Electronic Supplementary Material (ESI) for Nanoscale.

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Supporting Information

Volatile-Nanoparticle-Assisted Optical Visualization of Individual Carbon Nanotubes and Other Nanomaterials

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4. Supporting References

1. Supporting Figures

Fig. S1. An optical image of as-grown sample containing aligned CNTs on the substrate acquired by a digital camera. The CNTs cannot be observed in this image. Scale bar, 1 mm.

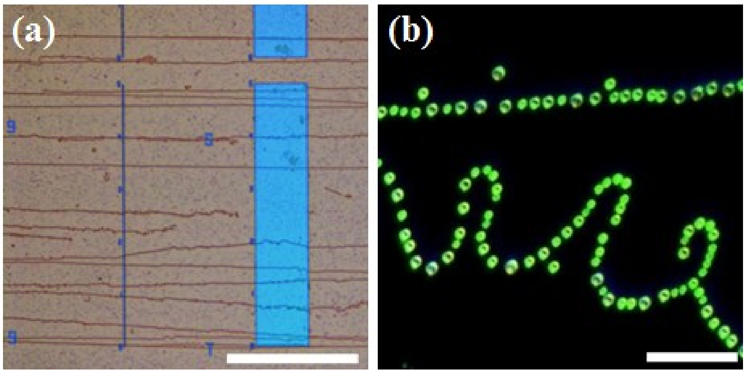

Fig. S2. Optical microscopy (OM) images of CNTs on a SiO_2/Si substrate decorated with sulfur NPs at low (a) and high (b) magnification. Scale bar, 500 µm in (a) and 10 µm in (b).

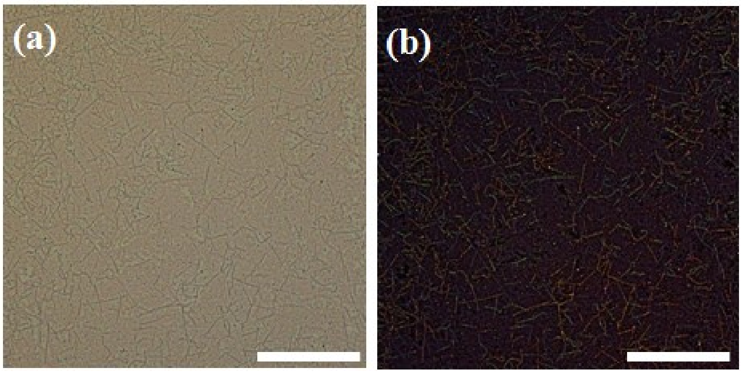

Fig. S3. OM images of randomly distributed short CNTs on substrates taken with bright-field mode (a) and dark-field mode (b). Scale bar, 200 µm.

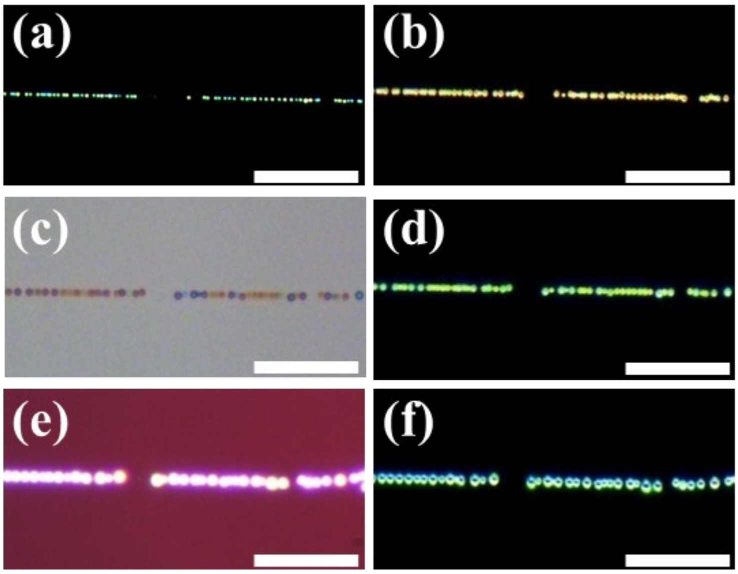

Fig. S4. OM images of suspended CNTs decorated with sulfur NPs at 120 °C with different deposition duration. (a) 1 min, (b) 5 min, (c-d) 10 min, (e-f) 20 min. Scale bar, 20 μm.

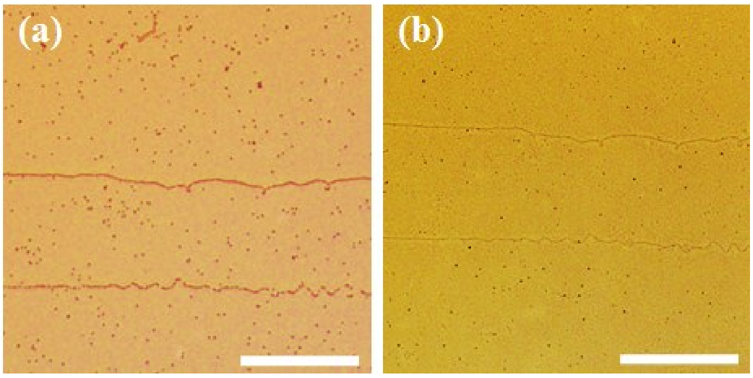

Fig. S5. OM images of CNTs decorated with sulfur NPs deposited at different conditions. (a) 80 °C for 30 min. (b) 150 °C for 45 s. Scale bar, 100 μm in (a) and (b).

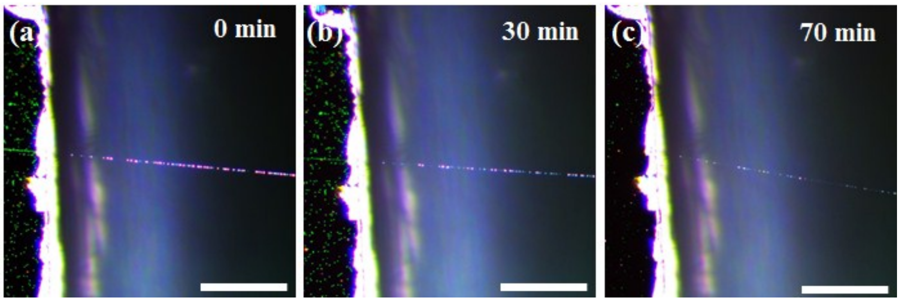

Fig. S6. Effective visualization duration of suspended CNTs decorated with sulfur NPs at 110 °C for 10 min. (a-c) OM images taken at (a) 0 min, (b) 30 min, and (c) 70 min at room temperature. Scale bar, 100 μm.

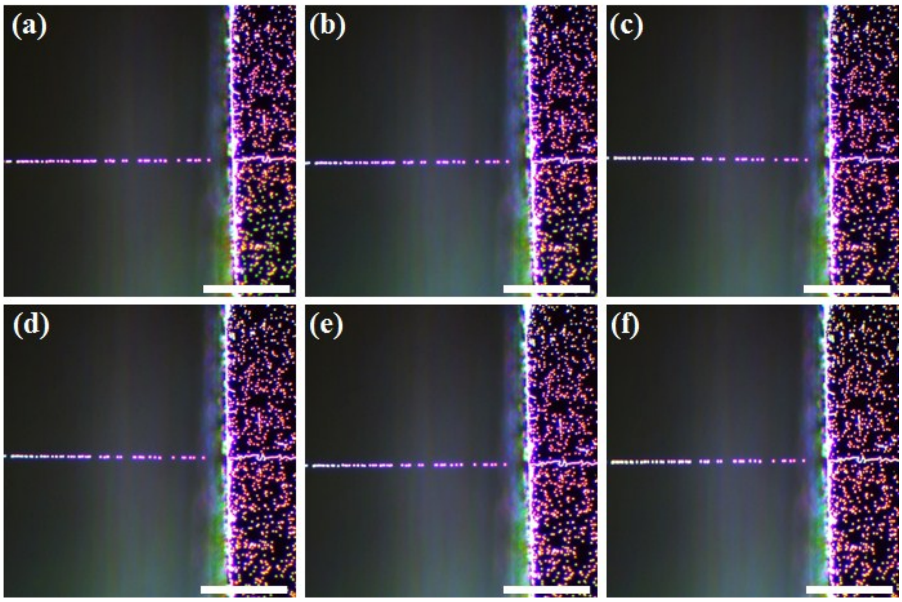

Fig. S7. Effective visualization duration of suspended CNTs decorated with sulfur NPs at 130 °C for 10 min. (a-f) OM images taken at (a) 0 min, (b) 60 min, (c) 100 min, (d) 120 min, (e) 180 min, and (f) 220 min at room temperature. Scale bar, 100 μm.

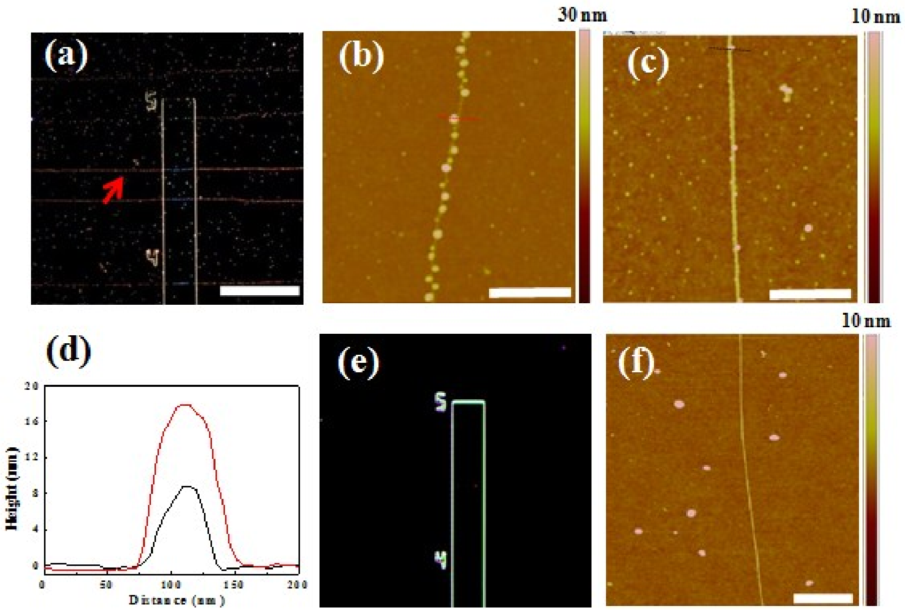

Fig. S8. The evolution of sulfur NPs on CNTs at room temperature on the SiO_2/Si substrate. (a) An OM image of CNTs decorated with sulfur NPs. Scale bar, 100 μm. (b, c) AFM images of CNT indicated by the red arrow in (a) after 3 and 4 hours at room temperature. Scale bar, 0.5 μm. (d) Height of sulfur nanoparticles indicated by dotted line in (b) and (c), which were about 19 nm and 8 nm，respectively. (e) An optical image of CNTs decorated with sulfur NPs after 3 hours at room temperature, showing the invisibility of CNTs. Scale bar, 100 μm. (f) An AFM image of the CNT after annealing at 450 °C for 30 min. Scale bar, 1 μm.

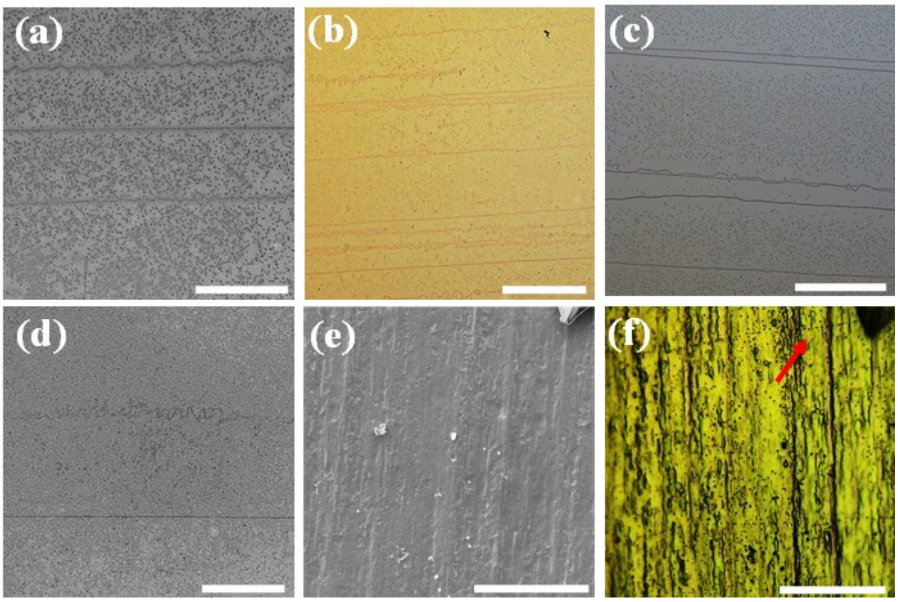

Fig. S9. Sulfur-assisted optical observation of individual CNTs on various substrates. (a-d) OM images of CNTs decorated with sulfur NPs on a Si substrate with a 300 nm oxide layer (a), a 110 nm oxide layer (b), a naturally oxide layer (c), and on a quartz substrate (d). Scale bar, 100 µm. (e) An SEM image of CNTs on a Mo foil. Scale bar, 50 µm. (f) An OM image of CNTs on the Mo foil substrate decorated with NPs corresponding to (e). The arrow indicates the CNT. Scale bar, 50 µm.

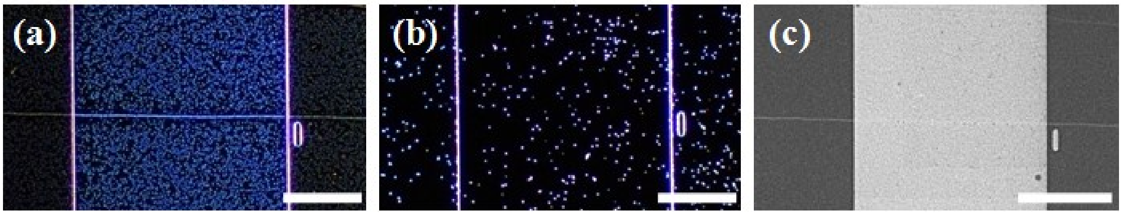

Fig. S10. (a) Optical image of a CNT which was decorated with sulfur NPs. (b) Optical image of the same CNT which was annealed at hydrogen atmosphere and then experienced the same process for deposition of sulfur NPs. (c) The corresponding SEM image of (b). Scale bar, 100 µm.

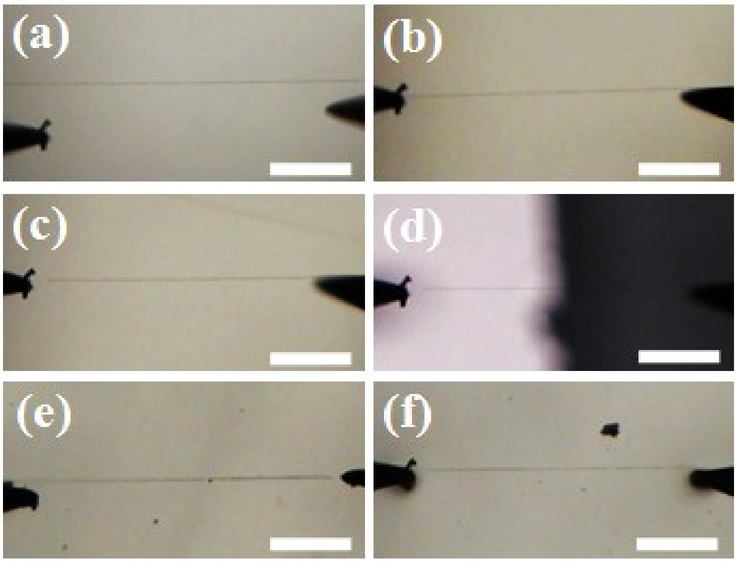

Fig. S11. Manipulation of individual CNTs with the assistance of NPs under an optical microscope. (a-d) The process of approaching, cutting and transferring of a CNT. (e) A CNT transferred to a polyethylene terephthalate (PET) substrate. (f) A CNT transferred to a a polydimethylsiloxane (PDMS) substrate. Scale bar, 200 μm in (a-f).

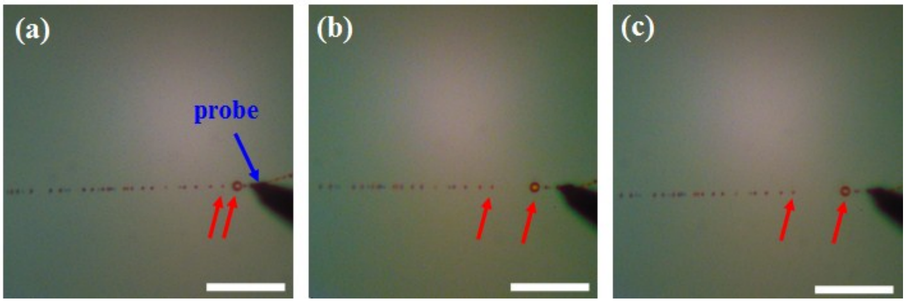

Fig. S12. OM images showing the process to pull out the inner shell of a multi-walled CNT. The arrows indicate two adjacent sulfur NPs, which can be used as markers to show the pulling out of the inner shell. Scale bar, 200 μm.

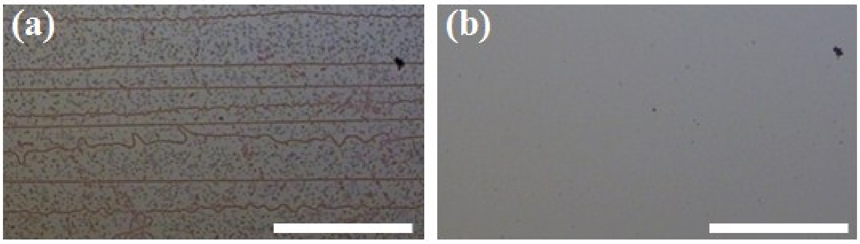

Fig. S13. Removing the sulfur NPs from CNTs on the SiO_2/Si substrate. (a) An OM image of CNTs decorated with sulfur NPs at 120 °C for 5 min. (b) An OM image of CNTs after heated at 120 °C for 1 min. Scale bar, 200 μm.

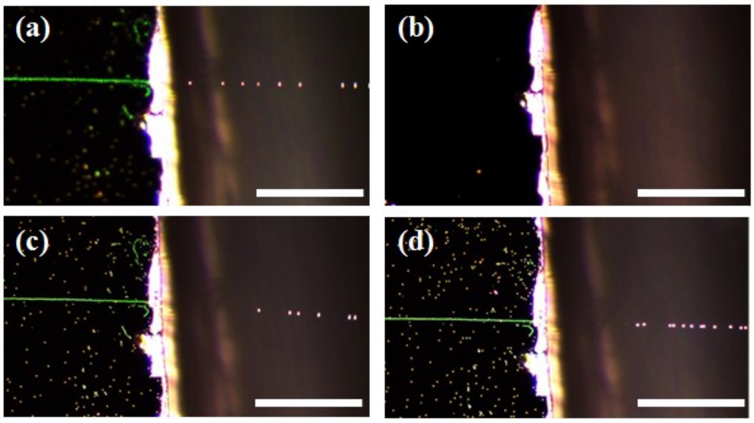

Fig. S14. The process of deposition and removal of sulfur NPs is repeatable. (a) The OM image of sample after deposition of sulfur at 120 °C for 5 min. (b) The OM image of the sample in (a) after heated for 5 min at 120 °C. (c) The OM image of the sample in (b) after deposition of sulfur at 120 °C for 5 min. (d) The OM image of the sample in (c) after the third deposition of sulfur at 120 °C for 5 min. Before deposited of NPs, the sample was heated at 120 °C for 5 min in order to remove the NPs. Scale bar, 200 μm.

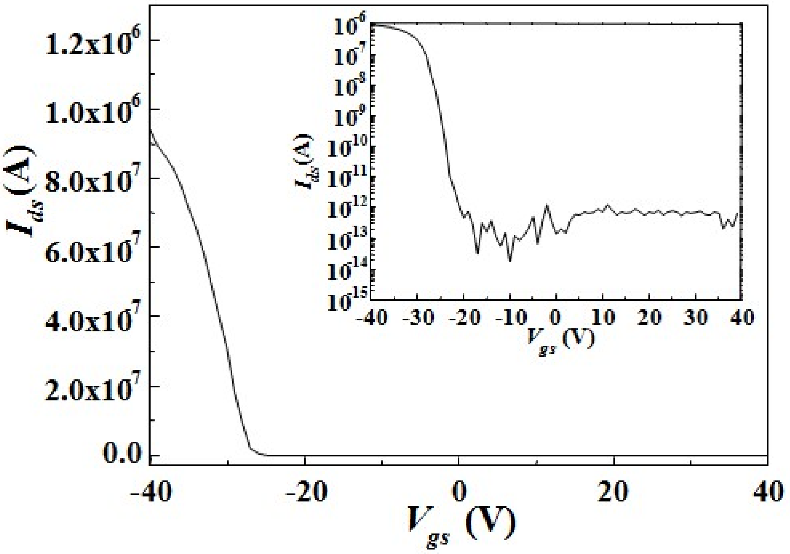

Fig. S15. I_{ds}-V_{gs} curve for V_{ds}=5 V. The inset curve shows that the gate can modulate the conductance by more than 6 orders of magnitude.

The mobility μ of the CNT field-emission-transistors (FET) can be obtained by[1]

$$\mu = \frac{L^2}{CV_{ds}} \cdot \frac{\partial I_{ds}}{\partial V_{gs}}$$

where L is the channel length and C is the gate capacitance. In addition, C can be obtained by

$$C \approx \frac{2\pi\varepsilon\varepsilon_0 L}{\ln(2h/r)}$$

where ε and h are the average dielectric constant and thickness of the device, respectively, r the CNT radius and ε the vacuum dielectric constant. Using L=80 µm, r=1.31 nm, h=300 nm, ε≈2.5, V_{ds}=5 V, the mobility of the device is 510 $\text{cm}^2/\text{V}\cdot\text{s}$ at room temperature, which is close to the mobility of ultralong single-walled CNTs.[2]

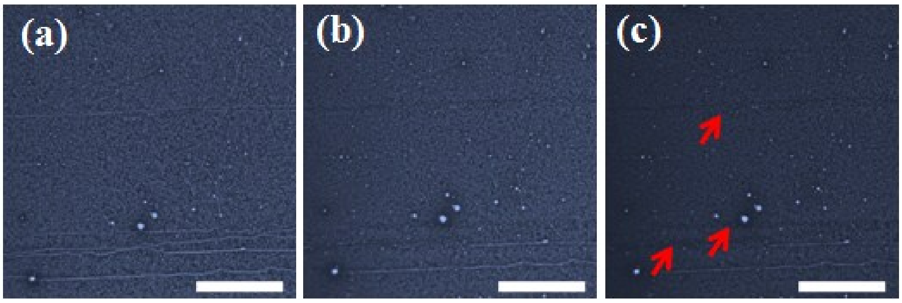

Fig. S16. Evolution of OM images of CNTs decorated with sulfur NPs when applying a voltage (36 V) on the CNTs, showing the different behavior of semiconducting and metallic CNT. (a) CNTs with sulfur NPs deposited at 120 °C for 5 min. (b) After 5 min. (c) After 13 min. The red arrows show the obvious changes along some CNTs. Scale bar, 200 µm in (a-c).

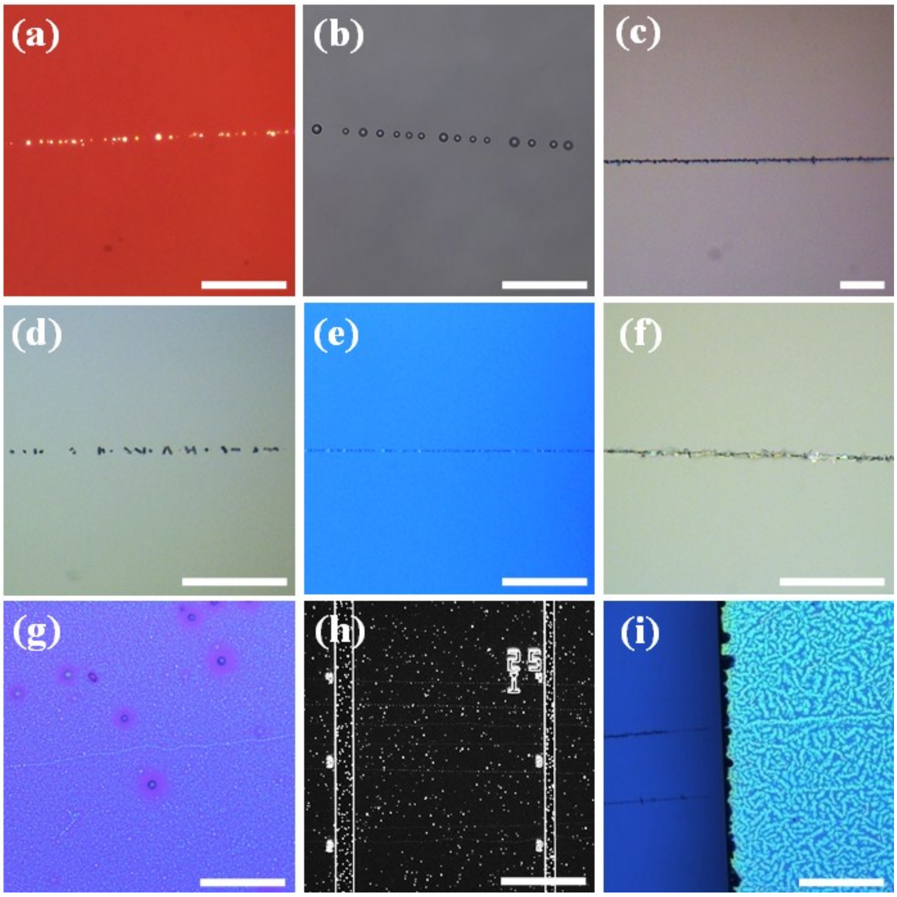

Fig. S17. OM images of suspended or supported CNTs decorated with other materials. (a-f) OM images of suspended CNTs decorated with NH_4Cl NPs at 150 °C for 10 min (a), CH_3COONH_4 at 80 °C for 10 min (b), HCl and $NH_3 \cdot H_2O$ at room temperature for 7 s (c), $CO(NH_2)_2$ at 70 °C for 10 min (d), hexadecanoic acid ($C_{15}H_{31}COOH$) at 100 °C for 10 min (e), octadecanoic acid ($C_{17}H_{35}COOH$) at 100 °C for 6 min (f). Scale bar, 50 μm in (a, d, f), 100 μm in (b, e), 20 μm in (c). (g-i) OM images of supported CNTs decorated with $(NH_4)_2SO_4$ at 150 °C for 10 min (g), abietic acid ($C_{20}H_{30}O_2$) at 120 °C for 9 min (h), dodecanoic acid ($C_{11}H_{23}COOH$) at 80 °C for 5 min (i). Scale bar, 20 μm in (g), 200 μm in (h, i).

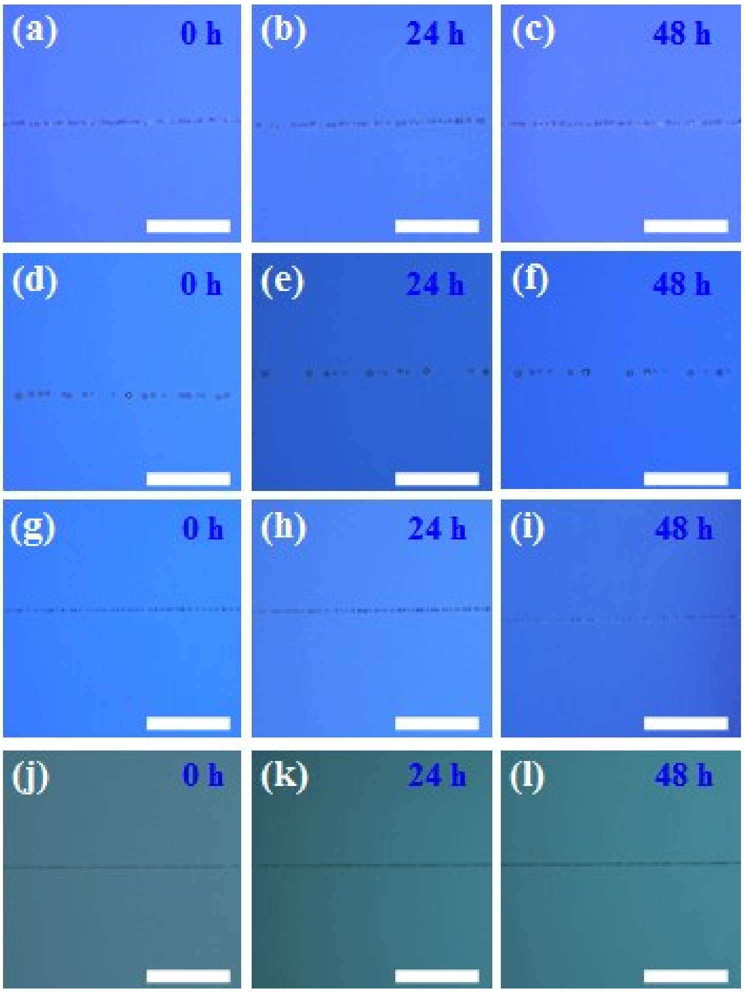

Fig. S18. Effective duration of optical observation by decorated with other substances on the CNTs (Part I). (a-c) OM images of an individual CNT decorated with $(NH_4)_2SO_4$ particles deposited at 150 °C for 10 min taken at 0 h (a), 24 h (b), 48 h (c). OM images of an individual CNT decorated with NH_4NO_3 NPs synthesized from nitric acid (HNO_3) and ammonium hydroxide ($NH_3 \cdot H_2O$) in water (deposited at room temperature for ~7 s) taken at 0 h (d), 24 h (e), 48 h (f). (g-i) OM images of an individual CNT decorated with heating paraffin wax at 150 °C for 4 min taken at 0 h (g), 24 h (h), 48 h (i). (j-l) OM images of an individual CNT decorated with heating abietic acid at 120 °C for 2 min taken at 0 h (j), 24 h (k), 48 h (l). Scale bar, 50 μm.

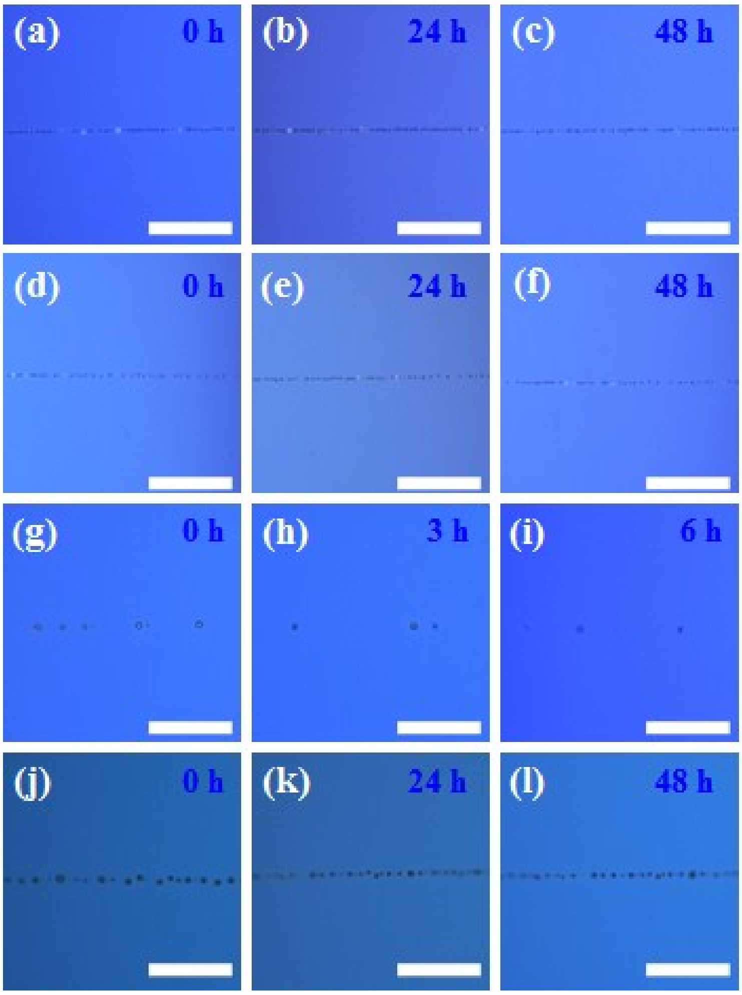

Fig. S19. Effective duration of optical observation by decorated with other substances on the CNTs (Part II). (a-c) OM images of an individual CNT decorated with heating hexadecanoic acid at 100 °C for 10 min taken at 0 h (a), 24 h (b), 48 h (c). (d-f) OM images of an individual CNT decorated with heating octadecanoic acid at 100 °C for 10 min taken at 0 h (d), 24 h (e), 48 h (f). (g-i) OM images of an individual CNT decorated with heating dodecanoic acid at 80 °C for 5 min taken at 0 h (g), 3 h (h), 6 h (i). (j-l) Optical images of suspended CNT decorated with the reaction product of HCl and $NH_3 \cdot H_2O$ taken at 0 h (j), 24 h (k), 48 h (l). Scale bar, 50 μm.

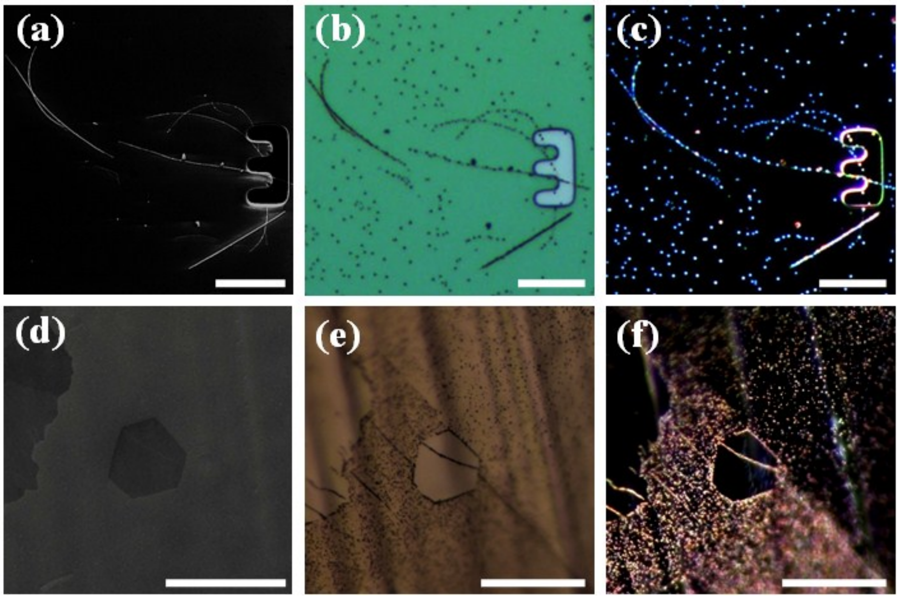

Fig. S20. Sulfur-assisted optical observation of Cu NWs and graphene under an OM. (a) An SEM image of Cu NWs on a SiO_2/Si substrate. (b) A bright-field OM image of Cu NWs decorated with sulfur NPs at 120 °C for 5 min. (c) Corresponding dark-field mode image of (b). Sulfur NPs distributes along to the Cu NWs. Scale bar, 20 μm in (a-c). (d) An SEM image of graphene on a Cu foil. The darker zone is graphene. (e) A bright-field OM image of the sample after deposition of sulfur NPs. (f) Corresponding dark-field mode image of (e). As-grown graphene has a clean surface and almost no contaminants, so the sulfur NPs are inclined to nucleate on the Cu surface and the edge of graphene. Scale bar, 50 μm in (d-f).

2. Supporting Table

Table S1 Summary of volatile substances which can assist the optical visualization of individual CNTs.

Substances		**Property**	**Results**		**Lifetime**
			Suspended CNTs	**on the substrate**	
Elementary substance	**Sulfur**	Bright yellow crystalline solid at room temperature; melting point, 115 ˚C	Y [a]	★★★★★[b]	> 3 h (120 °C, 10 min)
Ammonium salt	**NH_4Cl**	White crystalline salt; melting point, 338 ˚C	Y	N [c]	> 48 h (150 °C, 10 min)
	$(NH_4)_2SO_4$	White crystalline salt; melting point, >280 ˚C	Y	★★★★	> 48 h (150 °C, 10 min)
	$NH_4C_2H_3O_2$	White crystalline salt; melting point, 110~114˚C	Y	N	~15 s (80 °C, 10 min)
	$NH_3{\cdot}H_2O$ and HCl	White crystalline salt; melting point, 338 ˚C	Y	N	>48 h (5~7 s)
	$NH_3{\cdot}H_2O$ and HNO_3	White crystalline salt; melting point, 169.9 ˚C	Y	N	>48 h (5~7 s)
	$NH_3{\cdot}H_2O$ and CH_3COOH	White crystalline salt; melting point, 110~114 ˚C	Y	N	~15 s (5~7 s)
Organic compound	**Urea ($CO(NH_2)_2$)**	Melting point, 133~135 ˚C	Y	★	14 h (100 ˚C, 10 min)
	Paraffin wax	A mixture of hydrocarbon molecules containing between twenty and forty carbon atoms, melting point, >37 ˚C	Y	★★★	>48 h (150 ˚C, 10 min)
	Octadecanoic acid（$C_{18}H_{36}O_2$）	Saturated fatty acid, melting point, 69.3 ˚C	Y	★★	> 48 h (100 ˚C, 10 min)
Organic compound	**Hexadecanoic acid（$C_{16}H_{32}O_2$）**	Saturated fatty acid, melting point, 62.9 ˚C	Y	N	> 48 h (100 ˚C, 10 min)
	Dodecanoic acid（$C_{12}H_{24}O_2$）	Saturated fatty acid, melting point, 42.8 ˚C	Y	★★	~11 h (80 ˚C, 10 min)
	Abietic acid ($C_{20}H_{30}O_2$)	Organic compound that occurs widely in trees, melting point, 172~175 ˚C	Y	★★★★	> 48 h (120 ˚C, 10 min)
Organometallic compound	**Ferrocene ($Fe(C_5H_5)_2$)**	Melting point, 172.5 ˚C	Y	★	~3 h (100 , 10 min)

a) 'Y' stands for Yes, indicating that this substance is effective for the optical visualization of individual CNTs. In other word, the CNT can be observed under an optical microscope by deposition of this substance;

b) '★' stands for the effect degree of optical visualization. The more the number of this star has, the better effect of optical observation obtains.

c) 'N' stands for No, indicating that this substance has little effect on the optical visualization of nanomaterials.

3. Supporting Discussions

According to reference,[3] the vapor pressure of the rhombic sulfur is:

$$\lg(p\,/\,\mathrm{Pa})\text{=13.7889-5166(K/ T)} \quad (1)$$

The vapor pressure of monoclinic sulfur is:

$$\lg(p\,/\,\mathrm{Pa})\text{=13.4889-5082(K/ T)} \quad (2)$$

When the temperature is 25 °C, the sulfur is rhombic sulfur, so its vapor pressure is:

$$\lg(p_1\,/\,\mathrm{Pa})\text{=13.7889-5166(K/ T)} = 13.7889 - \frac{5166}{(273.15+25)} = -3.5479 \text{ , } p_1 = 2.9\times10^{-4}\,\mathrm{Pa}$$

When the temperature is 120 °C, the sulfur is monoclinic sulfur, so the vapor pressure is:

$$\lg(p_2\,/\,\mathrm{Pa})\text{=13.4889-5082(K/ T)} = 13.4889 - \frac{5082}{(273.15+120)} = -0.5625 \text{ , } p_2 = 3.65\,\mathrm{Pa} \text{ ,}$$

and

$$\frac{p_2}{p_1} = 1.3\times10^4$$

Besides, on the basis of experimental results,[4-6] the vapor pressure of sulfur is 1.59×10^{-4} Pa at 25 °C, while that is 4.05 Pa at 120 °C. Therefore, the radio of vapor pressures of sulfur at 120 °C and 25 °C is 2.55×10^{4}.

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