ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Zhu, J. Hiltz, R. B. Lennox and R. Schirrmacher, *Chem. Commun.*, 2013, DOI: 10.1039/C3CC46325G.



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSCPublishing

www.rsc.org/chemcomm Registered Charity Number 207890 Published on 10 September 2013. Downloaded by Laurentian University on 17/09/2013 05:47:37.

Cite this: DOI: 10.1039/c0xx00000x

ARTICLE TYPE

Chemical Modification of Single Wall Carbon Nanotubes with Tetrazine-tethered Gold Nanoparticles via a Diels-Alder Reaction

Jun Zhu^{a,b} Jonathan Hiltz,^b R. Bruce Lennox,^{*, b} Ralf Schirrmacher ^{*,a}

Received (in XXX, XXX) Xth XXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

A versatile methodology for the modification of single wall carbon nanotubes (SWCNT) through an inverse electron demand Diels-Alder reaction with tetrazine-AuNP (1-AuNP) under ambient conditions is described. A robust covalently 10 bonded hybrid nanocomposite is formed.

Both single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs) continue to be of great interest because of their many applications in the fabrication of advanced nanomaterials.^{1,2} Carbon nanotubes surface-modified with metal ¹⁵ nanoparticles (NP; mainly gold or silver) are of particular interest because of their application in catalysis, imaging contrasting agents, and drug delivery.^{3,4} Metal nanoparticles can be incorporated onto CNT through physical adsorption or covalent bonding. Physical adsorption of NP onto CNT can be achieved ²⁰ either by in-situ reduction of the corresponding metal ion or through electrostatic interactions, van der Waals interactions, or aromatic interactions of pre-formed gold nanoparticles (AuNPs) with the CNT. However, these inherently weak interactions result in poor stability of the resulting nanostructures. Covalent

- ²⁵ modification of CNT with the ligand shell of the NP can however significantly improve the stability of the nanocomposites. Most importantly, using pre-formed AuNPs enables control of the shape, size, and functionality of the NPs. One drawback of most CNT chemical modification methods is that the process usually
- ³⁰ involves an initial oxidation of the CNT with concentrated nitric acid and sulfuric acid, leading to the formation of various oxygen containing groups (mainly carboxyl group) on the defect sites.^{5,6} Esters or amides are often prepared in follow-up reactions.^{7,8,9,10} This activation process results in a series of derivative sites on
- ³⁵ CNT with little or no regiospecificity, mainly occurring at defects or edges. The result is a poorly-controlled modification. Moreover, reactions involving the most common AuNPs, thiolate-protected AuNPs, only tolerate mild ambient conditions because of the relative lability of the Au-S bond. Harsh
- ⁴⁰ conditions, such as heating at high temperature (>100 °C for prolonged periods) or photo-irradiation can cause severe degradation of the ligand shell and ultimately, the NP. Obvious entries to chemical derivatization that do not require oxidative activation, such as Diels-Alder reactions, unfortunately often ⁴⁵ involve reaction conditions that are incompatible with the thiolate
- AuNP, although CNT can serve as a dienophile in possible Diels-Alder reactions.^{8,11,12} Harsh conditions, including reflux or

microwave heating, are required to facilitate the completion of these reactions. An efficient covalent-bonding methodology for

- ⁵⁰ the preparation of CNT-AuNP nanocomposites using catalystfree and room temperature is thus much desired. We note that similar constraints arising in polymer-grafting–CNT synthesis and Diels-Alder reactions have been effectively used in this regard.¹³
- 55 Tetrazines react with strained dieneophiles in a rapid, atom efficient, and catalyst free-manner. The inverse electron demand Diels-Alder reaction of highly electron-deficient tetrazines with strained alkenes or acetylenes has been widely explored.^{14,15,16,17} 3,6-Diaminotetrazines, for example, have been applied to the
- ⁶⁰ modification of MWCNT at elevated temperatures.¹⁸ The resulting amino-tethered MWCNT can be used as a crosslinker to improve the wear performance of an MWCNT/epoxy resin.¹⁹ The application of the tetrazine click chemistry to nanoparticle modifications has however received relatively little attention. Han
- 65 et al. demonstrated the application of tetrazine-dienophile Diels-Alder chemistry to functionalize nanoparticles by attaching tetrazine-modified dyes/biomolecules to dienophile (norbornene) containing ligand-protected quantum dots.²⁰ Audebert et al. prepared tetrazine-doped silica nanoparticles to study the 70 fluorescence emission properties of these NP.²¹ Here we report the facile synthesis of a tetrazine-terminated AuNP (tetrazine-AuNP or 1-AuNP), and the development of an efficient and reproducible methodology to modify SWCNTs via the reverse electron demand Diels-Alder reaction with these tetrazine-AuNP. 75 The tetrazine-AuNP can react with SWCNTs in ambient conditions (room temperature and catalyst-free) to form a AuNP-SWCNT complex. Covalent bonding of AuNP to CNT not only increases the chemical and physical stability of the nanocomposites, but also provides a versatile methodology for 80 further modification of CNTs through the thiol exchange reaction.

The synthesis of the gold nanoparticle grafted single wall carbon nanotubes is shown in **Scheme 1**. To prepare the tetrazine-AuNP (1-AuNP), the undecanolthiolate-terminated gold ⁸⁵ nanoparticles (MUD-AuNP) were prepared by following a standard place-exchange procedure involving mixing 11mecaptoundecanol (MUD) with dodecanethiolate protected AuNP, at a ligand ratio of 1:1, for 1h. The MUD-AuNP were purified by washing with ethanol and acetonitrile. ⁹⁰ Characterization by ¹H-NMR spectroscopy reveals the absence of

This journal is © The Royal Society of Chemistry [year]

65

sharp ligand peaks, indicating the purity of the product AuNP. The pure MUD-AuNP are soluble in THF, chloroform, DCM, and toluene. 3,6-Dichlorotetrazine (1) was then prepared following a previous reported procedure with an overall yield of s 80%.^{14,22,23} Triaminoguanidine (3) was first synthesized by refluxing guanidine hydrochloride (2) and hydrazine monohydrate in dioxin for 2 hour, followed by treatment with 2,4-pentanedione to form the dihydrotetrazine precursor (4). The precursor 4 was then oxidized by sodium nitrite to yield 3,6-¹⁰ bis(3,5-dimethyl-1H-pyrazol-1-yl)-s-tetrazine (5). The 3,6dichlorotetrazine (1) was subsequently generated by treatment of 5 with hydrazine and trichloroisocyanuric acid. 3,6dichlorotetrazine (1) is a very hygroscopic compound and is readily hydrolyzed when exposed to moisture. To protect the 15 integrity of the tetrazine moieties and maintain their high reactivity toward the dienophile, the chlorotetrazine was introduced onto the hydroxyl-terminated MUD-AuNP in the last step, under anhydrous conditions. The tetrazine-capped AuNP (1-AuNP, 1.9±0.3 nm, Fig.1b) are synthesized by mixing the MUD-

²⁰ AuNP with excess of tetrazine 1 at room temperature for 2 h.

Published on 10 September 2013. Downloaded by Laurentian University on 17/09/2013 05:47:37.



Scheme 1. Synthesis of tetrazine-AuNP (1-AuNP) and the Diels-Alder reaction between tetrazine-AuNP and SWCNT to prepare AuNP-SWCNT.

Whereas most (the exception being the aforementioned ²⁵ polymer CNT conjugates¹³) published chemical modification methods of SWCNTs require pre-treatment and relatively harsh conditions, SWCNTs react with tetrazine-AuNP under ambient conditions, without any pre-treatment. A stock suspension of SWCNT in dry THF was first prepared by sonication of 5 mg of ³⁰ SWCNT in 5 mL of anhydrous THF. A tetrazine-AuNP/THF solution was immediately prepared before use by dissolving 1 mg of **1**-AuNP in 5 mL of dry THF. 1mL of a SWCNT suspension

- and different volumes of the tetrazine-AuNP solution (50 μ L and 500 μ L for this study) were mixed for 2 h at room temperature to ³⁵ allow for the completion of the Diels-Alder reaction. The reaction mixture was then centrifuged (5 min, 12,000 rpm); the upper black supernatant was then removed. The resulting AuNP-SWCNT pellet was re-suspended in THF, bath sonicated for 5 min and centrifuged again, discar0064ing the supernatant. This
- ⁴⁰ purification procedure was repeated with THF, DCM, toluene, and acetonitrile, 10 times per solvent until the supernatant was clear and colorless. The pure AuNP-SWCNT sample was then suspended in THF for further characterization. The reaction between the tetrazine-AuNP and SWCNT was confirmed by

45 TEM, EDX, Raman spectroscopy, and XPS.

HR-TEM images of SWCNT before (Figure 1a) and after (Figure 1 c,d) the Diels-Alder reaction with tetrazine-AuNP for 2h demonstrate the association between CNT and AuNP. An increase in the reactants ratio of tetrazine-AuNP to SWCNT leads ¹²⁰ to a greater density of AuNP attached onto the SWCNT surface. Interestingly, the AuNP remain quite evenly distributed along the CNT. Covalent bonding of AuNP to SWCNT is confirmed by a control experiment. MUD-AuNP and SWCNT were mixed under the same reaction conditions. As expected, the MUD-AuNP ¹²⁵ without tetrazines do not react with SWCNT and only underivatized SWCNT were isolated after purification (Supporting information, Figure S10.d). Energy dispersive X-ray (EDX) spectrum analysis confirms the presence of Au, S, Cl, and N in the AuNP-SWCNT sample (Figure S11).



Fig. 1. HR-TEM of (a) SWCNT, (b) 1-AuNP, (c) low 1-AuNP loading AuNP-SWCNT sample and (d) high 1-AuNP loading AuNP-SWCNT sample.

Raman spectroscopy provides evidence for the chemical modification of carbon nanotubes.²⁴ The HeNe laser line at 633 195 nm was used in the characterization of AuNP-SWCNT in order to avoid the strong extinctions of AuNP at 488 nm and 514 nm, which are otherwise common excitation wavelengths for Raman spectroscopy. The Raman spectrum of pristine SWCNTs (Supporting information Figure S12a) is consistent with data 200 reported in literature, with two prominent features: a weak D band and a strong G band around 1325 cm⁻¹ and 1580 cm⁻¹. respectively.²⁴ The spectrum of AuNP-SWCNT nanocomposites (Figure S12.b,c) shows significant changes compared to that of SWCNT alone. The decrease in the G/D ratio from 20/1 for the 205 pristine SWCNT (Figure S12.a) to 8/1 for the low AuNP loading AuNP-SWCNT sample (Figure S12.b) is consistent with sidewall modification of the SWCNT.5,25 The D and G bands almost disappear in the case of the high AuNP loading sample (Supporting information Figure S12.c). At the same time, new 210 bands associated with the AuNP-SWCNT were observed (Table 1). New peaks at 429 cm⁻¹ (ring deformation), 705 cm⁻¹ (C-S stretching mode), 810 cm⁻¹ (C-Cl stretch mode, broad) and a broad peak around 1090cm⁻¹ (C-C-C stretching mode) are observed. The characteristic features of a C-N stretch mode, a 215 tetrazine ring stretch mode, and the C=N stretch mode were also observed around 1270 cm⁻¹, 1390 cm⁻¹ and 1660 cm⁻¹, respectively. These new Raman bands in the functionalized SWCNT sample confirm the presence of the AuNP on the surface

Published on 10 September 2013. Downloaded by Laurentian University on 17/09/2013 05:47:37

of the SWCNTs.

Table 1. Summary	of the raman	bands of the	AuNP-SWCNT
------------------	--------------	--------------	------------

Raman Shift (cm-1)	Vibrational mode	
429	ring deformation	
705	C-S stretch	
810	C-Cl stretch	
1090	C-C-C stretch	
1270	C-N stretch	
1390	tetrazine ring stretch	
1660	C=N stretch	
a) 1200 1000 000 600 400 200 0.	C) 400 - 300 - 200 - 100 - 0 Biedrog Energy (W)	
b) 1200 1000 800 600 400 200 0 Energy (PV)	d) 400 400 454 422 400 300 300 304 30 Boding Deceny (47)	

Figure 2. XPS survey scan of (a) AuNP-SWCNT, and (b) SWCNT. (c) is the s zoom in of AuNP-SWCNT for peak assignment. (d) is the high resolution N1s spectra of AuNP-SWCNT.

The AuNP-SWCNT and SWCNT were also characterized by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of AuNP-SWCNT (Figure 2.a,c) compared with that of ¹⁰ pristine SWCNT (Figure 2.b) clearly shows the appearance of new peaks from the Diels-Alder adduct. The Au 4d (336 eV) and Au 4f (doublet around 89.0-89.5 eV) are clearly resolved but the S2p peak overlaps with the Si2p peak of the Si wafer sample support). EDX however confirms the presence of S in AuNP-¹⁵ SWCNT. A high resolution N1s XPS signal shows two peaks at 402.2 eV and 400.8 eV, one assigned to the nitrogen of the Diels-Alder adduct and the other to unreacted tetrazine on AuNP-SWCNT surface.

Conclusions

- 20 SWCNT are shown to be efficiently functionalized with tetrazine-AuNP through a versatile reverse electron demand Diels-Alder reaction under ambient conditions, e.g. room temperature, no irradiation, and catalyst-free. The loading of tetrzaine-AuNP on the SWCNT sidewall could be readily
- 25 controlled by varying the ratio of these two reactants. The tetrazine-AuNP can react directly with the sidewalls of SWCNTs and no pre-treatment of the nanotubes is required. More importantly, the high reactivity of tetrazine-AuNP with SWCNT provides for an accurate derivatization of 2D or 3D-based carbon
- ³⁰ materials. The covalent bonding greatly increases the stability of these nanocomposites compared to their analogues formed via non-covalent interactions.

Notes and references

^a Montreal Neurological Institute & Hospital, McGill University, 3801

³⁵ University Street, Montreal, QC H3A 2B4, Canada . Fax: +1 514-340-7502; Tel: +1-514-398-1857; E-mail: ralf.schirrmacher@mcgill.ca ^b Department of Chemistry and Centre for Self-Assembled Chemical Structures, McGill University, 801 Sherbrooke St. West, Montreal, QC H3A 2K6, Canada. Fax: +1 514-398-3797; Tel: +1-514-398-5244; E-40 mail: bruce.lennox@mcgill.ca

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

This work was supported by grants from CHIR (RS), NSERC (RS, 45 RBL) and FQRNT (RBL).

- 1 S. Iijima and T. Ichihashi, Nature, 1993, 363, 603.
- 2 S. Auvray, V. Derycke, M. Goffman, A. Filoramo, O. Jost and J. P. Bourgoin, *Nano Lett.*, 2005, 5, 451.
- 3 K. Welsher, Z. Liu, S. P. Sherlock, J. T. Robinson, Z. Chen, D. Daranciang and H. Dai, *Nat. Nanotechnol.*, 2009, 4, 773.
- 4 L. Minati, V. Antonini, M. D. Serra and G. Speranza, *Langmuir*, 2012, 28, 15900.
- 5 J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund and R. C. Haddon, *Science*, 1998, **282**, 95
- 6 M. Burghard and K. Balasubramanian, Small, 2005, 1, 180.
- 7 J. L.Delgado, P. de la Cruz, F. Langa, A.Urbina, J. Casado and J. T. Lopez Navarrete, *Chem. Commun.*, 2004, **40**, 1734.
- 8 L. Zhang, J. Yang, C. L. Edwards, L. B. Alemany, V. N. Khabashesku and A. R. Barro, *Chem. Commun.*, 2005, **41**, 3265.
- 9 C. Menard-Moyon, F. Dumas, E. Doris and C. Mioskowski, J. Am. Chem. Soc., 2006, **128**, 14764
- 10 L. Zhang, S. J. Zhen, Y. Sang, J. Y. Li, Y. Wang, L. Zhan, L. Peng, J. Wang, Y. F. Li and C. Z. Huang, *Chem. Commun.*, 2010, **46**, 4303.
- 11 G. Sakellariou, H. Ji, J. W. Mays, N. Hadjichristidis and D. Baskaran, *Chem. Mater.*, 2007, **19**, 6370.
- 12 J.Sun, L.Zhao, C.Hong and C. Pan, *Chem. Commun.*, 2011, **47**, 10704.
- 13 B.Yameen, C. Rodriguez-Emmenegger, I. Ahmed, C. M. Preuss, C. J. Dürr, N. Zydziak, V. Trouillet, L. Fruk and C. Barner-Kowollik, *Chem. Comm.*, 2013, 49, 6734 and reference therein.
- 14 G. Clavier and P. Audebert, Chem. Rev., 2010, 110, 3299.
- N. K. Devaraj, R. Weissleder and S. A. Hilderbrand, *Bioconjugate Chem.*, 2008, **19**, 2297; T. Reiner, E. J. Keliher, S. Earley, B. Marinelli and R. Weissleder, *Angew. Chem. Int. Ed.*, 2011, **50**, 1922; G. Budin, K. S. Yang, T. Reiner, and R. Weissleder, *Angew. Chem. Int. Ed.*, 2011, **50**, 9378; M. R. Karver, R. Weissleder and S. A. Hilderbrand, *Angew. Chem. Int. Ed.*, 2012, **51**, 920.
- 16 M. L. Blackman, M. Royzen and J. M. Fox, J. Am. Chem. Soc., 2008, 130, 13518; D. S. Liu, A. Tangpeerachaikul, R. Selvaraj, M. T. Taylor, J. M. Fox and A. Y. Ting, J. Am. Chem. Soc., 2012, 134, 792; J. L. Seitchik, J. C. Peeler, M. T. Taylor, M. L. Blackman, T. W. Rhoads, R. B. Cooley, C. A. Refakis, J. M. Fox and R. A. Mehl, J. Am. Chem. Soc., 2012, 134, 2898.
- 17 C. F Hansell, P. Espeel, M. M. Stamenovic, I. A. Baker, A. P. Dove, F. E. Du Prez and R. K. O'Reilly, *J. Am. Chem. Soc.*, 2011, **133**, 13828.
- 18 H. Hayden, Y. K. Gun'ko and T. S. Perova. *Chem. Phys. Lett.*, 2007, **435**, 84.
- 19 A. Zhang, W. Liu, M. Li and Y. Zheng, J. Reinf. Plast. Compos., 2009, 28, 2405.
- 20 J. Schoch, M. Wiessler and A. Jaeschke, J. Am. Chem. Soc., 2010, 132, 8846.
- 21 J. Malinge, C. Allain, L. Galmiche, F. Miomandre and P. Audebert, *Chem. Mater.*, 2011, 23, 45990.
- 22 D. E. Chavez and M. A. Hiskey, J. Heterocycl. Chem., 1998, 35, 1329;
 D. E. Chavez and M. A. Hiskey, J. Energ. Mater., 1999, 17, 357;
 D. E. Chavez, M. A. Hiskey and R. D. Gilardi, Angew. Chem. Int. Ed., 2000, 39, 1791.
- 23 Y. Gong, F. Miomandre, R. Meallet-Renault, S. Badre, L. Galmiche, J. Tang, P. Audebert and G. Clavier, *Eur. J. Org. Chem.*, 2009, 35, 6121.
- 24 A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon; A. Thess, R. E. Smalley, G. Dresselhaus and M. S. Dresselhaus, *Science*, 1997, 275, 187.
- 25 H.Hu, B. Zhao, M. A. Hamon, K. Kamaras, M. E. Itkis and R. C. Haddon, J. Am. Chem. Soc. 2003, **125**, 14893.