge test tube. The supernatant was removed, and the decorated CNT bundles were dispersed in acetone, sonicated for 10 minutes and centrifuged. Subsequently, acetone was substituted with dichloromethane (DCM) and the washing procedure (sonication in DCM and centrifugation) was repeated twice more. The success of the interfacial Michael addition reaction between SWCNT-SH and Maleimide-AuNP was confirmed by XPS, IR spectroscopy, and by transmission electron microscopy (TEM) images. The XPS survey of SWCNT-AuNP (Fig. 1c) clearly shows the appearance of the peaks related to gold at 83 eV (4f), 334–353 eV (4d), 547–643 eV (4p), and 762 eV (4s). The Au 4f<sub>7/2</sub> core line is at 84.19 eV (Fig. S3, ESI<sup>†</sup>) and results shifted upwards from that of bulk gold (83.95 eV) due to the nanoparticle size effect.<sup>26,27</sup> The high resolution C 1s spectrum (Fig. S3, ESI<sup>†</sup>) shows a new component at 285.30 eV related to the C-O-C of the AuNP glycol units. Most notably, the S 2p core line now shows the appearance of a new doublet related to the Au-S bonds with binding energies of 162.64 eV (S 2p<sub>3/2</sub>) and 163.82 eV (S 2p<sub>1/2</sub>), and the components related to the C-S-C bond (S 2p<sub>3/2</sub> at 163.58 eV and S 2p<sub>1/2</sub> at



**Fig. 2** TEM images of (a) SWCNT-AuNP; (b) control experiment (SWCNT-SH + Me-EG<sub>3</sub>-AuNP).

164.76 eV) formed through the expected interfacial Michael addition reaction (Fig. 1e). The IR spectrum of the hybrid nanomaterial (Fig. S1, ESI<sup>†</sup>) shows the appearance of the carbonyl stretching at 1704 cm<sup>-1</sup> due to the presence of the AuNP's Maleimides. Transmission electron microscopy (TEM) images of the hybrid nanomaterial (Fig. 2a) confirm that AuNP are linked to the surface of CNT bundles, that they kept their original size distribution, and that there are no unbounded particles present, confirming the efficiency of our washing procedure. Indeed, the use of sonication favours the detachment of those AuNP that are physisorbed on the CNT leaving just those that are covalently bonded.<sup>8</sup>

To exclude the possibility of unspecific bonding of the AuNP to the SWCNT-SH, a control experiment was carried out under identical conditions and following the same experimental procedure but using the model Me-EG<sub>3</sub>-AuNP. The Me-EG<sub>3</sub>-AuNP, because of the absence of the Maleimide functionality, are not expected to react with the thiol-modified CNT because they cannot undergo the Michael addition reaction. Fig. 2b is related to this control experiment and shows, as expected, completely clean CNT, confirming the successful synthesis of AuNP-decorated SWCNT through the Michael addition reaction between SWCNT-SH and Maleimide-AuNP.

Sonication was employed to test the stability and resilience of the final hybrid material. A fraction of SWCNT-AuNP was dispersed in water and sonicated for one hour. Its TEM images were then compared with those of the freshly prepared SWCNT-AuNP and they did not show any appreciable difference either in the density of chemisorbed AuNP or in the AuNP size distribution. This supports the efficiency of our synthetic approach and the resilience of the resulting AuNP-CNT hybrid.

In summary we have shown for the first time that water-soluble Maleimide-AuNP can be efficiently attached to thiol-modified CNT through a versatile interfacial Michael addition reaction. Because of the ability to run the chemistry in water, due to the solubility of the Maleimide-AuNP, the rate of the Michael addition is fast and results in a hybrid material that is densely covered with AuNP. The robustness of this AuNP-CNT hybrid is due to the covalent bond linking the nanoparticle to the CNT and because the functionalization reaction involves the ligand of the organic shell of the nanoparticle and not due to

its gold core. Our methodology presented here can be exploited to functionalize any carbonaceous material (*i.e.* graphene, nanodiamonds, glassy carbon) with AuNP or any other functional molecular material as long as the appropriate PEG-Maleimide can be prepared. It is possible to take advantage of the intrinsic presence of carboxylic group on the surfaces of these materials to introduce thiol functionalities through the coupling reaction described here. These thiol-modified materials would then be able to bind Maleimide functionalities through the Michael addition reaction as shown in this work.

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## Notes and references

- 1 S. Iijima, *Nature*, 1991, **354**, 56.
- 2 D. Connolly, S. Currihan and B. Paull, *Proteomics*, 2012, **12**, 2904.
- 3 W. R. Yang, P. Thordarson, J. J. Gooding, S. P. Ringer and F. Braet, *Nanotechnology*, 2007, **18**, 412001.
- 4 E. Frackowiak and F. Béguin, *Carbon*, 2002, **40**, 1775.
- 5 I. Capek, *Adv. Colloid Interface Sci.*, 2009, **150**, 63.
- 6 R. Zanella, E. V. Basiuk, P. Santiago, V. A. Basiuk, E. Mireles, I. Puente-Lee and J. M. Saniger, *J. Phys. Chem. B*, 2005, **109**, 16290.
- 7 N. Chauhan, A. Singh, J. Narang, S. Dahiya and S. C. Pundir, *Analyst*, 2012, **137**, 5113.
- 8 P. Gobbo, S. Ghiassian, M. Hesari, K. G. Stamplecoskie, N. Kazemi-Zanjani, F. Lagugné-Labarthe and M. S. Workentin, *J. Mater. Chem.*, 2012, **22**, 23971.
- 9 J. Huang, X. Xing, X. Zhang, X. He, Q. Lin, W. Lian and H. Zhu, *Food Res. Int.*, 2011, **44**, 276.
- 10 D. Cai, Y. Yu, Y. Lan, F. J. Dufort, G. Xiong, T. Paudel, Z. Ren, D. J. Wagner and T. C. Chiles, *BioFactors*, 2007, **30**, 271.
- 11 Y. Guo, S. Guo, Y. Fang and S. Dong, *Electrochim. Acta*, 2010, **55**, 3927.
- 12 L. Jiang and L. Gao, *Carbon*, 2003, **41**, 2923.
- 13 K. Jiang, A. Eitan, L. S. Schadler, P. M. Ajayan, R. W. Siegel, N. Grobert, M. Reyes-Reyes, H. Terrones and M. Terrones, *Nano Lett.*, 2003, **3**, 275.
- 14 A. V. Ellis, K. Vijayamohan, R. Goswami, N. Chakrapani, L. S. Ramanathan, P. M. Ajayan and G. Ramanath, *Nano Lett.*, 2003, **3**, 279.
- 15 L. Han, W. Wu, F. L. Kirk, J. Luo, M. M. Maye, N. N. Kariuki, Y. Lin, C. Wang and C.-J. Zhong, *Langmuir*, 2004, **20**, 6019.
- 16 B. R. Azamian, K. S. Coleman, J. J. Davis, N. Hanson and M. L. H. Green, *Chem. Commun.*, 2002, 366.
- 17 J. Hu, J. Shi, S. Li, Y. Qin, Z. X. Guo, Y. Song and D. Zhu, *Chem. Phys. Lett.*, 2005, **401**, 352.
- 18 X. Hou, L. Wang, X. Wang and Z. Li, *Diamond Relat. Mater.*, 2011, **20**, 1329.
- 19 H. Ismaili, F. Lagugné-Labarthe and M. S. Workentin, *Chem. Mater.*, 2011, **23**, 1519.
- 20 K. E. Snell, H. Ismaili and M. S. Workentin, *ChemPhysChem*, 2012, **13**, 3185.
- 21 Z. Liu, Z. Shen, T. Zhu, S. Hou, L. Ying, Z. Shi and Z. Gu, *Langmuir*, 2000, **8**, 3569.
- 22 L. Minati, G. Speranza, S. Torrenzo, L. Toniutti, C. Migliaresi, D. Maniglio, M. Ferrari and A. Chiasera, *Surf. Sci.*, 2012, **604**, 1414.
- 23 P. Gobbo and M. S. Workentin, *Langmuir*, 2012, **28**, 12357.
- 24 M. D. Best, *Biochemistry*, 2009, **48**, 6571.
- 25 W. R. Algar, D. E. Prasuhn, M. H. Stewart, T. L. Jennings, J. B. Blanco-Canosa, P. E. Dawson and I. L. Medintz, *Bioconjugate Chem.*, 2011, **22**, 825.
- 26 H. Liu, B. S. Mun, G. Thornton, S. R. Isaacs, Y.-S. Shon, D. F. Ogletree and M. Salmeron, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 155430.
- 27 C. R. Henry, *Surf. Sci. Rep.*, 1998, **31**, 231.

# Facile Synthesis of Gold Nanoparticle (AuNP)- Carbon Nanotube (CNT) Hybrids through an Interfacial Michael Addition Reaction

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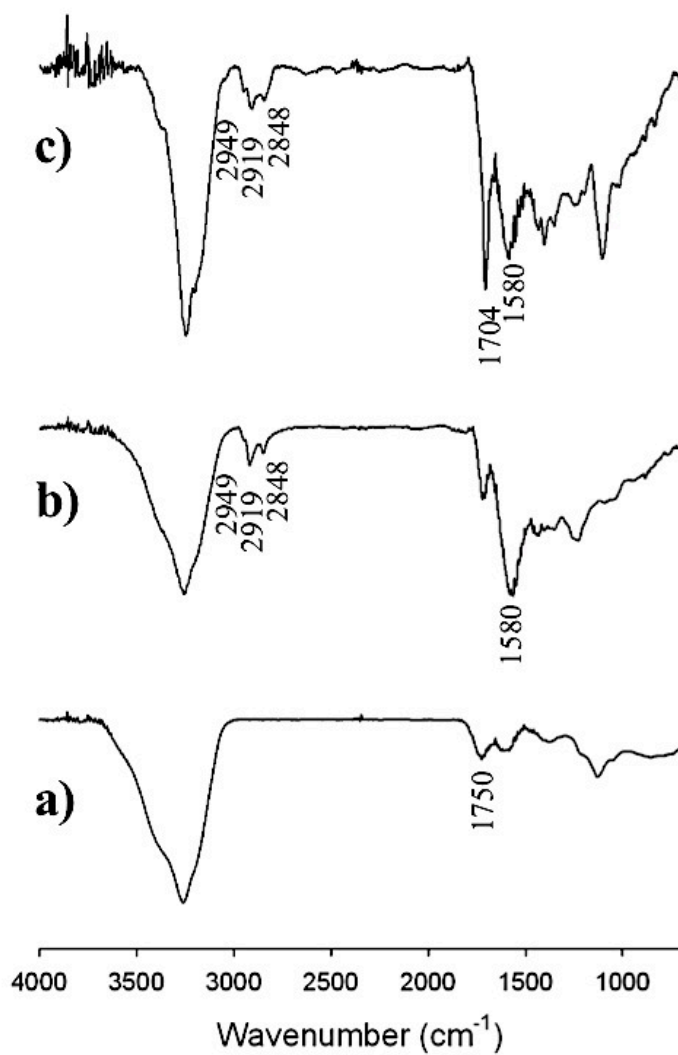
## Supporting Information

## General Materials and Methods

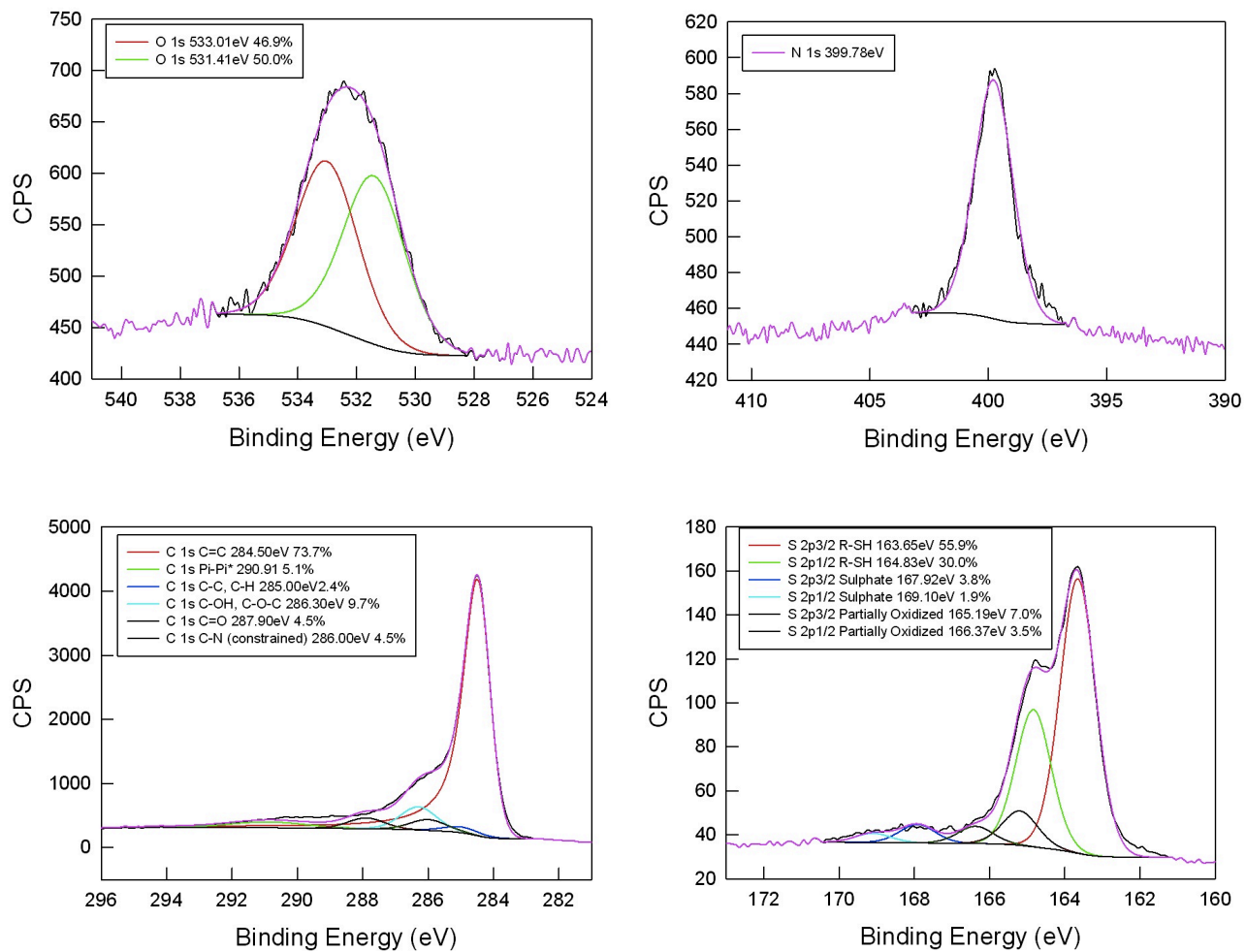
The following reagents were used for the synthesis of the compounds in this article. Potassium thioacetate, triethylene glycol monomethylether, tetraethylene glycol, 4-dimethylaminopyridine (DMAP), sodium borohydride, p-toluenesulfonyl chloride, Gold(III) chloride trihydrate, O-Benzotriazole-N,N,N',N'-tetramethyl-uronium-hexafluoro-phosphate (HBTU), N,N-Diisopropylethylamine (DIPEA), and single wall carbon nanotubes (carbon >90 %, 50-70% carbon as SWCNT, D = 1.2-1.5 nm, L = 2-5  $\mu$ m) were purchased from Aldrich. All common solvents, dry methanol, hydrochloric acid, sodium hydroxide, triethylamine, and magnesium sulfate were purchased from Caledon. Glacial acetic acid (99.7%) was purchased from BDH. Ethanol and methanol were purchased from Commercial Alcohols. Dialysis membranes (MWCO 6000-8000) were purchased from Spectra/Por.

Transmission electron microscopy (TEM) images were recorded from a TEM Philips CM10. Infrared spectra were recorded using a Bruker Vector33 spectrometer and making a thin film of sample onto a KBr disk.

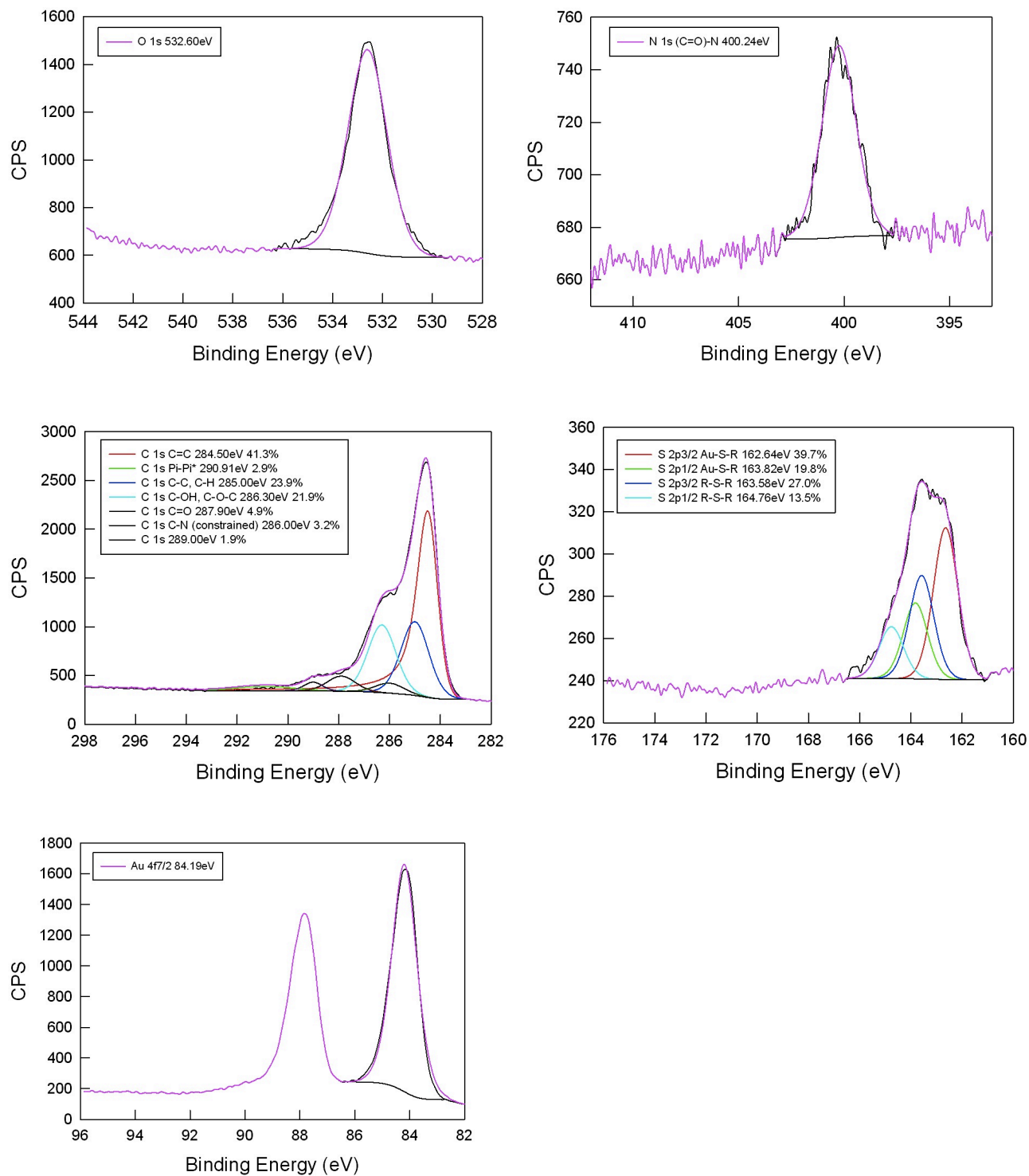
The XPS analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al K(alpha) source (15mA, 14kV). XPS can detect all elements except hydrogen and helium, probes the surface of the sample to a depth of 5-7 nanometres, and has detection limits ranging from 0.1 to 0.5 atomic percent depending on the element. The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f<sub>7/2</sub> line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p<sub>3/2</sub> line of metallic copper. Specimens were mounted on a double side adhesive and the Kratos charge neutralizer system was used on all specimens. Survey scan analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 160 eV. High resolution analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 20 eV. Spectra have been charge corrected to the main line of the carbon 1s spectrum set to 284.5 eV for graphitic/nanotube type species. Spectra were analyzed using CasaXPS software (version 2.3.14).



**Figure SII:** IR spectra of a) SWCNT starting material; b) SWCNT-SH; c)SWCNT-AuNP hybrid material.



**Figure SI2:** High resolution XPS spectra for SWCNT-SH.



**Figure SI3:** High resolution XPS spectra for SWCNT-AuNP hybrid material.