

# One-dimensional heterostructure: The selective decoration of single-walled carbon nanotube tips with metallic nanoparticles

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A straightforward protocol is presented to covalently bond gold nanoparticles exclusively at the tips of single-walled carbon nanotubes. This approach exploits the sterical hindrance given by a polymer and surfactant, preventing the attachment of non-functionalized gold nanoparticles onto the main nanotube body. These novel heterostructures have promising potential for applications in photonics and electronic devices.

Semiconducting single-walled carbon nanotubes (SWNTs) are visualized as one of the most promising materials for the next generation of electronic and photonic devices.<sup>1–8</sup> Similarly, metallic SWNTs can also play an essential role in developing device interconnections.<sup>9–11</sup> The quality of the carbon–metal contacts is a crucial issue that influences the device’s overall performance. This metal–carbon junction has been widely studied theoretically, demonstrating that the quality of the contact strongly depends on the metal type,<sup>12,13</sup> the nanotube chirality,<sup>14,15</sup> and how the nanotube is contacting the electrodes.<sup>16</sup> Experimentally, Seidel et al.<sup>17</sup> developed a multilayer structure for growing nanotubes *in situ* over electrodes, allowing very high on-currents of the order of several milliamperes and on/off ratios exceeding 500. Nosho et al.<sup>18</sup> investigated the response of SWNT field-effect transistors (FETs) with

diverse metal contacts, demonstrating that the conduction type and the drain current are dependent on the metal–work function. Moreover, FETs with nanotubes are projected to be more beneficial than the fin-FETs (a non-planar FET, with a channel contacted by the gate in at least two sides<sup>19</sup>) in terms of clock frequency and energy consumption.<sup>20</sup> Despite the expected performance, the metal–nanotube contact resistance has to be improved if desired to exploit the nanotubes’ performance in electronic devices. Therefore, it is fundamental to engineering the contact resistance at the atomic/molecular scale.<sup>21–23</sup> A standard procedure for fabricating SWNT-based devices is contacting the nanotube on the top of metal electrodes or, inversely, depositing the metallic electrodes over the nanotube.<sup>12,24,25</sup> This methodology is guided by weak van der Waals bonds between the electrodes and SWNTs,<sup>12,15</sup> resulting in a

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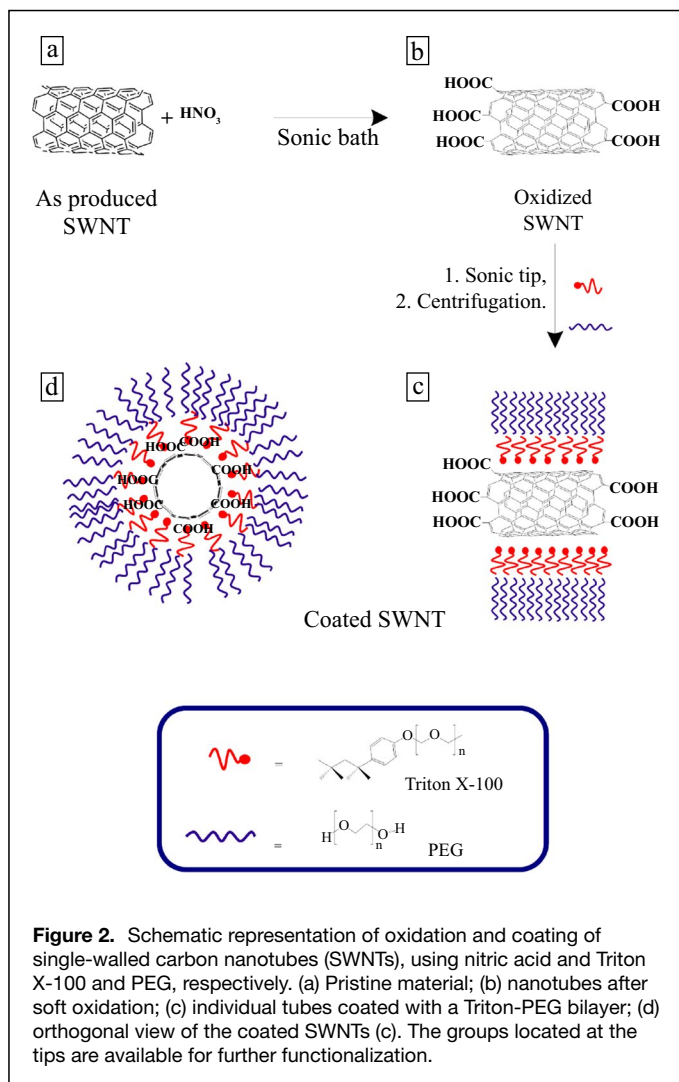
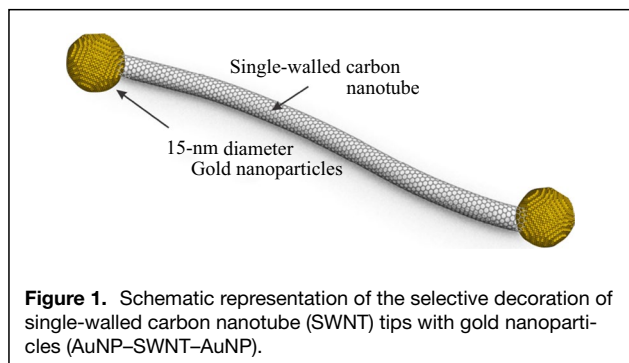
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weak assembly with a considerable barrier for electronic conduction (the Fermi level between the metal electrode and the nanotube does not perfectly align resulting in a gap between their energy levels, which is dependent on the metal type and their oxide barriers),<sup>26–28</sup> thus inducing high contact resistances. Additionally, the placement of a nanotube on the top of electrodes is a strategy that prevents further applications



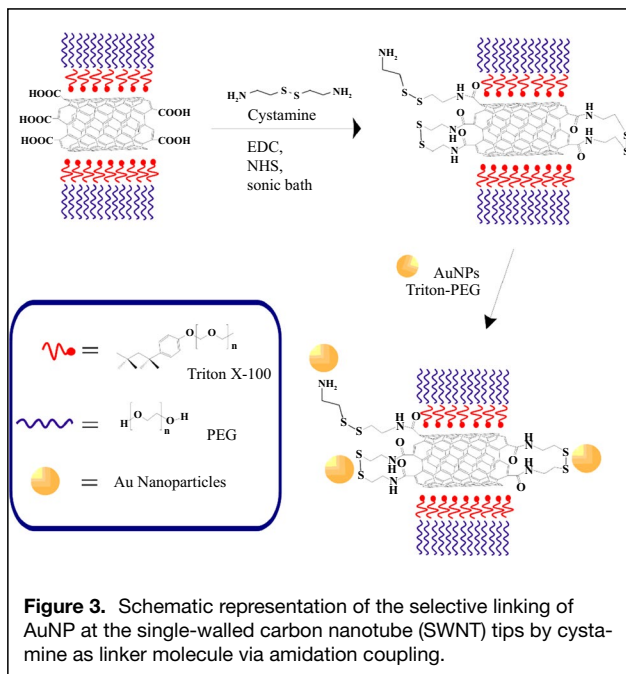
because it is quite complex to scale it up. Lowering the contact resistance will enhance the on/off ratio.<sup>15,26,29–31</sup> This means that it could be possible to have faster devices with lower power consumption. Much effort has been made to improve the contact between SWNTs and metal electrodes, for example, fusing by annealing the metal electrodes to obtain a carbide-metal junction<sup>3,32,33</sup> or exposing the electrodes to high energy beams.<sup>17</sup> However, all these protocols are not focused or applied exclusively on the metal-nanotube junctions, jeopardizing the integrity of other components.

Following the bottom-up approach, few groups have attempted to attach metallic moieties to semiconductor nanostructures. In this context, Deng et al.<sup>34</sup> have theoretically demonstrated that the presence of a covalent bond between graphene and metal particles increases its electric and mechanical performance considerably. These authors suggested that the functional groups (e.g.,  $-\text{COO}-$  and  $-\text{CON}-$ ) at the junction can reduce the electric resistance even 40 and 60 times, respectively. Interestingly, Weizmann et al.<sup>35</sup> achieved the linking of the as-purchased (custom-made) amine mono-functionalized gold nanoparticles attached exclusively to the nanotube tips. This approach, however, is expensive due to the time/cost of production of the mono-functionalized gold nanoparticles. Herein, we propose a chemical approach for the attachment of gold nanoparticles (AuNPs) on the tips of SWNTs (**Figure 1**). This strategy involves (1) mild oxidation of SWNT tips; (2) wall protection by polymeric bilayer; (3) introduction of thiol groups on both ends of SWNTs; and (4) covalent anchoring of AuNPs.

Because pristine SWNTs are chemically inert, they require mild treatment to ensure reactivity (opening) on the tips.<sup>36–38</sup> By following well-established protocols for SWNT oxidation,<sup>39</sup> we found that the treatment with nitric acid at a reduced time (2 h) is sufficient to oxidize the tips, and the final SWNT length is  $233 \pm 166$  nm (see electronic supporting information, ESI). To ensure reactivity exclusively at the tips, in the subsequent synthesis steps, the main body of the nanotubes was protected with a Triton-PEG mixture (see ESI for further details), preventing thus undesired wall functionalization (**Figure 2**). In our approach, the Triton X-100 prevents the nanotube bundling and aggregation, and the bulky and hydrophilic PEG enhances the steric stabilization by its long polymer chain.<sup>40,41</sup>

Cystamine is selected as a suitable molecular linker between the SWNT and AuNP. The presence of amine functional groups in cystamine, on the one hand, allows the selective functionalization of the nanotube by mild sonication. On the other hand, the affinity of disulphuric bonds toward the metallic surface is maintained. The schematic representation of the functionalized cystamine-SWNT (Cys-SWNT) is depicted in **Figure 3**.

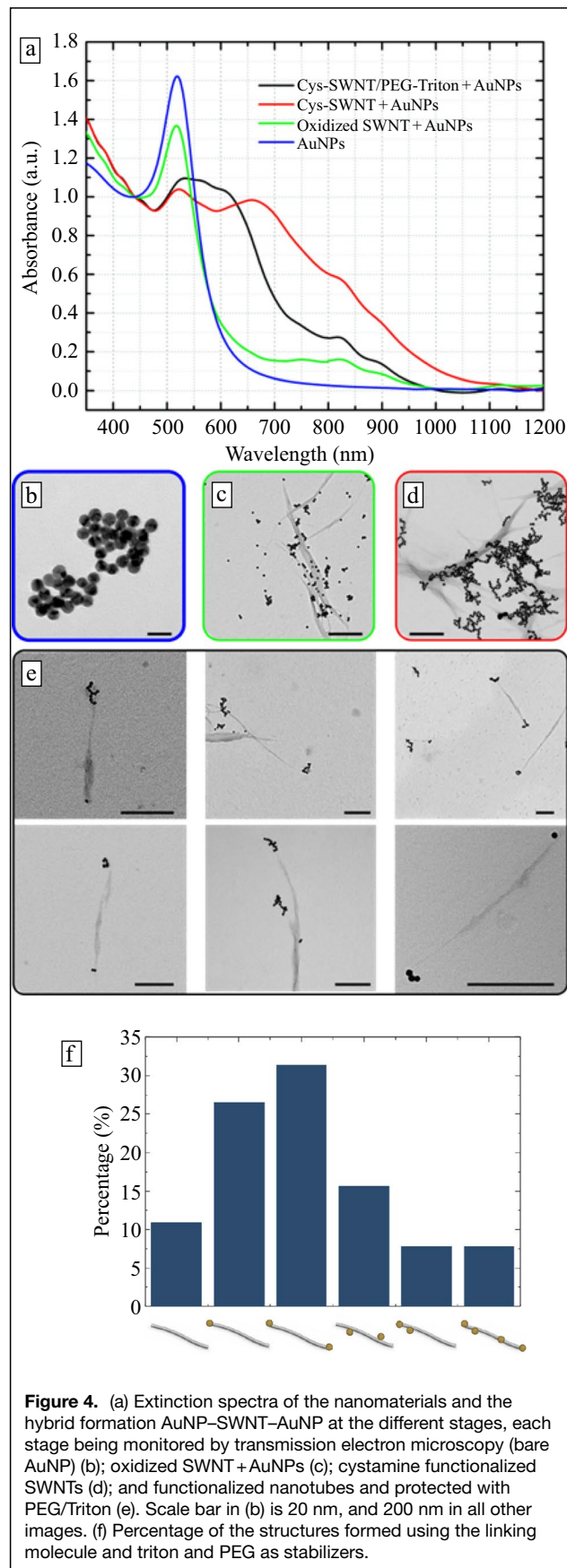
Gold nanoparticles ( $15 \pm 1.5$  nm) stabilized with citrate ions can be easily exchanged in further steps.<sup>42</sup> To minimize nonspecific interactions between AuNPs and the main body of the SWNTs, the AuNPs were pretreated



**Figure 3.** Schematic representation of the selective linking of AuNP at the single-walled carbon nanotube (SWNT) tips by cystamine as linker molecule via amidation coupling.

with the PEG solution (AuNP@PEG) (Figure 4b). The PEG addition also prevents the aggregation between other AuNPs (Figure S2). Combining the dispersion of Cys-SWNTs and AuNP@PEG, the selective anchoring of the metal nanoparticles to the SWNT tips by covalent bonds (Figure 3) was achieved. The formed heterostructures of AuNP–SWNT–AuNP were stored in an aqueous solution for further characterization.

Optical characterization of the sample at different experimental stages provided information on the interaction between carbon nanotubes and nanoparticles (Figure 4a). The UV–vis spectrum of the mixture containing oxidized SWNTs (not-functionalized with cystamine) and AuNPs showed intense localized surface plasmon resonance (LSPR) with the maximum at 517 nm and broad absorption bands at 800 nm, corresponding to characteristic Van Hove singularities of SWNTs (Figure 4a, green line).<sup>43,44</sup> Because the absorption curve shape of LSPR was the same as the original nanoparticles (Figure 4a, blue line), we deduced weak or non-interaction between the AuNPs and the SWNTs. TEM analysis confirmed the random distribution of nanoparticles and SWNTs (Figure 4c). The successful selective attachment of AuNP to SWNT tips was observed only when using Cys-SWNT coated with Triton/PE (reaching 33% of AuNP–SWNT–AuNP heterostructures formed, Figure 4f). The LSPR redshifted and dumped suggest changes in the colloidal stability of nanoparticles (Figure 4a, black line). TEM analysis revealed the presence of many AuNP–SWNT–AuNP heterostructures (Figure 4e) and confirmed the broadening of the LSPR due to the formation of small clusters containing few particles attached to SWNT tips. To further confirm the importance of the Triton/PEG shell around SWNT walls in the formation of



**Figure 4.** (a) Extinction spectra of the nanomaterials and the hybrid formation AuNP–SWNT–AuNP at the different stages, each stage being monitored by transmission electron microscopy (bare AuNP) (b); oxidized SWNT + AuNPs (c); cystamine functionalized SWNTs (d); and functionalized nanotubes and protected with PEG/Triton (e). Scale bar in (b) is 20 nm, and 200 nm in all other images. (f) Percentage of the structures formed using the linking molecule and Triton and PEG as stabilizers.

AuNP–SWNT–AuNP structures, control experiments using Cys–SWNT (without the Triton/PEG shell) and gold nanoparticles are performed. Observing the formation of chain-like aggregates containing nanoparticles, as confirmed by UV–vis characterization—broad LSPR band with the maximum at 650 nm (Figure 4a—red line and Figure 4d). These chain-like aggregates are formed due to free cystamine that can partially replace PEG to form linear structures.<sup>45</sup>

From TEM images, the formation of different structures was monitored. The histogram in Figure 4f indicates that the formation of the complete structures (i.e., AuNP–SWNT–AuNP) scores 32 percent. It is essential to highlight that the sample preparation for characterization promotes the aggregation of nanotubes and particles.

We have demonstrated that it is relatively simple to take advantage of organo-chemistry tools to build complex nanostructures with potential applications in photonic and electronic devices. The selective attachment of AuNPs to SWNT tips was successfully demonstrated. Whereas covalent chemistry was used to activate the carboxylic groups on the SWNTs, a soft supramolecular approach was used to protect lateral parts. The synthesis of such complex nanohybrid is a promising step toward the controllable and specific functionalization of SWNTs, with the potential for applications as the channel in FETs, sensors, or nano-interconnections. Moreover, further coating of lateral parts with dielectric materials (i.e., SiO<sub>2</sub>, TiO<sub>2</sub>) may open new doors for the fabrication of smart self-assembled nanodevices.

## Author contributions

Conceptualization: AEDRC, MG. Data curation: AEDRC, LS, MQ, MG. Founding MP. Supervision MQ, MP., Writing, editing and reviewing all the authors.

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## Data availability

Available in the supporting information.

## Code availability

Not applicable.

## Conflic of interest

The authors declare no conflict of interest.

## Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1557/s43577-022-00308-3>.

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