Research Article

Al–CNT–Ni composite with significantly increased strength and hardness

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Abstract
In this study, aluminium–carbon nanotube–nickel (Al–CNT–Ni) composite was prepared by powder metallurgy from pure Al powder and Ni-encapsulated CNT. Previously, carbon nanotubes were coated with nickel following ultraviolet-assisted electroless deposition method. Tensile strength and hardness of the composites were found to increase in proportion to the CNTs addition. For an addition of 7 wt.% Ni-coated CNTs containing 2.5 wt.% nanotubes of 8–15 nm diameter (Ni to CNT ratio was 1–0.357), resultant tensile and yield strength were increased by 129.26% and 157.48% respectively compared to pure aluminium. Hardness was also increased by 171.39%. These results were obtained while conventional sintering was followed by further consolidation by Hot Isostatic Pressing (HIP). Enhanced mechanical properties are attributed to the well dispersion of CNTs in aluminium matrix and strong interfacial bonding between CNT and aluminium. Well dispersion of CNTs and strong interfacial bonding was resulted from the uniform Ni-encapsulation as verified by red shift in Raman Spectroscopy.

Keywords Al/CNT composite · Ni-encapsulation · Electroless deposition · Interfacial bonding · Raman spectroscopy

1 Introduction

Light and strong metallic materials with good electrical conductivity are greatly needed in automobiles and aerospace applications as well as in power grids (hanging lines). Aluminium is a traditional light metal conductor (density 2.7 g/cm^3) with the fourth best conductivity (only after silver, copper and gold). However, strength of pure aluminium is relatively low which is not sufficient for application like power transmission lines. Although alloying can significantly increase its strength, this results in simultaneous reduction in electrical conductivity. Therefore, other ways to increase the strength meanwhile without decreasing electrical conductivity is important. Recently carbon nanotubes (CNTs) have been added to aluminium due to CNT's exceptional mechanical, electrical and thermal properties [1, 2] including high young's modulus (1.0–1.8 TPa), high tensile strength (30–200 GPa) and high elongation at break (10–30%) [3–6]. Moreover, CNT's thermal conductivity is comparable to that of diamond and electrical conductivity is like that of metals [7]. Thus, Al/CNT composites are considered as the novel attractive conductive materials due to their light weight coupled with potential high strength and high conductivity [8–12].

The ways of adding CNTs into aluminium include ball milling associated with powder metallurgy, mixing CNTs into molten aluminium and casting as well as high-pressure torsion etc. [12–15]. Based on published results all these methods are unable to disperse CNTs from bundles due to strong van der waals force in nanoscale range, therefore the resultant mechanical strength is not as high as expected and the resultant conductivity is lower than pure aluminium. Also, week interfacial bonding of CNT with aluminium matrix is of high concern.

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In this paper, authors have developed Al–CNT–Ni composite by powder metallurgy where nickel encapsulated multi-walled carbon nanotubes (MWCNTs) were mixed with pure aluminium powders. Resultant mechanical properties i.e. strength and hardness together with electrical conductivity were investigated for different diameter CNTs addition and different consolidation methods including Hot Isostatic Pressing (HIP). Nickel encapsulation was used to reduce the effect of strong van der waals force in nanoscale range and strengthen interfacial bonding of CNT with aluminium matrix.

2 Experimental

MWCNTs with purity greater than 95% were purchased from Cheap Tubes Inc. Two different diameter CNTs were used for this study: diameter between 30 and 50 nm with axial length between 10 and 20 µm and diameter between 8 and 15 nm with axial length between 10 and 50 µm. CNTs were first purified to get rid of impurities such as amorphous carbon, metal catalyst and smaller fullerenes by ultrasonically dispersing in an aqueous solution of HNO_3 (70%) at 80 C for 2 h [16, 17]. HNO_3 treatment also modifies surface properties to get better dispersion in the electrolyte with high-density activation sites for subsequent reactions [18]. After acid treatment CNTs become hydrophilic to adsorb metallic particles easily onto CNT's surface [18–20]. MWCNTs were then rinsed with deionized (DI) water until the solution was neutral.

Functionalized MWCNTs were then dispersed in an electroless nickel electrolyte for nickel encapsulation. In same amount of electrolyte almost double amount (weight) of smaller diameter CNTs were added compared to that of larger diameter CNTs. CNTs were first ultrasonically dispersed in the electrolyte solution under an ultra-violate (UV) exposure (a UV lamp of 100 W) for 20 min (Fig. 1a). The UV exposure results in emission of electrons from valance band as free electrons on CNT's surface (Fig. 1b) and attract nickel ions in the electrolyte to the vicinity of CNTs due to coulombic force (Fig. 1c). $NaBH_4$ solution was then added into the electrolyte to trigger Ni^O atoms reduced on CNT's surface (Fig. 1d) [21]. After rinsing with DI water thoroughly the activated CNTs were dipped into a standard Ni electroless solution at 50 C for 20 min. Finally, the Ni-encapsulated CNTs were received (Fig. 1e) after being washed with DI water, filtered off and dried. Composition of the electroless nickel electrolyte is shown in Table 1. Ammonia solution was used to adjust pH to 8.5. Coating morphology of Ni-encapsulated CNTs was studied using Zeiss ULTRA-55 Field Emission Gun Scanning Electron Microscope (FEG-SEM), as shown in Fig. 2a. Electroless nickel deposition on CNTs without UV exposure was also carried out (Fig. 2b). It's evident that UV assisted Ni-encapsulation resulted in uniform nickel coating on CNT's surface.

Ni-coated CNTs were then ultra-sonicated for 2 h in ethyl alcohol and after adding Al powders the mix was ultra-sonicated for another 2 h. Following drying, the mixture of Al and Ni-coated CNTs was pressed into pellet of 13 mm diameter under a unidirectional pressure of 400 MPa. Pure Al pellets were also prepared similarly. All the pellets were sintered in nitrogen atmosphere at 600 C for 2 h. HIP was also used for further consolidation of 8–15 nm diameter CNTs reinforced composites. HIP was conducted at 550 C for 90 min at 200 MPa pressure.

Archimedes principle was used to measure density using distilled water as an immersion medium. Effects of Ni-coated CNTs addition on the resultant tensile strength and micro-hardness were investigated. Tensile specimens were prepared with rectangular cross-sectional area as per ASTM E8/E8M–09. Tensile test was conducted using Mechanical Testing and Simulation (MTS) Tytron Tester.

Table 1 Composition of Ni electrolyte

Chemicals	Concentration (g/L)
$NiSO_4{\cdot}6H_2O$	35
NaH_2PO_2	35
$C_6H_5Na_3O_7$	18
NH_3 solution	For pH adjustment

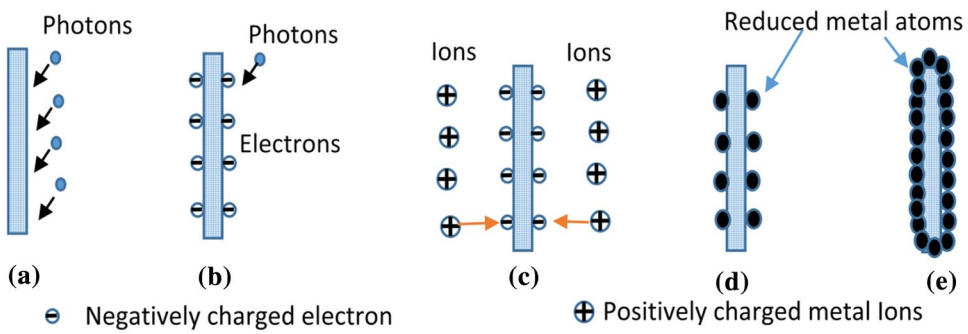

Fig. 1 Sketch of electrochemical deposition of nickel on CNTs stimulated by photon radiation, **a** photons radiation on CNTs, **b** electrons emitted on CNT's surface, **c** metal ions in electrolyte attracted to CNTs by coulombic force, **d** metal atoms reduced after reaction between ions and electrons and **e** Ni-encapsulated CNTs

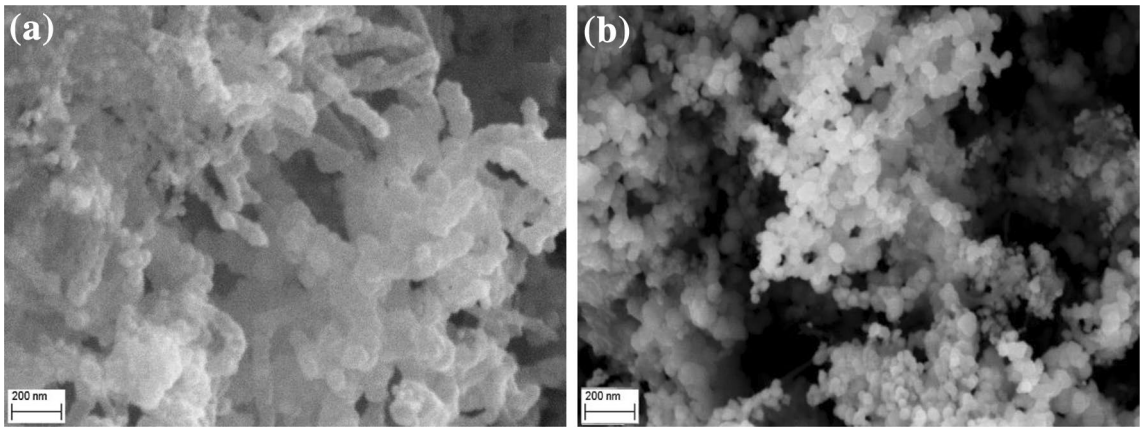

Fig. 2 Ni-encapsulated CNTs **a** with UV exposure and **b** without UV exposure

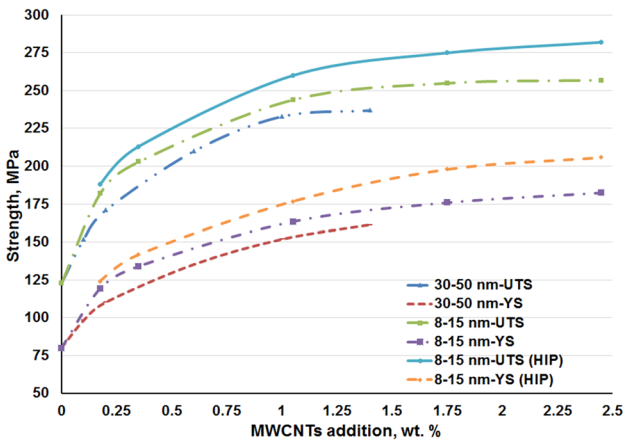

Fig. 3 Effect of CNTs addition on strength

Fracture surfaces were studied using Zeiss ULTRA-55 FEG-SEM. QV-1000 Vickers Hardness Tester was used to measure micro-hardness according to ASTM E-384 with an applied load of 50 g-force for 30 s. Diagonal lengths of the indentations were measured under SEM to calculate the hardness values.

3 Results and discussion

Figure 3 shows the effect of Ni-coated CNTs addition on both yield strength (YS) and ultimate tensile strength (UTS) of aluminium. CNTs coated with nickel under UV exposure (Fig. 2a) were only used to prepare the composites. A maximum of 7 wt.% Ni-coated CNTs (each of 30–50 nm and 8–15 nm diameter) was added in aluminium. Nickel to CNT ratio was 1–0.20 for 30–50 nm diameter CNT and 1–0.357 for 8–15 nm diameter CNT. Thus, 7 wt.% Ni-coated CNTs contain 1.4 wt.% actual CNTs when diameter of CNT is 30–50 nm (Al–1.4CNT–5.6Ni) and 2.5 wt.% actual CNTs when diameter of CNT is 8–15 nm (Al–2.5CNT–4.5Ni). For both type, addition of CNTs enhanced yield and ultimate tensile strength significantly. Strength was increased rapidly initially with addition of CNTs. Later, increase in strength was almost linearly proportional to any further addition. The smaller diameter CNTs resulted in greater strength values compared to the larger diameter ones. This is because for the same amount of CNTs addition, smaller diameter CNTs result in much finer inter particle distance and larger surface to volume ratio compared to that of the larger diameter CNTs. Later, HIP process was followed for 8–15 nm diameter CNTs reinforced composites. For Al–2.5CNT–4.5Ni composite (8–15 nm diameter) when conventional sintering was followed by HIP relative density was increased from 96.2 to 99.1%. Due to the further consolidation with HIP following conventional sintering, further increase in both yield and ultimate tensile strength were observed (Fig. 3). Compared to pure aluminium, YS and UTS of Al–CNT composites were increased maximum by 157.48% and 129. 26% respectively for Al–2.5CNT–4.5Ni composite (8–15 nm diameter) when conventional sintering was followed by HIP.

Figure 4 shows that micro hardness also increased continuously with increasing CNTs addition. Similar to tensile properties, micro hardness also increased rapidly with initial addition of CNTs. Later, with further addition hardness increased slowly. Compared to pure aluminium, micro hardness was increased maximum by 171.39% for Al–2.5CNT–4.5Ni composite (8–15 nm diameter) when conventional sintering was followed by HIP.

The fracture surface of pure Al and Al–CNT–Ni composites are shown in Fig. 5. Dimples on fracture surface indicates the ductile fracture mode of pure Al (Fig. 5a). At fracture surface of the Al–0.6CNT–2.4Ni composite (30–50 nm diameter), CNTs were observed to be

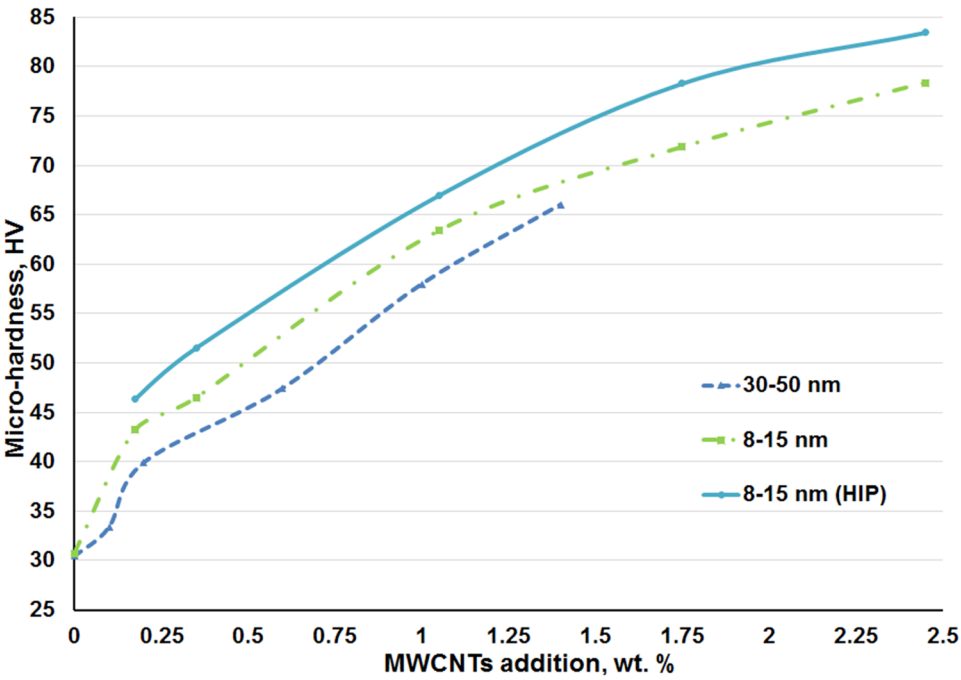

Fig. 4 Effect of CNTs addition on VH

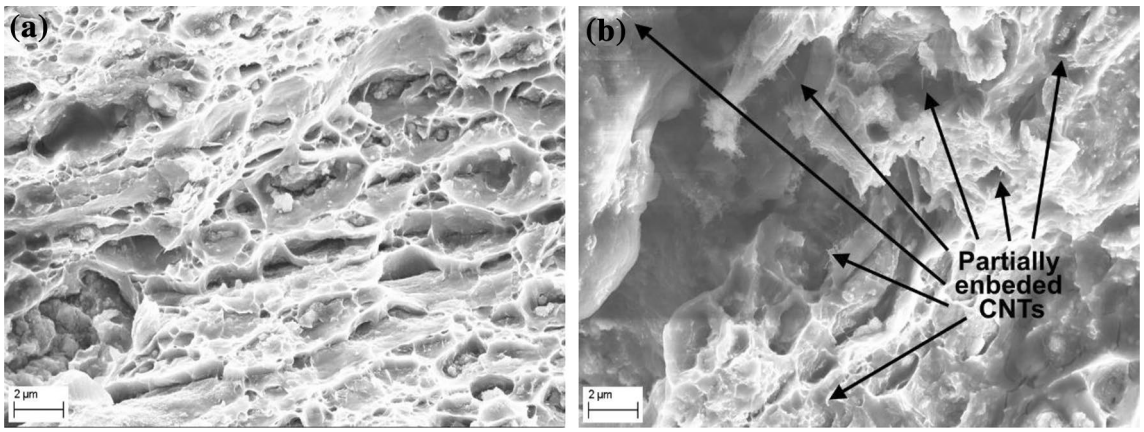

Fig. 5 SEM micrographs of fractured surfaces of **a** pure Al and **b** Al–0.6CNT–2.4Ni composite (30–50 nm diameter)

embedded partially in the Al matrix with short pull-out length (Fig. 5b). It's also evident that the Ni-encapsulated MWCNTs get dispersed well in the Al matrix. Ni coating prevents direct contact between CNTs by reducing van der waals force on CNT's surface and thus results in better CNT dispersion as well as better interfacial bonding between CNT and aluminium matrix. These results in the enhanced mechanical properties of the composites. In addition, the encapsulated nickel as shown in Fig. 5b appears in a chain of balls that forms "nailing" effects to increase the load bearing capability to prevent CNTs from withdrawing out. This indicates the strong interfacial bonding between Al matrix and CNT resulted from the uniform Ni-encapsulation [20]. Strong interfacial bonding results in partial embedment of CNTs in the matrix and short pull-out lengths.

Raman Spectroscopy was conducted for pristine CNTs, CNTs coated with nickel without UV exposure and CNTs coated with nickel with UV exposure (Fig. 6). It shows that after Ni-coating both D band and G band are shifted to the left. For Ni-encapsulation under UV exposure both band shifted further to the left. These results indicate the formation of strong interfacial bonding between CNT and Ni for UV-assisted Ni-encapsulation. D band is correspond to the distortion of SP^2 structure and G-band arises from the stretching of the C–C bond. When these bands shows red shift (towards lower frequency), it indicates strong C-metallic atom bond formation [23]. Later, Ni

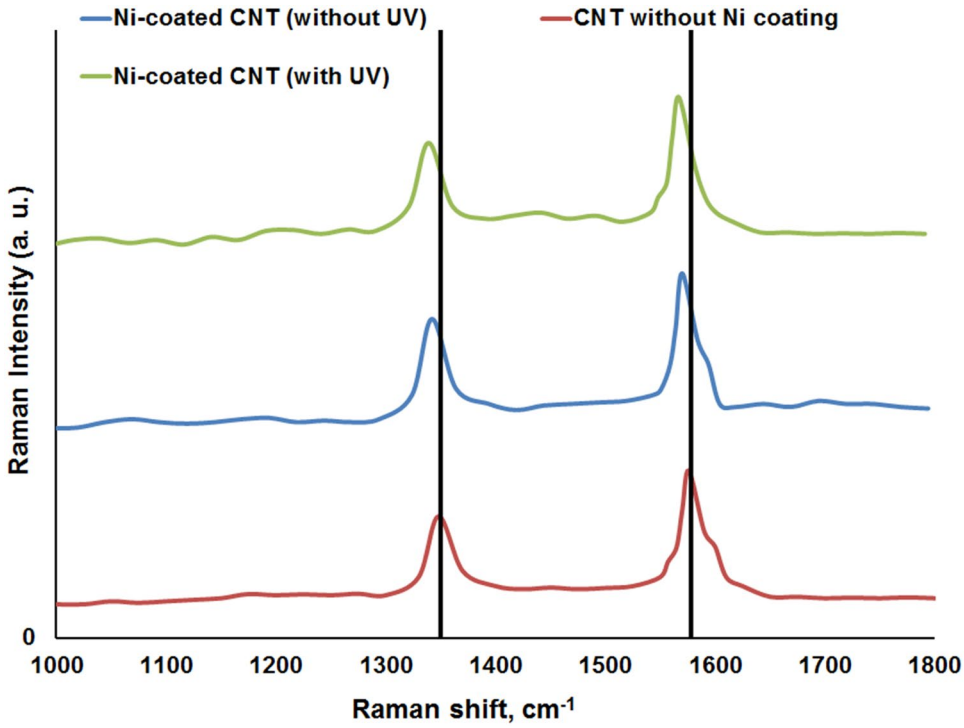

Fig. 6 Raman spectroscopy (red shift)

easily form metallic bond with aluminium matrix which is much stronger than CNT–Al (metal-non-metal) interfacial bonding.

In addition to the mechanical properties, resultant electrical conductivity of the Al–CNT–Ni composites was also investigated by using four-probe method (Fig. 7). Electrical conductivity was increased with addition of CNTs. Compared to pure aluminium, electrical conductivity was increased maximum to 112.5% for Al–2.5CNT–4.5Ni composite (8–15 nm diameter) when conventional sintering was followed by HIP. The increased electrical conductivity also implies a better interfacial bonding between CNT and Al matrix through uniform nickel encapsulation.

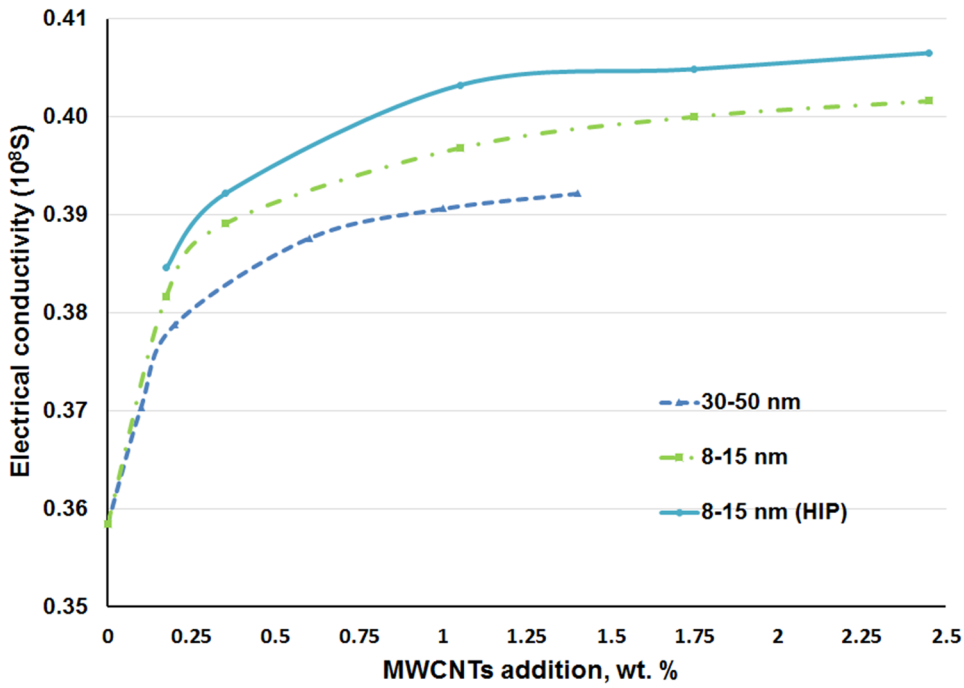

Fig. 7 Effect of CNTs addition on conductivity

Increase in tensile and yield strength of aluminium by CNTs reinforcement is reported in many studies so far. However, in most cases increase in YS strength was in the range of 110–160% and UTS in the range of 100–150% compared to pure aluminium [4–7]. In this context current study reported strength enhancement in the high end. However, the achievement of this study is not only enhancing the mechanical properties, rather to enhance electrical conductivity simultaneously unlike many other studies [22–25]. In most cases electrical conductivity was reported to drop with CNTs addition [22, 23].

4 Conclusions

Al–CNT–Ni composite was prepared by powder metallurgy method in which Ni-encapsulated CNTs were mixed with pure aluminium powder. Resultant yield strength and ultimate tensile strength of the composites were enhanced significantly. For Al–2.5CNT–4.5Ni composite (8–15 nm diameter) when conventional sintering was followed by HIP, yield strength and ultimate tensile strength were increased maximum by 157.48% and 129. 26% respectively. Micro hardness was also increased by of 171.39. More importantly, electrical conductivity was increased to 112.5% compared to that of pure aluminium. All these results are attributed to the well dispersed CNTs and the strong interfacial bonding resulted from uniform Ni-encapsulation on CNT's surface. Uniform nickel encapsulation was achieved by UV-assisted electroless deposition method. The good interfacial bonding was verified by red shift in Raman spectrometry.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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