Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 505292, 16 pages
http://dx.doi.org/10.1155/2013/505292

*Review Article*

# Highly Conductive, Transparent Flexible Films Based on Metal Nanoparticle-Carbon Nanotube Composites

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Received 28 February 2013; Revised 13 July 2013; Accepted 15 July 2013

Academic Editor: Sulin Zhang



Metallic nanoparticles decorated on MWCNTs based transparent conducting thin films (TCFs) show a cheap and efficient option for the applications in touch screens and the replacement of the ITO film because of their interesting properties of electrical conductivity, mechanical property, chemical inertness, and other unique properties, which may not be accessible by their individual components. However, a great challenge that always remains is to develop effective ways to prepare junctions between metallic nanoparticles and MWCNTs for the improvement of high-energy barriers, high contact resistances, and weak interactions which could lead to the formation of poor conducting pathways and result in the CNT-based devices with low mechanical flexibility. Herein, we not only discuss recent progress in the preparation of MNP-CNT flexible TCFs but also describe our research studies in the relevant areas. Our result demonstrated that the MNP-CNT flexible TCFs we prepared could achieve a highly electrical conductivity with the sheet resistance of ~100 ohm/sq with ~80% transmittance at 550 nm even after being bent 500 times. This electrical conductivity is much superior to the performances of other MWCNT-based transparent flexible films, making it favorable for next-generation flexible touch screens and optoelectronic devices.

## 1. Introduction

Flexible transparent conducting films (TCFs) with low electrical resistance and high optical transmittance have received considerable attention for niche applications in flexible or foldable displays, touch screens, solar cells, transistors, and transparent electrodes for liquid-crystal displays [1–3]. Deposition of indium-tin oxide (ITO) on plastic substrates for the preparation of flexible TCFs has been an attractive strategy owing to its transparency, conductivity, and wide usability [4, 5]. Nevertheless, ITO is costly and brittle, and the film transparency is poor in the near-infrared range. Therefore, a substitute for ITO is necessary.

The high flexibility, high specific surface area, low density, and excellent electrical, optical, and mechanical properties of carbon nanotubes (CNTs) have made them ideal candidates for next-generation flexible TCFs [3, 6, 7]. Among various CNT-based flexible TCFs, composites of zero-dimensional metallic nanoparticles (MNPs) decorated on one-dimensional CNTs (MNP-CNTs) have received most of attention because of their electrical conductivity, mechanical properties, chemical inertness, and other unique characteristics, which may not be shown by their individual components [8–10]. In practice, however, high-energy barriers, high contact resistances, and weak interactions between the CNTs and MNPs led to the formation of high-resistance ($10^4$–$10^9$ Ω) electrical contacts and poor conducting pathways [11], resulting in the development of MNP-CNT-based devices with low mechanical flexibility (without taking into account their intrinsic electronic properties) and leading to limitations on their application in flexible TCFs. Thus, methods to fabricate junctions for improving the adhesion between the MNPs and CNTs for the seamless connection of two CNTs have been explored. This chapter will discuss recent progress in the preparation of MNP-CNT flexible TCFs, organized as follows. First, we will introduce the synthesis methods for preparation of MNP-CNT nanocomposites. Next, selected approaches for the formation of MNP-CNT flexible TCFs will be discussed. Finally, we will review techniques of postmodification treatment for MNP-CNTs to

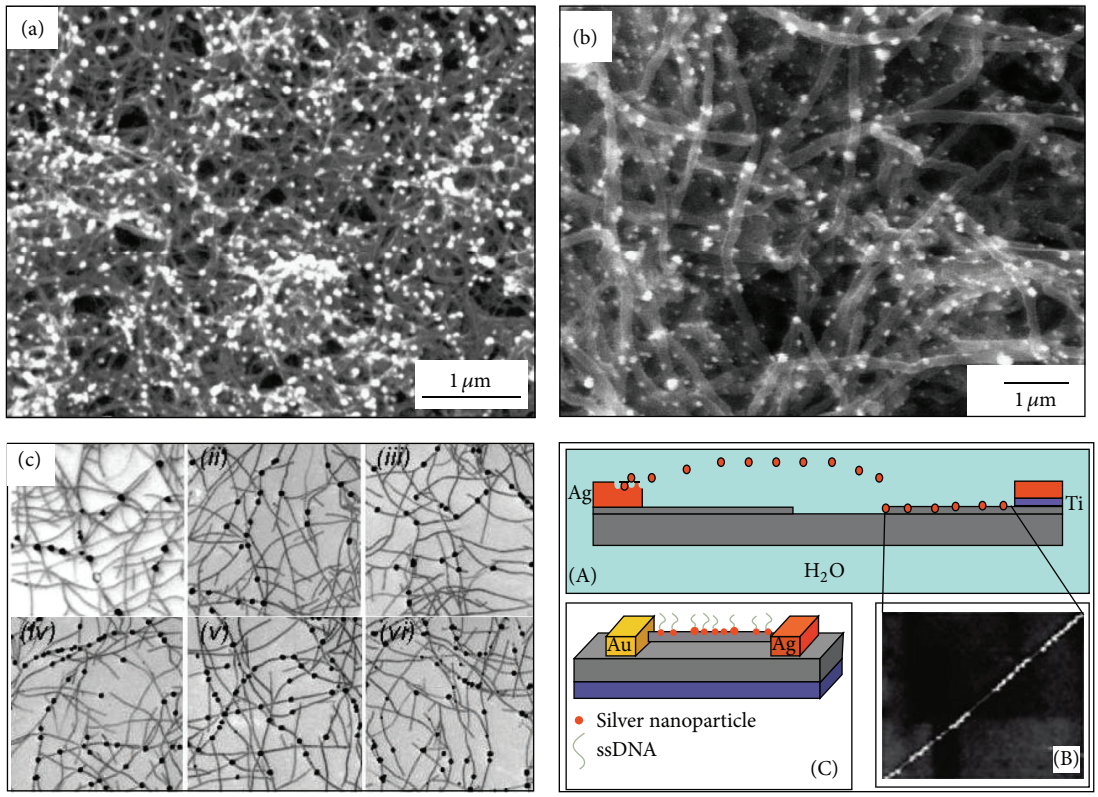



Figure 1: SEM images of various MNP-CNT nanocomposites prepared by the electrochemical deposition method. (a) Pt-CNT-graphite nanocomposite and (b) PtRu-CNT-graphite nanocomposite (reproduced with permission from [17, 18], Copyright ©2004 Elsevier). (c) FESEM images of Pd NPs decorated on the sidewalls of SWCNTs at different applied potentials between −0.1 and −0.35 V versus Ag/AgCl (reproduced with permission from [19], Copyright ©2011 American Chemical Society). (d) Decoration of Ag NPs along SWCNTs to form two-terminal electrical devices (reproduced with permission from [10], Copyright ©2011 American Chemical Society).

improve junctions between CNTs. In each section, after a brief introduction to recent results reported in the literature, we will describe our research studies in the relevant areas. In the final section, important results of electrical, optical, and mechanical performances in the MNP-CNT flexible TCFs we designed will be presented.

## 2. Synthesis Methods for MNP-CNT Nanocomposites

CNTs, which do not react with metal salts, have been widely used as supports for building MNP-CNT nanocomposites by depositing MNPs on the sidewalls of CNTs. Numerous methods that have been developed to synthesize MNP-CNT nanocomposites can be divided into physical, chemical, and electrochemical categories [12]. Among them, the liquid-phase synthesis route in the chemical and electrochemical categories, such as electrochemical deposition, the microwave-assisted approach, dispersion of MNPs onto the functionalized CNTs, and the polyol process, has been proven as a powerful tool for the fabrication of MNP-CNT nanocomposites (Table 1).

*2.1. Electrochemical Deposition Method.* The electrochemical deposition method involves simple reduction of metal ions on selected substrates from an electrolyte solution and enabling effective control on nucleation and growth procedure of material synthesis [13–15]. It is an excellent synthetic approach for preparing inorganic NPs and their relative CNT-metal nanocomposites because of the following advantages: (1) easy control of size distributions and densities of MNPs on CNTs by tuning the concentration of metal precursors and the electrochemical-deposition parameters of applied potential and deposition time; (2) large-scale synthesis; (3) short-term formation [16]. By using CNTs grown directly on substrates and electrochemically deposited high-purity MNPs, decoration of Pt or bimetallic Pt-Ru NPs with sizes of 60–80 nm on multiwalled carbon nanotubes (MWCNTs) was successfully carried out by He et al. [17, 18]. The process was utilized in the pregrowth of MWCNTs on a graphite disc by chemical vapor deposition and subsequent electrodeposition of Pt or bimetallic Pt-Ru NPs on the CNT-graphite electrode by the potentiostatic method at a saturated calomel electrode (SCE) deposition potential of −0.25 V (Figures 1(a) and 1(b)). Using a similar process, Day and coworkers electrodeposited Pd and Pt NPs on single-walled carbon nanotube (SWCNT)

Table 1: Methods for the synthesis of MNP-CNT nanocomposites.

| Synthesis method | Metal | Particle size (nm) | CNT type | Ref. |
|---|---|---|---|---|
| Electrochemical deposition | Pt | 60–80 | MWCNT on graphite disc | [18] |
| | Ag | ~100 | SWCNT on $Si/SiO_2$ | [10] |
| | Ni | hundreds | Functionalized MWCNTs | [16] |
| | Pd | 20–40 | SWCNT on $Si/SiO_2$ | [19] |
| | PtRu | 60–80 | MWCNT on graphite disc | [17] |
| Microwave-assisted reduction | Pt | ~5.0 | Bulk 3-D MWCNTs | [21] |
| | Ru | 1.8–2.6 | MWCNTs | [22] |
| | Au | 3.0 | Functionalized SWCNTs | [23] |
| | Pt | 2.5 | Functionalized SWCNTs | [23] |
| | Pd | 24.6 | Sulfonated MWCNTs | [24] |
| | Ni | 16.1 | Sulfonated MWCNTs | [24] |
| | Sn | 25.1 | Sulfonated MWCNTs | [24] |
| Dispersion of MNPs on functionalized CNTs | Pt | ~4.0 | Acid oxidation-MWCNTs | [29] |
| | Au | 3.0–7.0 | Dendrimer-modified MWCNTs | [30] |
| | Pd | 2.0 | Thiol group-functionalized MWCNTs | [26] |
| | PtPd | 2.0–4.0 | Polypyrrole-functionalized MWCNTs | [25] |
| | Pt | 33.8 | PSS-functionalized MWCNTs | [31] |
| | Pt | 1.8 | PVP-functionalized MWCNTs | [32] |
| Polyol process | Pt | 2.0–3.0 | Purified CNTs | [35] |
| | Pd | 5.4 | Acid oxidation-MWCNTs | [36] |
| | Pt | ~2.3 | Purified MWCNTs | [39] |
| | Sn | 3–5 | Acid-treated MWCNTs | [38] |
| | Au | <10 | Purified MWCNTs | [39] |
| | PtPd | 2.4–5.4 | Acid oxidation-MWCNTs | [36] |
| | PtRu | 3.0 | Acid oxidation-MWCNTs | [37] |
| | PtAg | ~3.8 | Purified MWCNTs | [39] |

networks pregrown on the surface of a $SiO_2$ layer on a Si substrate ($Si/SiO_2$), using a microcapillary electrochemical cell at an applied potential in the range of −0.1 to −0.4 V (Ag/AgCl); in addition, they discovered that the density, distribution, and size of the MNPs could be controlled through the deposition potential and time (Figure 1(c)) [19]. Sahoo et al. further demonstrated that the Ag NPs could be synthesized and decorated along CNTs and the coverage densities of Ag NPs could be changed under the control of deposition time, applied voltage, and location of CNTs with respect to the anode (Figure 1(d)) [10]. However, large or random particle size of MNPs in MNP-CNT nanocomposites was always obtained through electrochemical deposition owing to the contradiction between a larger driving force for nuclei formation and an inhibitive mechanism for crystal growth.

*2.2. Microwave-Assisted Reduction.* Microwave-assisted reduction, providing direct energy for effective heating of a reaction mixture by transferring electromagnetic energy into thermal energy, has been considered a convenient and rapid heating technique in the synthesis of MNP-CNT nanocomposites [20]. Minett's group successfully took advantage of bulk three-dimensional (3D) MWCNT architecture as the support and decorated Pt NPs measuring ~5 nm in size on CNTs by microwave-assisted reduction performed on an $H_2PtCl_6$ precursor and ethylene glycol mixture (Figure 2(a)) [21]. Zhang et al. further demonstrated that the twinned Ru NP-CNT nanocomposites could be fabricated by microwave treatment of a mixture of $Ru_3(CO)_{12}$ and CNTs pretreated in an Ar flow for 2 h in a quartz-tube reactor; the structure of Ru NPs could be rearranged into single crystals as the microwave heating proceeded [22]. Furthermore, microwave-assisted hydrothermal synthesis, a kind of improved microwave-assisted method, has also been developed for the preparation of MNP-CNT nanocomposites [23]. One of the representative works in microwave-assisted hydrothermal synthesis was reported by Ramulifho and coworkers, who prepared Pd, Ni, and Sn NPs decorated on the surface of sulfonated MWCNTs (Figure 2(b)) [24].

*2.3. Dispersion of MNPs onto Functionalized CNTs.* Introducing more binding sites and surface anchor groups to CNTs to benefit MNP decoration has been considered an effective tool for MNP-CNT nanocomposites synthesis [25], for which chemical functionalization of the CNT surface is essential. Among various techniques to modify the surface of CNTs, covalent attachment of functional groups such as carbonyl-, carboxyl-, and amine-groupson to the surface of CNTs is one of the most promising routes because of its capability

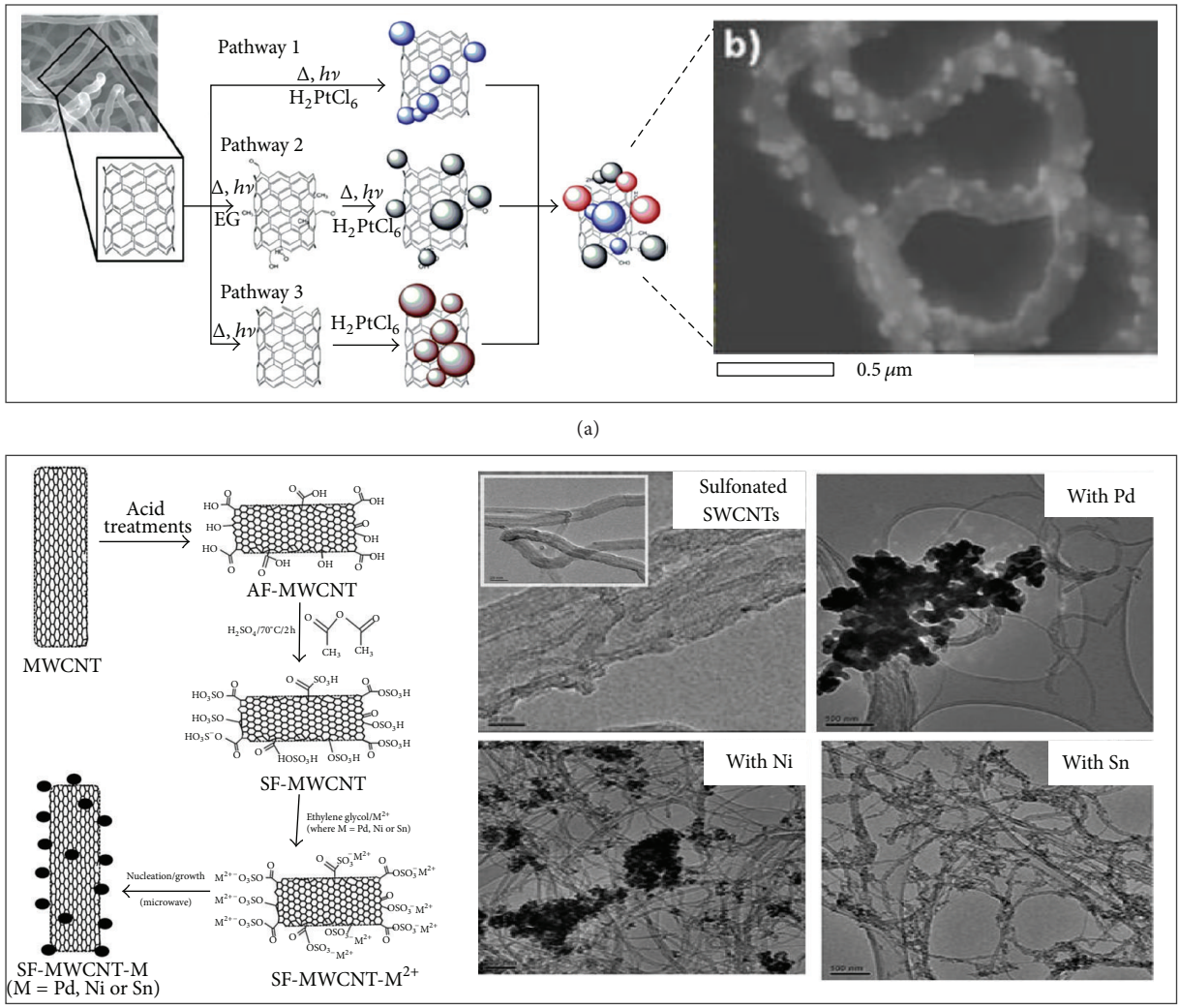



Figure 2: (a) Schematic illustration of microwave-assisted reduction for the preparation of Pt NP-MWCNT nanocomposites and image of the resulting product (reproduced with permission from [21], Copyright ©2010 The Royal Society of Chemistry). (b) Synthesis procedure and relevant TEM images of the prepared MNPs supported on sulfonated MWCNTs by using the microwave-assisted hydrothermal method (reproduced with permission from [24], Copyright ©2012 Elsevier).

to result in strong metal-CNT interactions, thereby giving stable MNP-CNT nanocomposites with heavily loaded MNPs [12, 26]. The addition of carbonyl and carboxyl groups on the surface of CNT is the most common covalent functionalization process for the modification of the CNT surface. By this process, CNTs are functionalized with –C=O, –COO–, and –COOH groups through pretreatment of CNTs in acidic aqueous solutions such as those of $O_3$ and $H_2O_2$, which provide nucleation sites for the deposition of MNPs [27, 28]. Hull et al. successfully used the sonochemical treatment method to functionalize the CNT surface with –C=O, –C–O–C–, –COO–, and –C–OH groups in an $HNO_3$-$H_2SO_4$ aqueous solution, allowing them to deposit Pt NPs with diameters of ~4 nm (Figure 3(a)) [29]. In another representative work reported by Lu and Imae, an MNP-CNT nanocomposite was created from MWCNTs modified with fourth-generation $NH_2$-terminated poly(amido amine) dendrimers (CNT-DEN) and controllable Au NPs (Figure 3(b)). Besides, several MNPs with controllable size of Ag, Cu, Pt, and Ag@Au supported on the surface of CNT/DEN were successfully obtained [30]. Polymers, wrapping around CNTs to introduce surface functional groups on the CNTs, have also been used to anchor MNPs supported on CNT surface to form MNP-CNT nanocomposites. For example, Pt nanoflowers could be immobilized on the surface of MWCNTs wrapped by poly(sodium 4-styrenesulfonate) (PSS-MWCNTs); Au and Pd NPs could also be decorated on the surface of PSS-MWCNTs (Figure 3(c)) [31]. Another representative work on

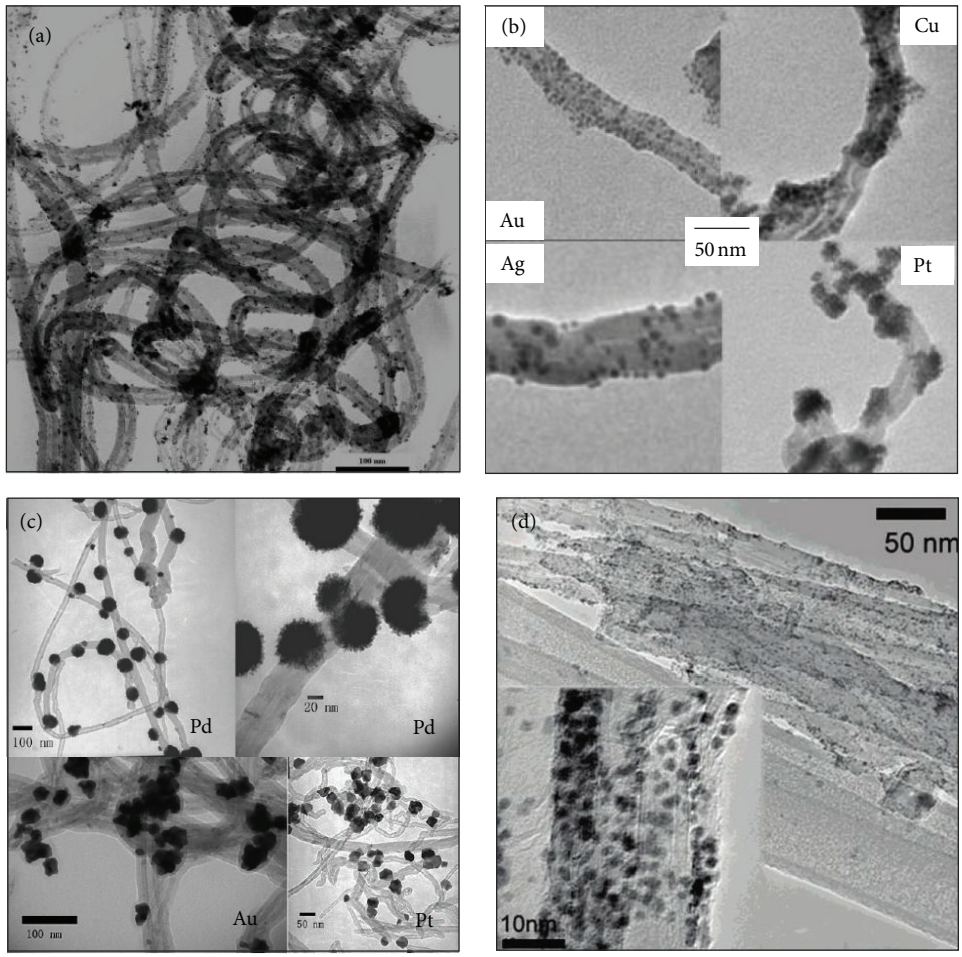
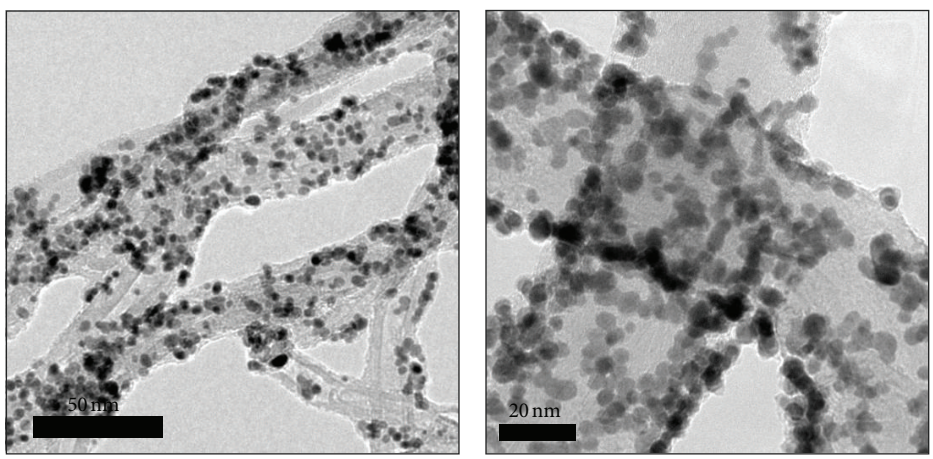



Figure 3: (a) TEM image of functionalized CNTs with –C=O, –C–O–C–, –COO–, and –C–OH groups by sonochemical treatment, followed by deposition of Pt NPs (reproduced with permission from [29], Copyright ©2006 American Chemical Society). (b) TEM images of CNT-DEM-NPs (reproduced with permission from [30], Copyright ©2007 American Chemical Society). (c) TEM images of Pd/PSS-MWCNTs, Au/PSS-MWCNTs, and Pt/PSS-MWCNTS (reproduced with permission from [31], Copyright ©2010 The Royal Society of Chemistry), (d) TEM image of Pt/PVP-MWCNTs (reproduced with permission from [32], Copyright ©2007 American Chemical Society).




(a) (b)

Figure 4: Representative HRTEM images of (a) Pt NPs and (b) bimetallic AgPt NPs attached on MWCNTs by using the polyol process in our work.

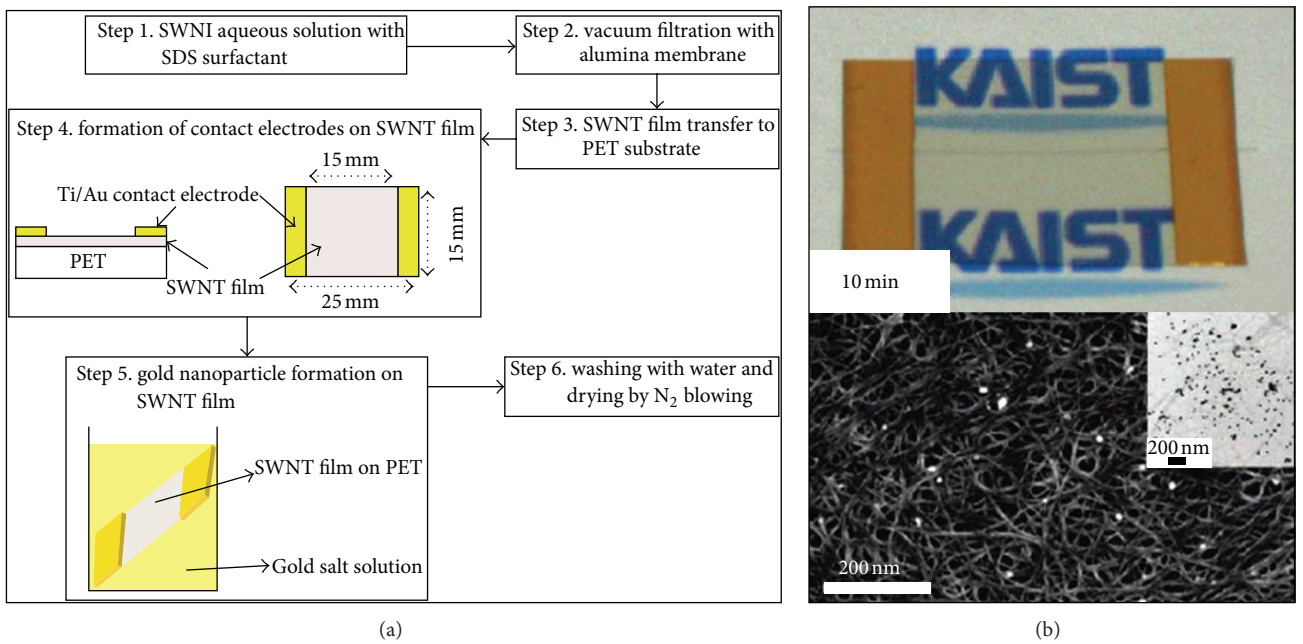



FIGURE 5: (a) Schematic illustration of the fabrication of Au-SWCNT films by the vacuum filtration method followed by electroless reduction of Au ions on the SWNT networks. (b) Optical image and TEM image of Au-SWCNT flexible TCFs (reproduced with permission from [43], Copyright ©2007 American Chemical Society).

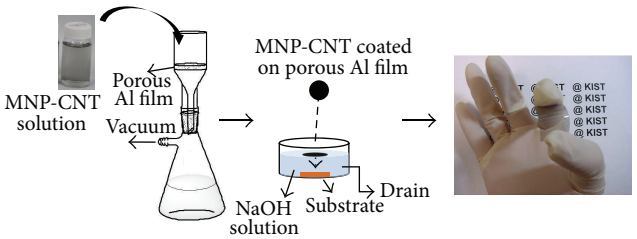



FIGURE 6: Schematic illustration of the vacuum filtration technique with subsequent process of Al membrane transfer for the formation of MNP-CNT flexible TCFs (reproduced with permission from [40], Copyright ©2010 Elsevier).

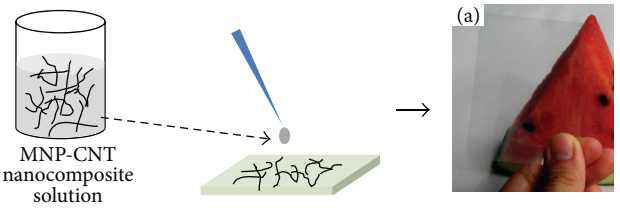
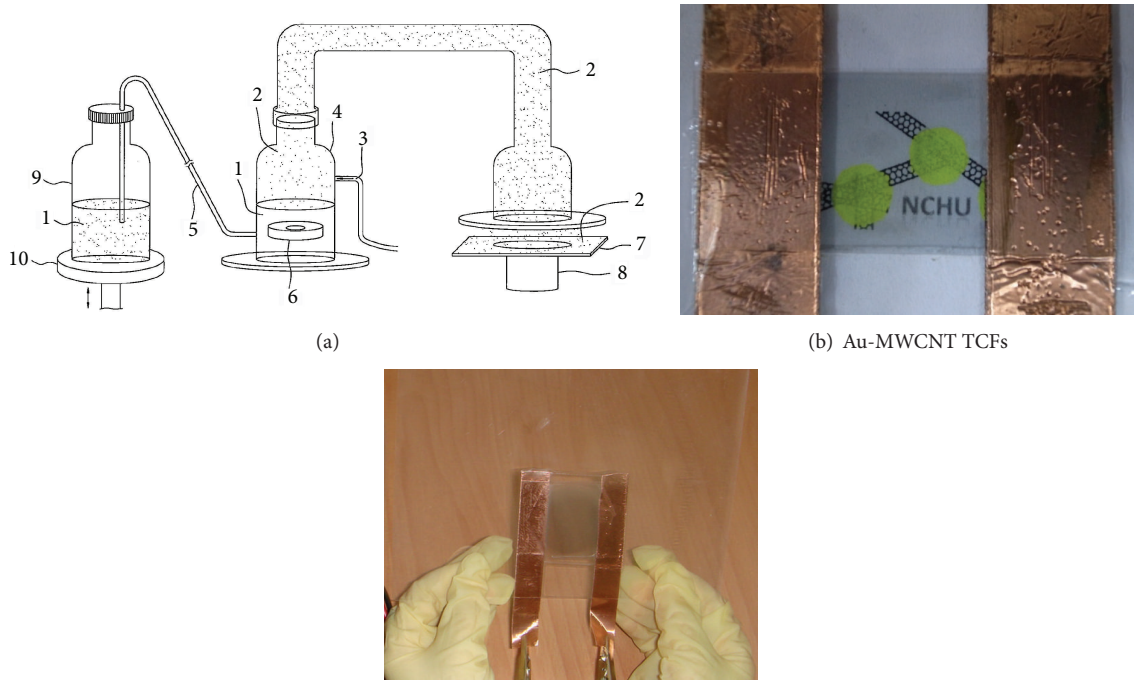



FIGURE 7: Schematic illustration of the drop-coating process for the formation of MNP-CNT flexible TCFs (reproduced with permission from [45], Copyright ©2012 Springer-Verlag).

the synthesis of Pt-MWCNT and PtRu-MWCNT nanocomposites using poly(vinyl pyrrolidone) (PVP) was carried out by Hsin and coworkers, where PVP not only helped form a homogenous CNT-dispersed aqueous solution but also served as the functional group binding the metal ions and MNPs (Figure 3(d)) [32].

*2.4. Polyol Process.* The polyol process, which involves the reduction of a metal salt precursor in a polyol, a compound containing multiple hydroxyl groups that serves as the solvent for the metal precursor and its reducing agent, has been widely used to synthesize inorganic nanostructures and their relative nanohybrids [33, 34]. Recently, preparation of MNP-CNT nanocomposites through the polyol process attracted much interest because of the advantages of homogeneous reduction and nucleation, leading to narrow, small, and monodispersed MNPs supported on the surfaces of CNTs. Based on this method, several kinds of MNPs deposited on CNTs, such as Pt, Pd, and bimetallic PtPd and PtRu, were successfully obtained [35–38]. In our work, we also demonstrated the successful preparation of Au (<10 nm), Pt (~2.3 nm), and bimetallic AgPt NPs (~3.8 nm) supported on MWCNTs by using a simple polyol process with surfactant-assisted sonication (Figure 4) [39]. In brief, a known quantity of metallic precursor and a predetermined quantity of purified MWCNTs were mixed in ethylene glycol to obtain a homogeneous solution under a nitrogen atmosphere using a probe-type sonicator. The mixture solution was then heated to 160°C at a heating rate of 2°C/min and was maintained at this temperature for 2 h. More importantly, the size of the MNPs, the composition ratio of bimetals, and their loading amount and distribution on the sidewalls of CNTs could be controlled by the reaction time, formation temperature, and weight ratio of the precursors to CNTs.




(a) (b) Au-MWCNT TCFs

(c) AgPt-MWCNT TCFs

Figure 8: (a) Schematic view of equipment we designed that combines an ultrasonic atomizer with a spin-coating apparatus for fabricating MNP-CNT TCFs. The CNT solution 1 is atomized at a supersonic atomizing frequency to form atomized particles 2 of various sizes, including the CNTs. Specifically, 1 is contained in an atomizing container 4 and is maintained at a constant level using a siphon 5 that connects 4 with a reservoir 9. Thus, a supersonic atomizing member 6 that generates the supersonic atomizing frequency is maintained at a constant depth below the level of 1 to produce the atomized particles 2 of desirable particle size. 9 is placed on an elevating device 10. The levels 1 in 4 can be controlled by adjusting the height of 10. Preferably, 9 can be provided with a probe-type sonicator (not shown) to maintain a homogeneous dispersion of 1 in 9. A carrier gas 3 is provided to carry 2 to a substrate 7 placed on a spin-coating equipment 8 for the formation of conductive, thin CNT films. (b) Au-MWCNT TCFs and (c) AgPt-MWCNT TCFs prepared from ultrasonic atomization with the spin-coating method.

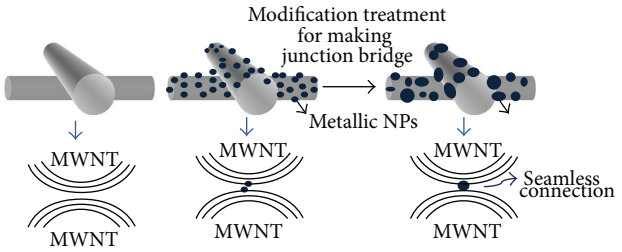



Figure 9: Schematic illustration of MNPs adhered to CNTs for making a junction bridge to connect CNTs seamlessly with the aid of modification treatments.

## 3. Methods for Fabricating MNP-CNT Flexible TCFs

Several approaches have been used to build MNP-CNT flexible TCFs through physical, chemical, and electrochemical processes. Among them, the solution-based deposition processes of vacuum filtration, drop coating, and ultrasonic atomization with the spin-coating method, followed by thermal treatment, have been widely applied to fabricate MNP-CNT flexible TCFs because of their competitive advantages of low cost, use without high vacuum requirements, low-temperature process, suitability for various substrates, and easy adaptability to mass production.

*3.1. Vacuum Filtration.* The vacuum filtration technique is a simple and cheap approach, which involves vacuum filtration of homogeneous suspensions with desired products under a low vacuum to create a relevant nanonetwork film on the surface of a filter. The technique uses a porous Al membrane and the subsequent transfer of resulting MNP-CNT film onto a desired substrate by dissolving the membrane [40–43]. By employing vacuum filtration to form SWCNT films and subsequent electroless reduction of Au ions ($Au^{3+}$) on the SWCNT networks, Kong and coworkers obtained Au-SWCNT flexible TCFs with highly conductive, high-density properties, as shown in Figure 5 [43]. Park et al. further demonstrated that Au-MWCNT hybrid films with improved flexible, transparent, and conducting properties could be synthesized by depositing an Au-NP-decorated MWCNT hybrid solution on poly(ethylene terephthalate) (PET) films by vacuum filtration followed by removal of the Al-membrane filtration filter (Figure 6) [40]. This method can offer uniform films with precise control of the MNT-CNT framework; it is not suitable for mass production, however.

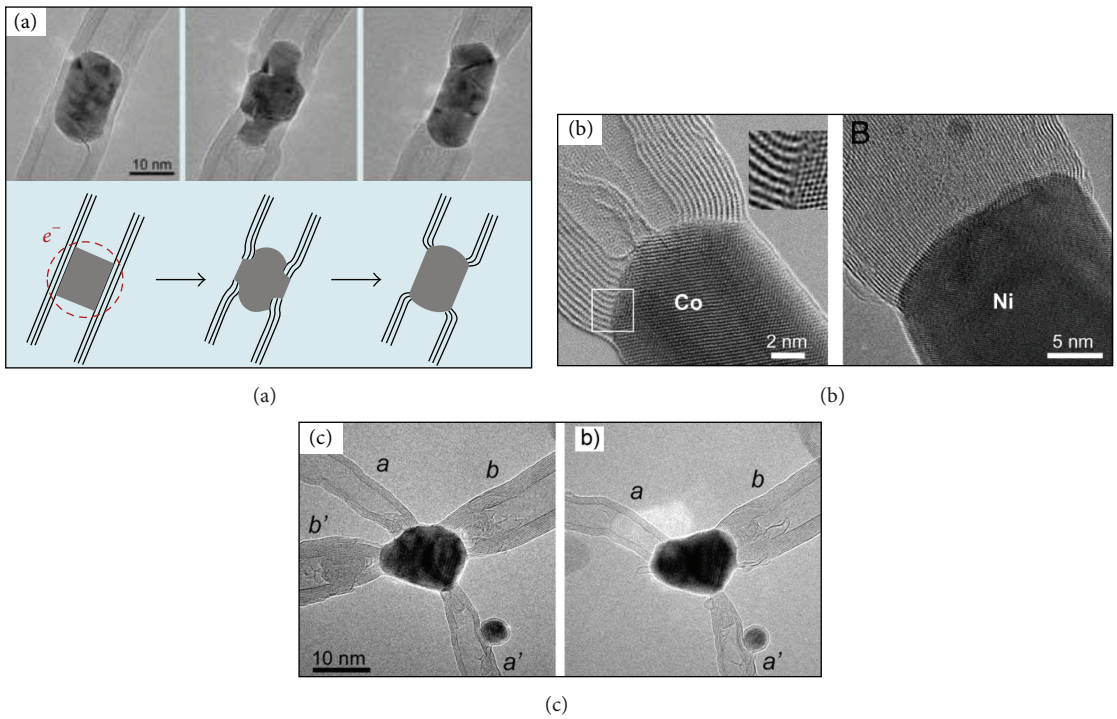



Figure 10: Formation of CNT-MNP-CNT heterojunctions with different metal nanoparticles through intense electron-beam irradiation at temperatures of 450–700°C (reproduced with permission from [50] Copyright ©2009 National Academy of Sciences and [51], Copyright ©2009 Wiley).

*3.2. Drop-Coating.* The drop-coating procedure, used to release droplets of a colloidal solution of MNP-CNT nanocomposites on a substrate, has been considered a good candidate for fabrication of MNP-CNT flexible TCFs because of its coffee-ring effect during the evaporation process, which can form a film of high conductivity and transparency [44]. Recently, flexible, hybrid transparent electrodes of Ag nanowires and single-walled CNTs with excellent conductivity and transmittance as well as long stability have been produced by Tokuno et al. through this method (Figure 7) [45]. Nevertheless, disadvantages of this method remain, such as low density and nonuniform thickness of films, limiting their suitability for scaling up to broader applications.

*3.3. Ultrasonic Atomization with Dip Coating.* Ultrasonic atomization, a technique of producing a fine spray from a liquid, is a relatively inexpensive technique for the continuous production of micron- and nanometer-sized materials to assist the production of large-scale films by spin coating [46]. It involves the generation and subsequent deposition of a mist of micron-sized droplets from a humidifier on the surface of a substrate. The water drops then evaporate, and the solute precipitates to form products. For the fabrication of MNP-CNT flexible TCFs, first, isolation of the MNP-CNT nanocomposites is necessary to form atomized particles from the homogeneous MNP-CNT solution with the desired viscosity. These atomized particles are subsequently transferred to spin-coating equipment with a carrier gas stream of nitrogen and then spin-coated on flexible substrates and rinsed with water several times to remove the remaining surfactants. The resulting films possess not only good mechanical flexibility but also excellent conductivity owing to its dense, compact frameworks. Recently, we have successfully prepared MNP-CNT flexible TCFs composed of Au and AgPt NPs supported on MWCNTs from a homogeneous MNP-MWCNT composite solution using our design of an ultrasonic atomization–spin coating tool (Figure 8(a)) [39]. The resulting Au-MWCNT and AgPt-MWCNT thin films exhibit good electrical conductivity (sheet resistance of 100–200 ohm/sq) and high transparency (transmittance of 80–85% at 550 nm), which are competitive with those of most other CNT-based films (Figures 8(b) and 8(c)). In addition, the optical transmittance and electrical conductivity of MNP-MWCNT films can be controlled by the deposition time of ultrasonic atomization [39].

## 4. Modification of MNP-CNT Nanocomposites

The disadvantages of high-energy barriers, high contact resistances, and weak interactions between the CNTs and MNPs make it difficult for them to form MNP-CNT TCFs because of the poor conducting pathways and low mechanical flexibility. It is well known that the electrical conductivity and mechanical stability of the CNT thin films are strongly dependent on the CNT network connections and densities. Therefore, junction fabrication for CNTs by cross-linked materials of MNPs to obtain well-defined electrical contacts and firmly attached CNTs have been explored (Figure 9).

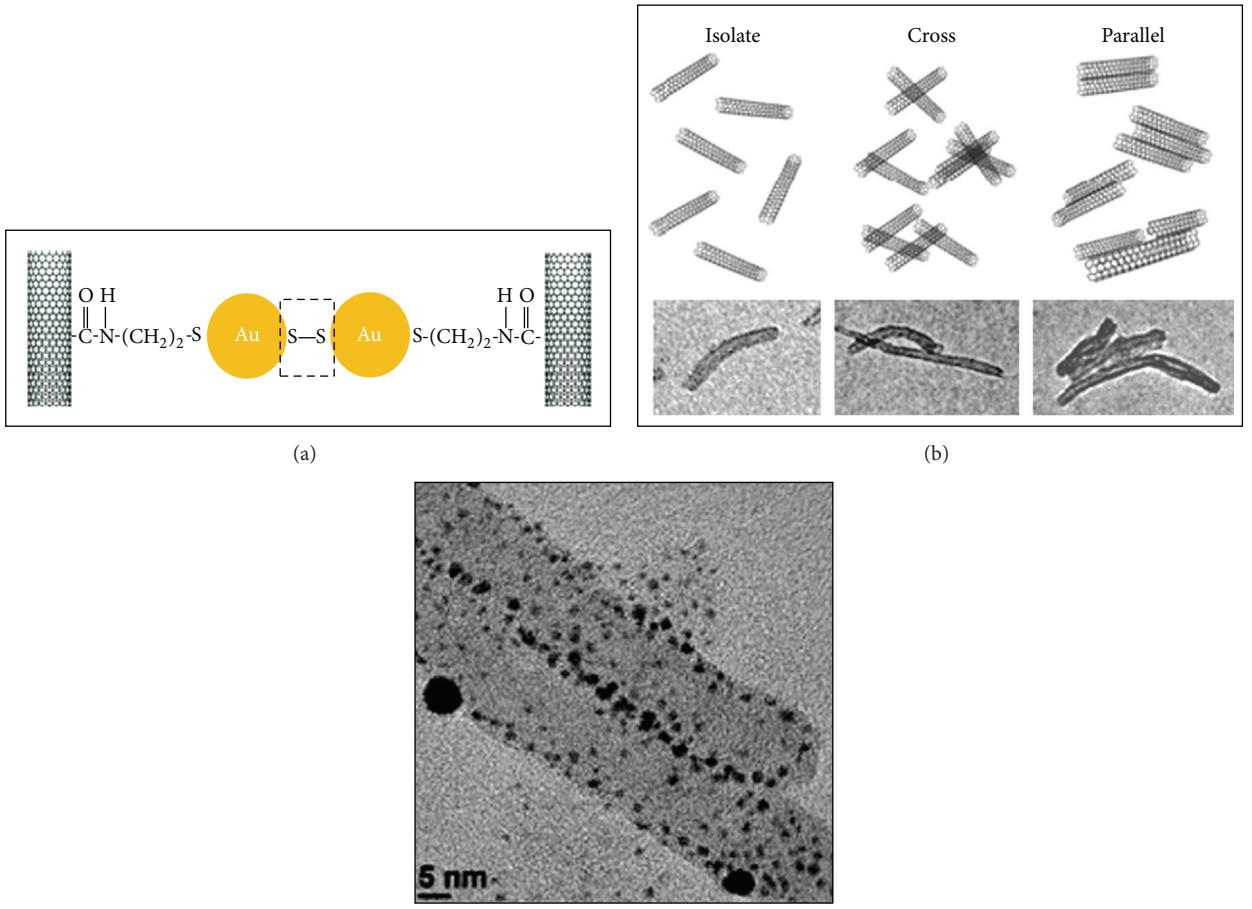



Figure 11: (a) Schematic illustration for cross-linking two CNTs by creating chemical bonding between thiol groups immobilized on the surface of AuNPs of different AuNP-CNTs. (b-c) TEM images of the assembly of AuNP-CNTs strands (reproduced with permission from [54], Copyright ©2011 American Chemical Society).

Postmodification treatment such as electron-beam welding, incorporation of polymers and surfactants, and microwave (MW) plasma irradiation, which can improve adhesion between the MNPs and CNTs to form junctions, have been used for the connection of two CNTs.

*4.1. Electron-Beam Welding.* Electron-beam welding, used to weld the CNTs and create contacts between them for the formation of interconnected CNTs through electron-beam irradiation [47–49], has been employed recently in welding of CNTs to metal NPs to form heterojunctions. This method can offer robust junctions between CNTs and metal NPs because of the formation of covalent metal-carbon bonds, allowing CNTs to firmly attach to the surface of metal NPs. Using this approach with intense electron-beam irradiation at temperatures of 450–700°C, Rodriguez-Manzo et al. successfully obtained strong MNP-CNT nanocomposites, composed of Fe, Co, Ni, and FeCo, with robust CNT and MNPs heterojunctions in which all the CNT layers were strongly bonded to the surface of MNPs (Figures 10(a) and 10(b)) [50]. Two-, three-, and four-terminal junctions of CNTs with a Co NP as the central node were also successfully prepared by further tailoring of the junction with a focused electron beam (Figure 10(c)) [51]. To effectively employ this method, it is essential to use a transmission electron microscope as well as maintain both ultrahigh energetic electron irradiation and high-temperature annealing.

*4.2. Creating Chemical-Bonding Bridges.* Creating chemical bonding between functional groups immobilized on the surface of MNPs of different MNP-CNTs to cross-link two CNTs has been demonstrated to reduce contact resistance between them, thus improving the electrical and mechanical performances of the CNT-based films [52, 53]. Recently, assembly of AuNP-CNTs into strands in an interconnected, parallel arrangement and cross-arrangement by cross-linking of the thiol groups attached on AuNPs have been carried out in Rhee's group. Their work involved the synthesis of AuNP-CNT nanocomposites by combining thiolated MWCNTs and Au NPs through sonication at 60°C for 1 h and subsequent interaction of the AuNP-MWCNTs with alkanedithriols through stirring at room temperature (Figure 11) [54]. It is a

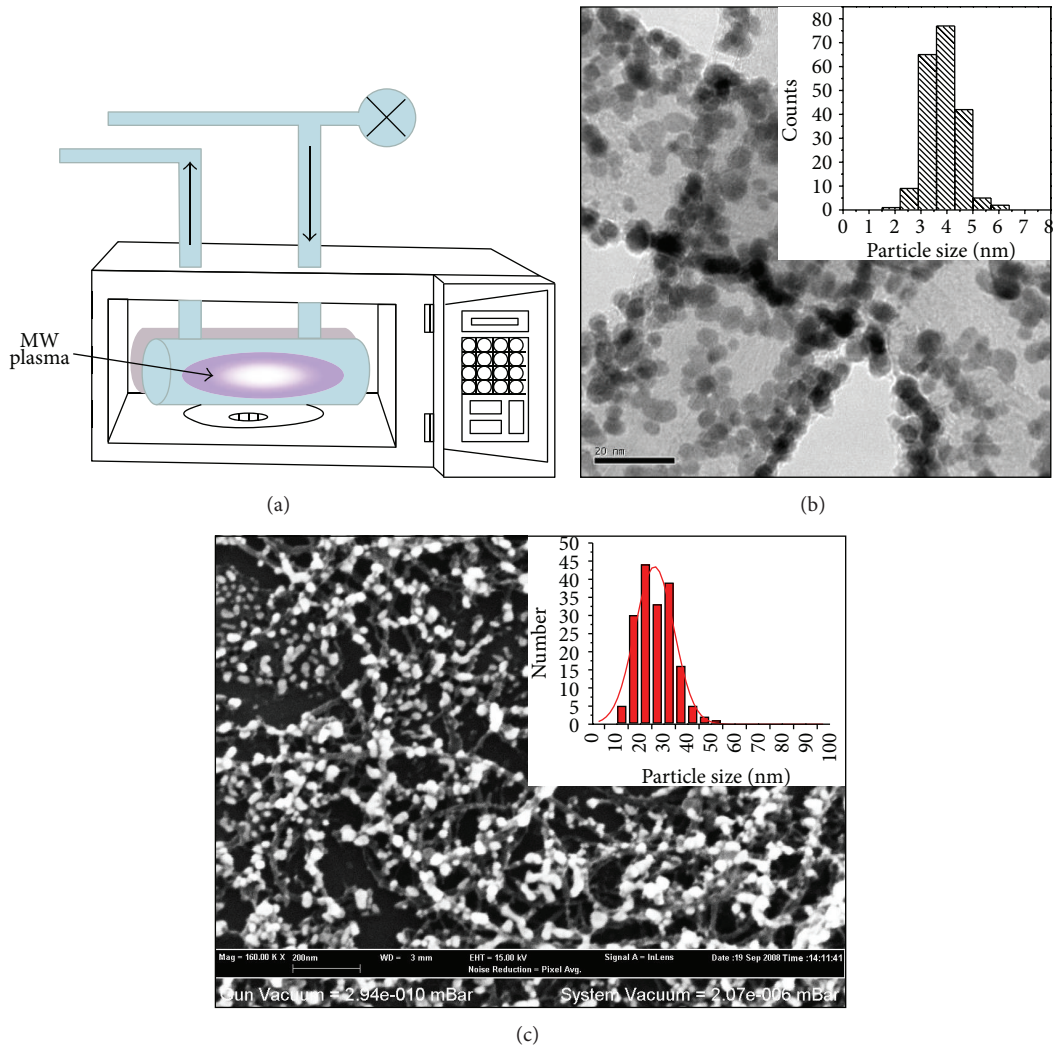
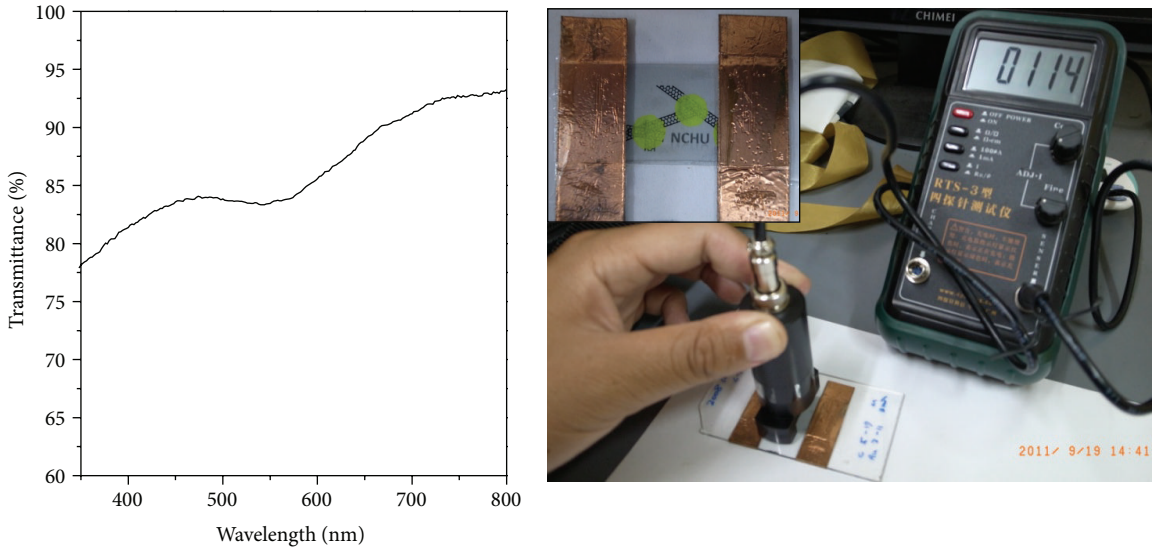



Figure 12: (a) Scheme of the MW plasma irradiation oven that we designed for postmodification treatment of MNP-MWCNT thin films. Morphology and size distribution of AgPt nanoalloys attached to AgPt-MWCNT flexible TCFs (b) before and (c) after postmodification MW plasma irradiation.

simple postmodification approach to bridge different MNP-CNTs to fabricate CNT-based thin films with high optical transparency and low electrical conductivity; however, lower thermal stability of the functional groups attached on the surfaces of MNPs would highly reduce the strength of the bridge junction, lowering their potential for TCF applications.

*4.3. Microwave (MW) Plasma Irradiation.* The constraints in the abovementioned postmodification treatments created limitations for large-scale production of MNP-CNT flexible TCFs. Thus, a simple but effective technique has yet to be realized. For this purpose, we developed a microwave (MW) plasma irradiation technique for the postmodification treatment of the prepared MNP-CNT flexible TCFs. MW plasma irradiation, which involves the generation of plasma cells by supplying energy to a neutral gas to form accelerating electrons or ions in the MW electromagnetic field, can provide rapid heating and uniform temperature distribution [55]. This irradiation method is known to be efficient for the following purposes: (1) treating carbon surfaces with damage-free processing to enhance the textural characteristics of the nanotubes and to improve their strength [56, 57]; (2) coating substrates with inorganic nanomaterials [58]; (3) synthesizing metallic NPs [59, 60]; (4) converting metallic thin films coated on substrates to NP structures [61]. However, very few studies have reported the use of MW plasma treatment for the fabrication of junctions between the CNTs and MNPs. Through postmodification MW plasma treatment, we observed, for the first time, smaller MNPs attached on MWCNTs of MNP-MWCNT nanocomposites that melted and fused into larger agglomerates [39]. For example, the average diameter of the observed AgPt alloy NPs of AgPt-MWCNT-PET films was approximately 26 ± 8 nm after MW plasma treatment, which was much larger than that of the as-produced NPs (3.8 ± 0.65 nm), as shown in Figure 12. More




(a) (b)

Figure 13: UV-Vis transmittance spectrum and sheet resistance analysis of prepared Au-MWCNT flexible TCFs.

importantly, the abovementioned coalescence can provide an additional advantage in that the MNPs strongly adhere to the walls of the MWCNTs to form the intra- or interjunctions between the MWCNTs and the MNPs, lowering the contact resistance between MWCNTs and resulting in improved mechanical integrity and excellent electrical conductivity.

## 5. Improved Performances of Our Synthesized MNP-CNT Flexible-TCFs

As shown by the above results, our group successfully fabricated flexible, transparent, and conducting composite thin films, constructed from MWCNTs, and supported single- or bimetallic NPs such as Au, Pt, and AgPt on a flexible PET substrate, through the combination of a polyol process for synthesizing nanocomposites of MWCNTs and MNPs with an ultrasonic atomization–spin coating method for preparing thin films. These nanocomposites were then exposed to microwave plasma irradiation, which could lower the contact resistance between the MNPs and CNTs and reinforce the network bridges. In the following section, we will briefly review some results on the optical, electrical, and mechanical performances of our prepared MNP-MWCNT flexible TCFs.

Au NPs, offering unique characteristics of high surface reactivity, biocompatibility, nontoxicity, and tunable optical properties, have been widely used in various applications [61–64]. In particular, the decoration of Au NPs on CNTs for applications in biosensors, transistors, and catalysis has been investigated extensively because of the synergistic effect of hybridization of CNTs with Au NPs [65–67]. We successfully obtained Au-MWCNT flexible TCFs with excellent transparency and electrical conductivity. Characterization of the films for optical transmission and electrical properties showed that the optical transmittance was 83–88% at 550 nm and the electrical resistance was 110–160 ohm/sq in four-probe measurements (Figure 13). These values were much better than those of the film that was not exposed to MW plasma treatment (Table 2), indicating that the junctions fabricated between the Au NPs and MWCNTs by MW-plasma heat-induced coalescence were effective in reducing the number of defects and in increasing the number of charge-transfer pathways, which in turn enhanced the optical transmittance and electrical conductivity.

The AgPt bimetallic-NP system has received enormous interest for the following reasons [68]: (1) there is a reduction in the poisoning effect; (2) there is a significant improvement in the catalytic and optical response properties; (3) silver-based materials render these NPs competitive alternatives to Au, Pt, and Pd nanocolloids in low-cost applications because silver is much more cost-effective than other noble metals; (4) the use of AgPt bimetallics as potential lead-free solder materials has been studied in recent years. Herein, we report the successful formation of large-scale AgPt-MWCNT TCFs (Figure 14(a)), where the AgPt-MWCNT composites were spin-coated on PET films using the ultrasonic atomizer technique in the presence of SDS surfactants. In addition, in order to enhance the electrical flexibility and to improve the mechanical property of the films, the AgPt NPs were annealed under MW plasma irradiation. Characterization of the films showed an optical transmittance of 80% at 550 nm and a two-probe electrical resistance of 154.36 ohm/sq (Figures 14(a) and 14(b)). We also analyzed the strain-dependent electrical resistance characteristics by a two-point bending test to explore the feasibility of the as-prepared films (Figure 14(c)). The test confirmed that the sheet resistance of the fabricated films reached a value as low as 154 ohm/sq, which was consistent with the two-probe measured data. It is interesting

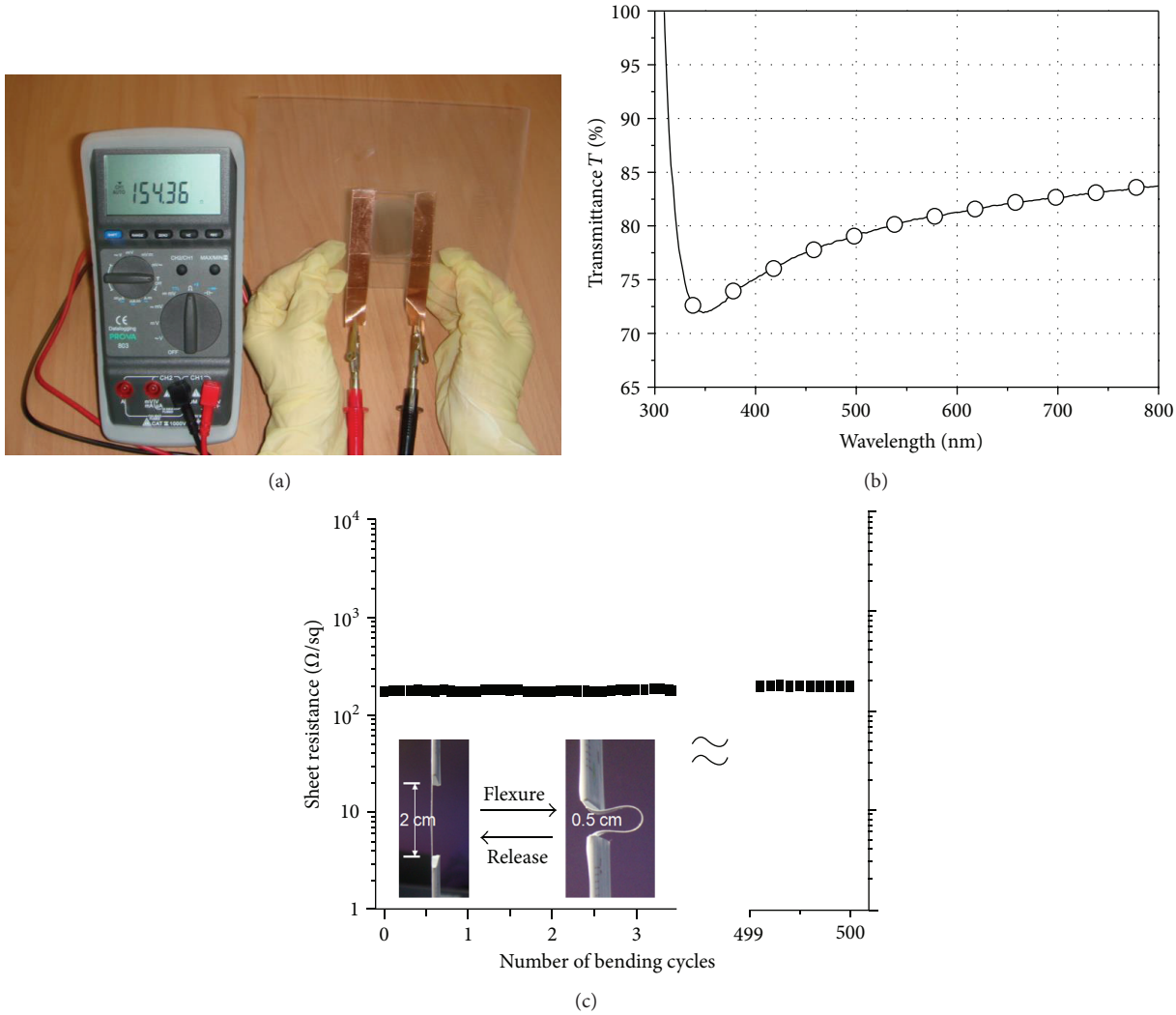



Figure 14: (a) Photograph and sheet resistance analysis, (b) UV-Vis transmittance spectrum, and (c) flexibility test of the representative AgPt-MWCNT flexible TCFs.

Table 2: Optical transmittance and electrical conductivity of prepared Au-MWCNT flexible TCFs with and without post-modification MW plasma irradiation treatment.

| | | Sample 1 | Sample 2 |
|---|---|---|---|
| Before MW plasma irradiation | Sheet resistance (ohm/sq) | 246.7 | 283.7 |
| | Transmittance at 550 nm (%) | 75.1 | 71.4 |
| After MW plasma irradiation | Sheet resistance (ohm/sq) | 152.2 | 156.8 |
| | Transmittance at 550 nm (%) | 87.9 | 83.5 |

to note that the conductivity of the films did not decrease even after 500 bending cycles; the sheet resistance remained at approximately 154 (±1%) ohm/sq.

The resulting performances of flexible tests of CNT-based flexible TCFs made from MWCNT, Au-MWCNT nanocomposites, and AgPt-MWCNT nanocomposites with the postmodification treatment of MW plasma irradiation are summarized in Table 3. The electrical conductivity of the as-produced MNP-MWCNT thin films was higher than that of films without decorating MNPs, which is attributed to the junction fabricated between the MWCNTs and MNPs to increase the number of effective charge-transfer pathways and reduce the contact resistance. In addition, the films could be bent without causing a decrease in the electrical conductivity of MW-plasma-treated Au-MWCNT and AgPt-MWCNT flexible TCFs. However, the MWCNTs, whose sheet resistance dramatically increased to 3400 ohm/sq from 200 ohm/sq owing to the destruction of charge-transfer pathways and the increase in contact resistance after the bending tests, did not exhibit this characteristic. This result

Table 3: Sheet resistance (ohm/sq) of the prepared flexible TCFs of MWCNT, Au-MWCNT, and AgPt-MWCNT before and after the flexibility test by two-point bending measurement.

| Bending cycles | Original | 100 | 250 | 500 |
|---|---|---|---|---|
| MWCNT | 200 | 3.4 K | 3.6 K | 3.7 K |
| Au-MWCNT | 157 | 157 | 155 | 158 |
| AgPt-MWCNT | 175 | 179 | 176 | 177 |

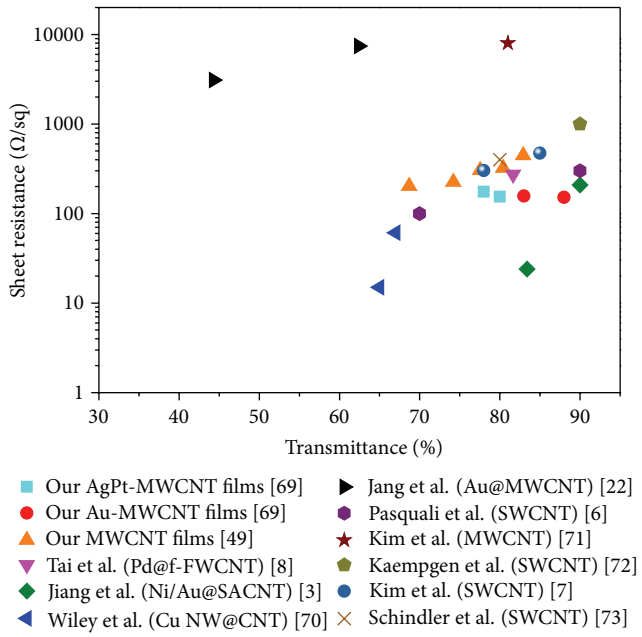



Figure 15: Comparison of the sheet resistance of our AgPt-MWCNT, Au-MWCNT, and MWCNT thin films after MW plasma treatment (two-probe resistance) with that of other CNT-based thin films with or without metallic NPs decoration reported in the literature, as a function of the transmittance at 550 nm.

indicates that the existence of MNPs can provide strong adhesion to the sidewalls of the MWCNTs through the intra- or interjunctions, thereby forming a robust MNP-MWCNT network of effective conducting pathways and enhanced mechanical ability.

## 6. Conclusion

Flexible, transparent, and conducting composite thin films, constructed from CNT-supported MNPs, have attracted a lot of attention owing to their potential in various applications. In this chapter, in addition to reviewing some of the synthesis processes for MNP-CNT flexible TCFs reported in the recent literature, we have also introduced our research results in this area. Through the combination of a polyol process for synthesizing composites of MWCNTs and MNPs with an ultrasonic atomization–spin coating method for preparing flexible thin films, we have successfully prepared Au NP-MWCNT, Pt NP-MWCNT, and AgPt NP-MWCNT flexible TCFs. More importantly, by subsequently exposing these nanocomposites to microwave plasma irradiation, improved optoelectronic and mechanical properties of the films could be achieved owing to the formation of junction bridges between MWCNTs with MNPs, leading to lower contact resistance between the NPs and CNTs and reinforced frameworks. It is worth noting that our results are competitive with other MWCNT-based composite flexible transparent films (Figure 15) [3, 6–8, 40, 46, 69–73]. Synthesis of MNP-CNT flexible TCFs by our inexpensive, effective, convenient, and feasible method can offer a potential means for the development of various CNT-based substrates decorated with several different MNPs, which is favorable for industrial scalability and for use in next-generation flexible touch screens and optoelectronic devices.

## Acknowledgment

The authors gratefully acknowledge the support through the National Science Council of Taiwan, Taiwan, under Project nos. NSC-101-2113-M-005-014-MY3 and NSC-101-2622-M-005-002-CC2.

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