

# Preparation of gold nanoparticle/single-walled carbon nanotube nanohybrids using biologically programmed peptide for application of flexible transparent conducting films

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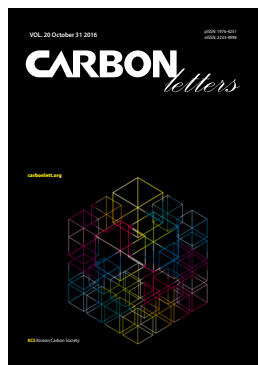
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## Abstract

In this study, we report a general method for preparation of a one-dimensional (1D) arrangement of Au nanoparticles on single-walled carbon nanotubes (SWNTs) using biologically programmed peptides as structure-guiding 1D templates. The peptides were designed by the combination of glutamic acid (E), glycine (G), and phenylalanine (F) amino acids; peptides efficiently debundled and exfoliated the SWNTs for stability of the dispersion and guided the growth of the array of Au nanoparticles in a controllable manner. Moreover, we demonstrated the superior ability of 1D nanohybrids as flexible, transparent, and conducting materials. The highly stable dispersion of 1D nanohybrids in aqueous solution enabled the fabrication of flexible, transparent, and conductive nanohybrid films using vacuum filtration, resulting in good optical and electrical properties.

**Key words:** carbon nanotube, gold nanoparticle, peptide, transparent film

## 1. Introduction

The creation of nanoscale building blocks, which are precisely defined with unique functions, structures, and properties, is a central challenge to the “bottom-up” approach to the construction of next-generation optical, electronic, and magnetic materials and devices [1-4]. Biomolecules such as DNA, peptides, and proteins are particularly promising candidate biotemplates and structure-guiding components for the synthesis and assembly of nanomaterials and their integration into organic or inorganic materials [5]. The development of metal binding peptides using genetic engineering approaches has resulted in several biological strategies to tailor nanoparticle (NP) physicochemical properties and to assemble NPs at multiple length scales by utilizing the sequence programmability, selective molecular recognition ability, and multi-functionality of metal binding peptides [6-9]. In addition, fusion peptides with two domains have been used to synthesize bimetallic NPs [10]. The elaborate features of biomolecules in nanomaterial science and engineering have encouraged researchers to design and fabricate novel surfaces of building blocks for wide-ranging applications [11]. Based on three fundamental principles of molecular recognition, self-assembly, and genetic engineering of peptide sequences, one dimensional nanohybrid building blocks were achieved by assembly of gold NPs on gold binding peptide wrapped-carbon nanotubes [7,12].

Progress in the development of carbon nanotubes (CNTs)-NPs heterostructures as novel one-dimensional (1D) building blocks has enabled the realization of numerous applications in the electronic, sensor, catalyst, and energy fields [13,14]. The controlled arrays and packing densities of NPs in 1D nanohybrids are important as unique properties that largely depend on discrete NPs on the surfaces of CNTs [15]. Generally, three strategies have been

used to deposit NPs on the side walls of CNTs, namely, covalent functionalization, non-covalent modification, and direct NP formation [16]. However, in most cases, these methods are limited in terms of 1D nanostructure applications because of CNT breakage, poor CNT processability, lack of specific-sites, and poor NP stability. To this end, biological molecules based on programmable component spacing and precise registry have been exploited to synthesize and deposit NPs directly on CNTs; examples include NP arrays on DNA-wrapped CNTs, virus-templated CNTs, and protein-functionalized CNTs [17-20]. Biological systems devised using nature's toolbox provide possibilities of high levels of NP organization, facile functionalization, self-assembly motif incorporation, and environmentally benign synthesis [5-7,21]. Nevertheless, despite extensive studies, the NP stability and the precision of the NP arrays remain substantial challenges for many applications [16].

In this study, based on site-specific interactions created by employing programmed peptides as linkers between Au NPs and CNTs, we report a new strategy toward effective 1D arrangement of Au NPs on single-walled CNTs (SWNTs). Programmed peptides containing phenylalanine and glutamic acid groups can serve as bifunctional entities that produce definable supramolecular conjugates of peptide-wrapped SWNTs (p-SWNTs) and can guide the 1D arrangement of Au NPs. In particular, we found that highly stable dispersions of NP conjugations with high electrical conductivity enable the preparation of transparent conductive flexible thin films by vacuum filtration. The AuNP/p-SWNT nanohybrid thin films produced in the present study showed good electrical and optical properties.

## 2. Experimental

### 2.1. Materials

SWNTs produced by high-pressure decomposition of CNTs (HiPco process) were purchased from Carbon Nanotechnologies Inc. (Houston, TX, USA). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%), hydrochloric acid (HCl, 37%), and sodium hydroxide (NaOH, 97%) were purchased from Junsei (Tokyo, Japan). Hydrogen tetrachloroaurate(III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) and ethanol were obtained from Aldrich (Darmstadt, Germany). Anodic aluminum oxide (AAO, 200 nm pore size, 47 mm diameter) membrane filters were purchased from Whatman International (Marlborough, MA, USA). Substrates consisting of untreated glass slides ( $75 \times 25 \times 1.1$  mm) were obtained from Paul Marienfeld (Lauda-Königshofen, Germany). All chemicals were used without purification or treatment, and deionized (DI) water (18 M $\Omega$  cm) purified by an ultrapure water system (Milli-Q; Millipore, Darmstadt, Germany) was used in all experiments.

### 2.2. Synthesis AuNP/p-SWNT nanohybrid films

Prior to preparing the AuNP/p-SWNTs, SWNTs (30 mg) were first sonicated with 40 mL of a  $\text{H}_2\text{SO}_4/\text{HNO}_3$  (3:1) mixture for 10 h. After sonication, the resulting suspension was filtered and rinsed with DI water. The collected SWNTs were re-dispersed in the  $\text{H}_2\text{O}_2/\text{HCl}$  (1:1) mixture and refluxed for 4 h at 70°C to

remove metal impurities. For the fabrication of the p-SWNTs, purified SWNTs (0.7 mg) were added to 1 mL of the designed peptide (100  $\mu\text{M}$ , (EGF)<sub>3</sub>-F) and then vortexed and sonicated in an ice water bath for 1 min, respectively (repeated three times). Following this, centrifugation was performed for 10 min at 13,000 rpm to remove aggregated nanotubes. The 1  $\mu\text{M}$  of  $\text{HAuCl}_4$  was mixed with the p-SWNT dispersion, then sonicated and centrifuged to obtain the AuNP/p-SWNT nanohybrid without unreacted species. The upper 50% of the supernatant was used to prepare p-SWNT and AuNP/p-SWNT network films on glass substrates by vacuum filtration method.

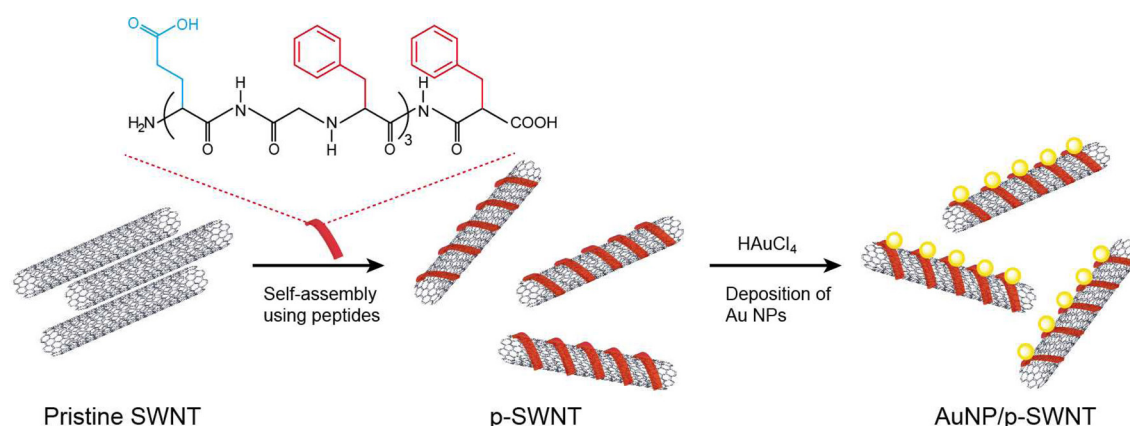
### 2.3. Characterization

Transmission electron microscopy (TEM) and elemental mapping images were collected on an EM-912  $\Omega$  energy-filtering TEM (JEM2100F; JEOL, Tokyo, Japan) at 200 kV. Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscope (S-4800; Hitachi, Tokyo, Korea) equipped with a Schottky emitter with high stability. Zeta potential measurements were performed on a Malvern Zetasizer NanoZS system. X-ray photoelectron spectroscopy (XPS) measurement was conducted using a Thermo MultiLab 2000 system. The Raman spectra were obtained using an ARAMIS Spectra spectrometer (Horiba Jobin Yvon, Longjumeau, France). The optical transmittance was measured at 550 nm using a ultraviolet-visible spectrophotometer (OPTIZEN 3320UV QX; MECASYS, Daejeon, Korea). Sheet resistance was measured using the standard 4-point probe technique (MCP-T610; Mitsubishi Chemical Analytech, Chigasaki, Japan). All electrochemical data were obtained at room temperature within an error range of  $\pm 5\%$ .

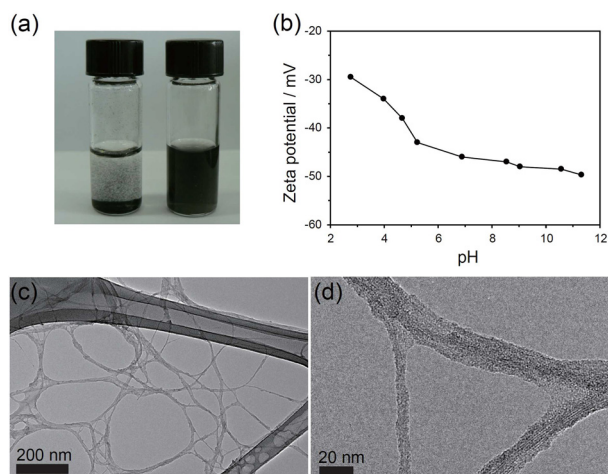
## 3. Results and Discussion

Fig. 1 illustrates the scheme of the organization of Au NPs on the p-SWNTs. We studied the assembly and functionalization of the nanohybrids using programmed peptide sequences containing repeating glutamate (E), glycine (G), and phenylalanine (F) units. The supramolecular formation of p-SWNTs was promoted by mutual interaction between the  $\text{sp}^2$  hybridized carbon surface and the aromaticity of the F sequences via  $\pi$ -stacking interaction under optimized conditions of sonication and stirring [22]. The strong affinity of the peptides for the SWNTs enabled the peeling of individual tubes from the tight bundled forms.

The p-SWNTs were readily dispersible in DI water; dispersions were stable for several months, presumably due to the functionalities of the surface peptides (Fig. 2a). On the other hand, in the absence of peptides, the SWNTs aggregated. Fig. 2b shows the zeta potential values as a function of the pH values ranging from 2.7 to 11.3. All zeta potential values were 30 mV, indicating, from a colloidal science perspective, highly stable colloidal dispersions of p-SWNT [23]. The highly individual p-SWNTs in DI water were visualized by TEM. Fig. 2c and d provide TEM images of the p-SWNTs with debundled, homogeneously distributed, non-aggregated SWNTs, unlike the typically observed structure for pristine SWNTs. High-resolution TEM (HR-TEM) images revealed details of the



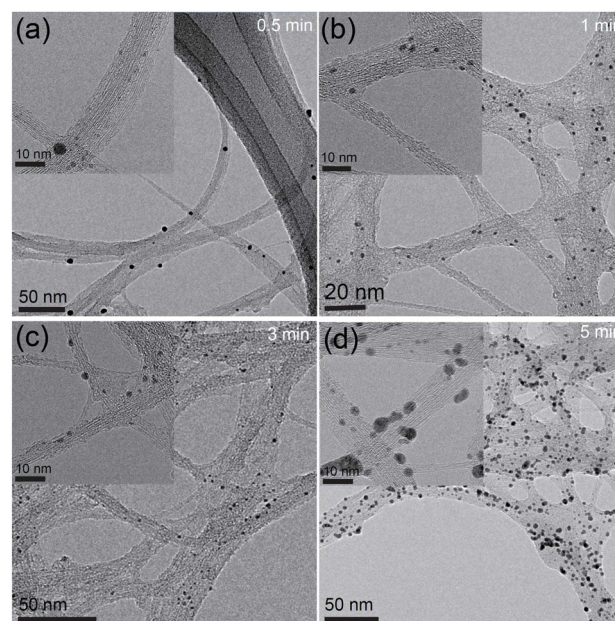
**Fig. 1.** Schematic illustration of the fabrication process for AuNP/p-SWNT nanohybrids. SWNT, single-walled carbon nanotube; p-SWNT, peptide-wrapped SWNT; NPs, nanoparticles.



**Fig. 2.** (a) Photo-images of pristine single-walled carbon nanotube (SWNT) dispersion (left) and AuNP/peptide-wrapped SWNTs (p-SWNT) dispersion (right). (b) Zeta potentials of p-SWNT as a function of pH values. (c, d) Transmission electron microscopy images of p-SWNT. AuNP, Au nanoparticle.

self-assembly of the SWNTs with peptides via  $\pi$ -stacking (Fig. 2d). The Y-junction image of the p-SWNTs indicated that the peptides aided the separation of the nanotubes into wrapped groups of one to two tubes by wrapping tubes. Non-covalent  $\pi$ - $\pi$  interaction between the SWNTs and peptides led to advantages in terms of maintaining the chemical structures, enhancing the electronic properties of the nanotubes, and inducing effective dispersion of the nanotubes [24].

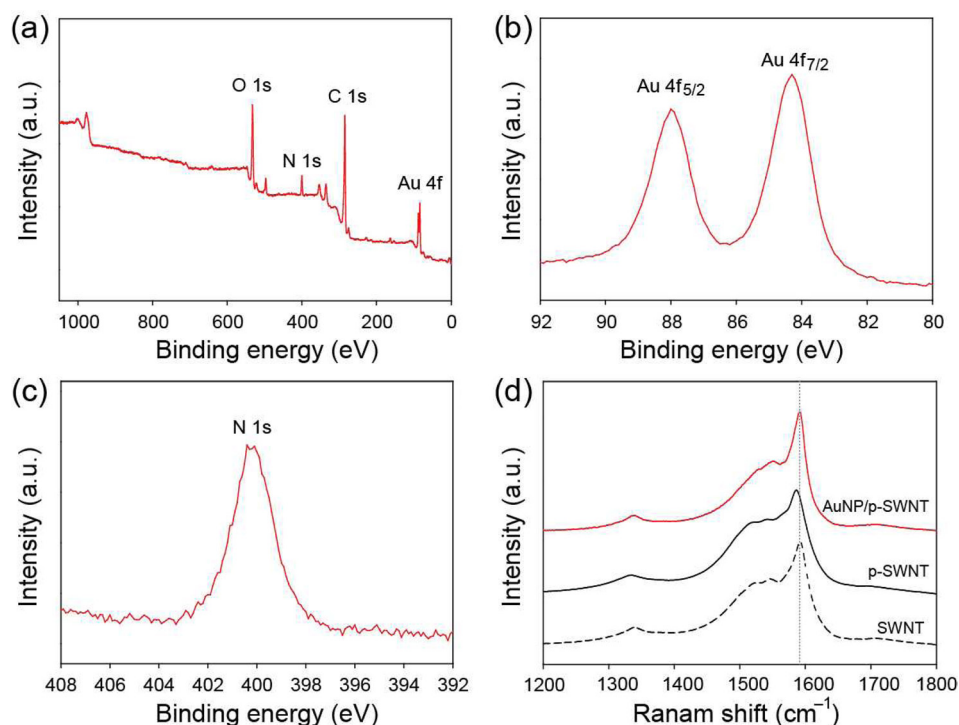
The well-designed p-SWNTs provided nanoscale building blocks for the nucleation and growth of Au NPs, yielding AuNP/p-SWNT nanohybrids. Valuable insight into the structural features of the AuNP/p-SWNTs and the sonication times required for Au growth were provided by TEM and HR-TEM (Fig. 3). Representative TEM images of the AuNP/p-SWNTs showed nanostructures of uniformly deposited Au NPs on the surfaces of the highly debundled p-SWNTs. The AuNPs became larger and their surface densities increased with increasing reaction time. Notably, the uniform



**Fig. 3.** Transmission electron microscopy images of AuNP/peptide-wrapped single-walled carbon nanotubes with different reaction times of (a) 0.5 min, (b) 1 min, (c) 3 min, and (d) 5 min.

distribution of the AuNPs on the p-SWNTs appeared to be due to the strong interaction between the Au precursors and the carboxylic acid functional groups of the peptides and to burst nucleation induced by ultrasonication. In contrast to the AuNP/p-SWNTs, the NPs aggregated on the non-treated, bundled SWNTs. HR-TEM images (inset of Fig. 3) revealed the presence of a thin layer of coating peptide on the isolated nanotubes, and Au NPs surrounded by peptides on the sidewalls of the nanotubes. This result indicates that the programmed peptide sequences with E, G, and F amino acids carried out two functions, through which phenylalanine non-covalently interacted with the SWNT side walls and the glutamate containing carboxylic acid molecules served as sites of nucleation for 1D arrays of Au NPs.

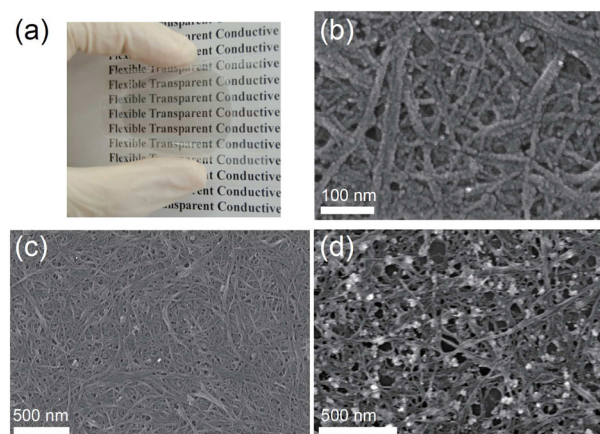




**Fig. 4.** X-ray photoelectron spectroscopy spectra of AuNP/peptide-wrapped single-walled carbon nanotubes (p-SWNT) nanohybrid: (a) survey scan, (b) Au 4f, and (c) N 1s. (d) Raman spectra of pristine SWNT, p-SWNT, and AuNP/p-SWNT nanohybrids. AuNP, Au nanoparticle.

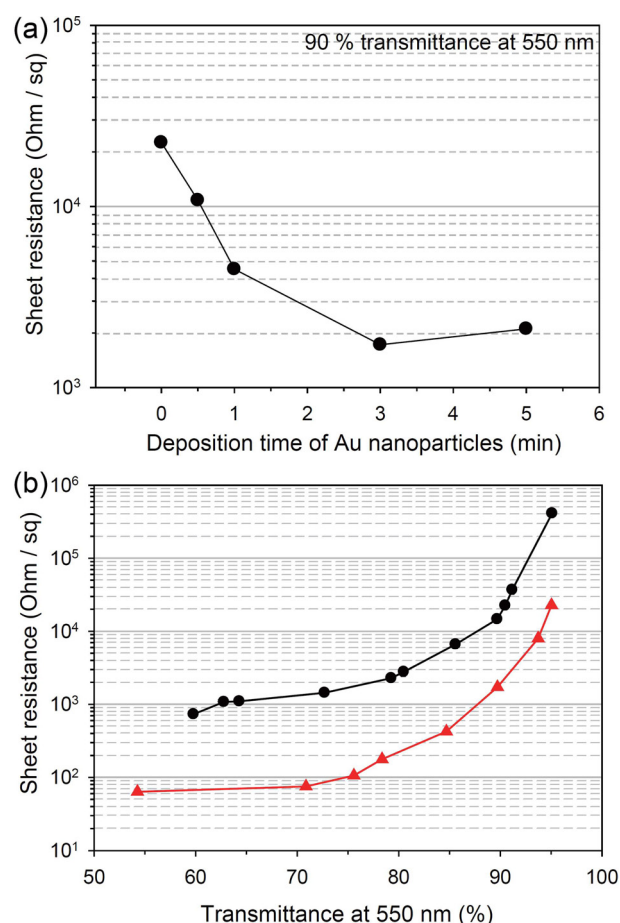
XPS analysis was carried out to determine the chemical state of the AuNP/p-SWNT nanohybrid. Fig. 4a reveals that the nanohybrid was mainly composed of C, O, N, and Au elements. The binding energies at 84.3 and 88.0 eV in Fig. 4b are assigned to the spin-orbital split components of the Au 4f level from metallic gold, thereby suggesting the successful formation of Au NPs [25,26]. However, the binding energy of Au 4f<sub>7/2</sub> is slightly larger than that of bulk Au (83.8 eV) [26]. This might be a consequence of the small size of Au NPs and the interaction between the Au NPs and p-SWNTs [25]. The N 1s peak at 400.2 eV confirmed the presence of peptides in the AuNP/p-SWNT nanohybrids (Fig. 4c). The electronic structures of the AuNP/p-SWNTs were also investigated by Raman spectroscopy (Fig. 4d). The G band of the pristine SWNTs was slightly downshifted from 1592 to 1586 cm<sup>-1</sup> after peptide wrapping. The band shifts observed here suggest that charge transfer between the SWNTs and the programmed peptide may occur through molecular-level interaction [27]. A small upshift (by 5 cm<sup>-1</sup>) of the Raman G-band in the nanohybrids compared to the p-SWNTs was observed; this is attributed to the phonon stiffening effect via p-type doping [28]. The negligible change of the intensity ratio of the D-band and G-band ( $I_D/I_G$ ) after peptide wrapping was due to non-covalent interaction between the side walls of the SWNTs and phenylalanine. This indicates that non-covalent functionalization by the peptide prevents the dramatic destruction of the intrinsic electronic properties of the SWNTs [29].

The attractive features of AuNP/p-SWNTs were demonstrated by applying them to a transparent electrode using a filtration and



**Fig. 5.** (a) Photo image of flexible AuNP/peptide-wrapped single-walled carbon nanotubes (p-SWNT) film. (b-d) Scanning electron microscopy images of AuNP/p-SWNT. AuNP, Au nanoparticle.

wet transfer method. Highly stable AuNP/p-SWNT dispersions in aqueous solution were prepared by mild sonication because of the water-favorable feature of the peptide on nanotubes. The dispersion state of the suspensions was very stable for over several months. Vacuum filtration of the AuNP/p-SWNT suspensions using AAO membranes allowed self-regulated, uniform nanoscale film formation. AuNP/p-SWNT nanohybrids on filter membranes were then transferred to a poly(ethylene terephthalate) (PET) substrate by dissolving the AAO membrane



**Fig. 6.** (a) Sheet resistance with different Au deposition times and (b) sheet resistance at 550 nm of AuNP/peptide-wrapped single-walled carbon nanotubes films. AuNP, Au nanoparticle.

with 2 M NaOH solution. Fig. 5a provides a photograph of a transparent flexible thin AuNP/p-SWNT film. SEM was used to observe the surface of the Au/p-SWNT hybrid film on PET, with results shown in Fig. 5b-d. The 1D nanohybrid was found to be tangled into 3D network structures by filtration. Au NPs on the side-walls of the peptide-wrapped nanotubes were observed as white spots. The diameters of the AuNP/p-SWNTs in the nanohybrid films were below 20 nm.

The optoelectronic properties of the AuNP/p-SWNT films were investigated by measuring the sheet resistance  $R_s$  at transmittance of 550 nm and room temperature. Fig. 6a presents the sheet resistances of the AuNP/p-SWNT films produced using different Au deposition times at 90% transmittance (wavelength 550 nm). In this preliminary test, we selected a reaction time of 3 min in order to optimize the optical and electrical properties of the AuNP/p-SWNT films. Fig. 6b provides a summary of the optical and electrical properties of the AuNP/p-SWNTs compared with the p-SWNT films. The introduction of the Au NPs dramatically reduced the sheet resistance of the p-SWNT films. Overall, the sheet resistance of the AuNP/p-SWNT films was much lower than that of the p-SWNT films. The formation of Au NPs on the SWNT network could alter the electronic

properties of the pristine SWNTs by electron transfer between SWNTs and Au NPs. The enhanced electrical conductivities of the SWNT networks were attributed to low tunneling resistance at the intertube junctions and electron transfer between the Au NPs and the nanotubes (acting as electron donor and acceptor, respectively) [30,31].

## 4. Conclusions

We developed a general method for the functionalizing of SWNTs with programmed peptides and the coating of these Au NPs. The chemical groups of peptides can be easily modulated by means of the design of amino acid sequences. Suitably designed peptides simultaneously debundled or exfoliated the CNTs via non-covalent interaction and served as templates for the controlled assembly of Au NPs on SWNTs via site-specific interaction between the cation precursors and the anion groups of the peptides. Furthermore, the successful dispersion of Au/p-SWNTs in DI water enabled transparent, conductive, flexible thin films to be easily fabricated. The strategy described provides a means of preparing nanohybrids consisting of carbon nanomaterials and NPs for application in flexible electronics, optoelectronics, biosensors, and optical devices.

## Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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