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# Strong and Stable Doping of Carbon Nanotubes and Graphene by MoO<sub>x</sub> for Transparent Electrodes

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**ABSTRACT:** MoO<sub>x</sub> has been used for organic semiconductor doping, but it had been considered an inefficient and/or unstable dopant. We report that MoO<sub>x</sub> can strongly and stably dope carbon nanotubes and graphene. Thermally annealed MoO<sub>x</sub>-CNT composites can form durable thin film electrodes with sheet resistances of 100  $\Omega$ /sq at 85% transmittance plain and 85  $\Omega$ /sq at 83% transmittance with a PEDOT:PSS adlayer. Sheet resistances change less than 10% over 20 days in ambient and less than 2% with overnight heating to 300 °C in air. The MoO<sub>x</sub> can be easily deposited either by thermal evaporation or from solution-based precursors. Excellent stability coupled with high conductivity makes MoO<sub>x</sub>-CNT composites extremely attractive candidates for practical transparent electrodes.



**KEYWORDS:** Transparent conductors, nanotubes, composites, doping

ransparent electrodes are crucial for touch screen, flat panel display, and solar cell technologies. A variety of materials, including transparent conducting oxides,<sup>1</sup> metal nanowires,<sup>2,3</sup> and conducting polymers<sup>4</sup> have been studied intensively for this application. Additionally, carbon nanotube (CNT) networks and graphene thin films have recently shown considerable promise. Unfortunately, as-deposited CNT and graphene films still typically fall short of expectation. The ideal transparent electrode needs a sheet resistance  $(R_{sq})$  of at most 10  $\Omega/sq$  at 85% transmittance,<sup>5</sup> and a good-quality, air-doped CNT network has a typical  $R_{sq}$  of about 200–300  $\Omega/sq$  at 85% transmittance.<sup>6,7</sup> In the case of CNTs, low conductivities can be due to tube defects,<sup>8</sup> low graphitization, or poorly dispersed films,<sup>9</sup> but in general the presence of high junction resistances and Schottky barriers between metallic and semiconducting carbon nanotubes poses the biggest challenge.<sup>10</sup>

Doping a carbon nanotube network theoretically improves network conductivity in two ways. First, an increase in the free carrier concentration in the networks is expected. Second, doping reduces the tube–tube junction resistance, as it allows carriers to pass more easily between metallic and semiconducting CNTs.<sup>11</sup> CNTs are doped mildly p-type by oxygen adsorption, and while more severe partial chemical oxidation can serve similar end, this process is difficult to control and is usually associated with the formation of considerable defects and loss of  $\pi$ -conjugation and conductivity in the carbon nanotube.<sup>12</sup>

There are a number of useful metrics to evaluate the performance of a transparent conductor.<sup>13–15</sup> In this work, we use one of the most common, the dc to optical conductivity

ratio.<sup>15</sup> This convenient single-value figure of merit enables direct comparison of the qualities of a wide variety of transparent conductors at a wide variety of optical densities.

Dopants for carbon nanotubes range from alkali metals<sup>16</sup> and halogens<sup>17</sup> to acidic liquid dopants such as chlorosulfonic acid,<sup>18</sup> HNO<sub>3</sub>,<sup>19</sup> H<sub>2</sub>SO<sub>4</sub>,<sup>20</sup> or SOCl<sub>2</sub>,<sup>21</sup> and redox dopants such as FeCl<sub>3</sub>,<sup>22</sup> AuCl<sub>3</sub>,<sup>23</sup> F4-TCNQ,<sup>24</sup> triethyloxonium hexachlor-oantimonate,<sup>13</sup> or bis(trifluoromethanesulfonyl)imide.<sup>25</sup> The strongest of these produce CNT network electrodes with very good performance (60–160  $\Omega$ /sq with transmission around 90%). While the record dc to optical conductivity ratio is 65 doped, these films were made with an unstable and moisturesensitive superacid dopant.<sup>18</sup> Most of the other results are unstable to air, chemicals, thermal stress, and/or humidity and also introduce mobile ions into the network, which can damage a device fabricated on top of the films. HNO<sub>3</sub> immersion, perhaps the most common CNT network doping method, typically generates networks with dc to optical conductivity ratios ranging from 7 to 40.<sup>6,26,27</sup> Nevertheless sheet resistances generally rise quickly after doping, reducing, for example, a film with a dc to optical conductivity of 40 to one with less than 20 in a matter of hours.<sup>27</sup>  $AuCl_3$  doped films have sheet conductances about 66% of their original doped value after 50 days and sheet conductances about 20% of their original doped value after heating to 200 °C.<sup>23</sup> Capping a doped film with PEDOT:PSS<sup>28</sup> or sol-gel<sup>29</sup> improves the doping stability

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Figure 1. Schematic showing the fabrication of MoO<sub>x</sub>-CNT transparent conductors.

in ambient but complicates processing, increases the film thickness, and in the latter case makes the CNT film difficult to address electrically.

Development of mild, stable, reliable, low toxicity doping is therefore critical for enabling carbon nanotube transparent electrode technology. In the case of Chandra et al., use of a nonvolatile metal chloride cation substantially improved the stability of a doped carbon nanotube network.<sup>13</sup> However, strong acid treatment was necessary in addition to dopant application to achieve good performance, and the films still degraded with sheet resistance suffering 15% increase over 100 h. Bis(trifluoromethanesulfonyl)imide also maintains nearly stable doping at room temperature.<sup>25,30</sup> Nevertheless very little ambient stability data, and no robust thermal (above 150 °C for at least several hours)<sup>18</sup> and chemical stability data have been reported to date for doped CNT networks or for graphene. Demonstrated mechanisms to strongly and stably dope carbon nanotubes and graphene, and to control their functionalization, remain rare and highly desirable.

In parallel, molybdenum oxides have long been interesting and useful electronic materials due to their ease of deposition from vapor or solution and their relatively accessible reduction and oxidation.<sup>31</sup> The filling of trap states left by partial reduction of Mo(VI) oxide are usually accompanied by considerable changes in the absorption and conductivity of the material, which makes it useful for sensing or electrochromic applications.<sup>32</sup> They have also been investigated as electrochemical storage, photocatalysis, and field emission agents.<sup>33</sup> Molybdenum oxides have received much renewed attention very recently as evaporable<sup>34</sup> or solution processable<sup>35</sup> p-type dopants and hole injection layers for wide band gap organic semiconductors, typically in organic light-emitting diodes or photovoltaic cells.<sup>36,37</sup> Some evidence exists for its ability to dope graphene.<sup>38,39</sup> Nevertheless it had been considered a weak dopant, because induced hole densities per wt %  $MoO_x$  have typically been low.<sup>40</sup> Furthermore, the stability of the doping effect in the presence of air and water has been questionable, especially as exposure to atmospheric oxygen is known to substantially degrade the work function of evaporated films of MoO<sub>x</sub>.<sup>41</sup>

In this work, we report the charge-transfer interaction between  $MoO_x$  and CNT networks. We employed this to develop stable p-doped  $MoO_x$ -CNT bilayer transparent electrodes. We found that the interaction could be strongly

enhanced by thermal activation, and we assessed the influence of annealing and  $MoO_x$  deposition method on the properties of these films. We then studied the efficacy and stability of the charge-transfer system compared with that of well-known molecular dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ).<sup>24,42,43</sup> Finally, we extended the usability of  $MoO_x$  doping to large-area CVD-grown graphene and to use in multilayers with conducting polymer PEDOT:PSS.

A basic process for fabricating  $MoO_x$ -CNT transparent conductors is illustrated in Figure 1. When a CNT network was airbrushed onto a glass surface in this work, we found that the dc to optical conductivity ratio ranged from 1.6 to 3.5 with an average of about 2.6. When airbrushed onto a vacuum-evaporated  $MoO_x$  surface on borosilicate glass or  $SiO_2$ , it ranged from 4 to 7 with an average of about 5.6. As deposited, the presence of the  $MoO_x$  already decreased network  $R_{sq}$  by about a factor of 2. When annealed at 450–500 °C for 3 h in argon, the bilayer performance improved further for an overall decrease in  $R_{sq}$  by a factor of 5–7 relative to an undoped, unannealed network. The final dc to optical conductivity ratios averaged about 15, but could be as high as 23, or 24 if capped with PEDOT:PSS.

The improvement associated with addition of  $MoO_x$  is illustrated in Figure 2a, showing data for  $R_{sq}$  versus transmittance of airbrushed CNT networks of various thicknesses, and the same after deposition and annealing on a glass surface modified with  $MoO_x$ . By comparison,  $MoO_x$  films of identical thickness on glass or SiO<sub>2</sub> without CNTs in all cases had sheet resistances of more than 300 M $\Omega$  both before and after annealing. Annealing an analogous CNT network without  $MoO_x$  resulted in  $R_{sq}$  improvement of 1.2–1.7, confirming that the observed effect was due to  $MoO_x$ -CNT interaction. For comparison, doping a CNT network with F4-TCNQ on glass led to only about a 1.3–1.5-fold decrease in  $R_{sq}$  for dc to optical conductivity ratios in the range of 3–4.  $MoO_x$ -CNT bilayer composites, especially after annealing, were thus notably superior to undoped and F4-TCNQ doped CNT networks.

It is of particular note that the most successful literature doping efforts begin with CNT networks which even before doping have very high dc to optical conductivities (7 or higher), compared with the networks in this work.<sup>6</sup> We obtained very competitive performance in our final films despite initial limitations in materials or network morphology. We anticipate,

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Figure 2. (a) Sheet resistance as a function of transmittance for annealed  $MoO_x$ -CNT composites is shown in red, for unannealed  $MoO_x$ -CNT composites in blue versus as-deposited CNTs is shown in black, and for various plain  $MoO_x$  thin films of 10 nm thickness or less is shown in green. (b) Transmittance spectra of  $MoO_x$ -CNT bilayer networks relative to undoped CNT networks of similar thicknesses. (c) Transmittance spectra of a CNT network doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane relative to an undoped CNT network of similar thickness. (d,e) Spectra as described in panels b,c converted to absorbance with a fitted CNT baseline of  $k/\lambda^b$  subtracted to show details of CNT van Hove transitions.

therefore, that our figures of merit do not represent the highest available with use of this technique.

 $MoO_x$  films of less than 10 nm thickness were essentially transparent in the visible as initially deposited from vacuum. Scanning electron microscopy images (Figure 3a) showed that after annealing the  $MoO_x$  layer dewetted from glass supporting substrates and did not remain continuous. Plain  $MoO_x$  thin films displayed a broad and rather variable absorbance in the 600-1250 nm range, indicative of the presence of slightly nonstoichiometric oxide. Annealing  $MoO_x$  in vacuum or inert environment is known to cause oxygen deficiency and the formation of electron traps.<sup>44</sup> Some of the electrons in these traps can be photoexcited into the  $MoO_x$  valence band, resulting in broad and widely variable low-wavelength absorbance and the increasing coloration of the  $MoO_x$  from light green to deep blue.

Absorbance data after annealing in the presence of a CNT adlayer were less variable. Transmittance of a representative Letter



**Figure 3.** (a) SEM micrograph of an annealed  $MoO_x$ -CNT composite film. (b) Raman spectra of a plain airbrushed CNT network and of similar networks doped with F4-TCNQ and with heat-treated  $MoO_{x}$ .

annealed  $MoO_x$ -CNT bilayer film is shown in Figure 2b with details of normalized absorption spectra shown in Figure 2c. The data resemble a typical CNT network spectrum with suppressed van Hove transitions overlaid on top of a broad spectrum of  $MoO_{3-x}$ . If the deposited  $MoO_x$  layer was thin enough, and the CNT network was dense enough, the absorbance of the film was dominated by CNTs, which was a necessary condition for the fabrication of high-quality transparent conductors. Practically, we could achieve this condition reliably with evaporated  $MoO_x$  films of less than 10 nm thickness and airbrushed CNT networks with transmittances of 75–90% before annealing.

Suppression of the van Hove transitions is consistent with strongly doped CNTs. Compared to air-doped CNT networks on glass, unannealed networks on  $MoO_x$  showed evidence of a small amount of charge transfer, and annealed networks had a larger response. With doping, the area attributable to the <sup>S</sup>E<sub>22</sub> CNT transitions decreased by roughly 10% for F4-TCNQ and 64% for annealed  $MoO_x$ .

For high-transmittance composites, the  $MoO_x$  layer was very thin, and in these composites no observable Raman signals could be attributed to  $MoO_x$  modes. Raman spectroscopy of F4-TCNQ and  $MoO_x$  doped composites at 633 nm excitation

Mo 3d O 1s 7000 1.2 Unannealed 6000 Annealed 1 bilayer bilayer A.U. (normalized) 9.0 9.0 9.0 9.0 9.0 5000 4000 A.U. 3000 2000 Plain 02 1000 CNT 0 0 235 237 239 525 530 535 229 231 233 Binding Energy (eV)

Figure 4. XPS Mo 3d and O 1s peaks for MoO<sub>x</sub>-CNT composites before and after annealing, compared with an untreated, airbrushed CNT network.

wavelength revealed the relative suppression of RBM and G'band intensity in the CNTs compared with the CNT G-band. Additionally, the CNT G-band both substantially narrowed and shifted toward longer wave numbers, which is consistent with substantial charge withdrawal from the CNTs.<sup>45</sup> For F4-TCNQ, the G<sup>-</sup>-band shifted by about 2 cm<sup>-1</sup> to 1597 cm<sup>-1</sup> compared to an as-deposited film. CNTs airbrushed onto MoO<sub>x</sub> before any heat treatment had G<sup>-</sup>-bands 3–5 cm<sup>-1</sup> higher in wavenumber than those sprayed onto plain glass in the same experiment. After heat treatment, this shift increased to 14–17 cm<sup>-1</sup> or to 1609–1611 cm<sup>-1</sup>.

The amount of Raman G<sup>-</sup>-band upshift for a particular semiconducting CNT and excitation wavelength is known theoretically and experimentally to directly depend on the amount of charge removed per carbon atom; greater shift implies more charge withdrawn, although not linearly. In several studies,<sup>45,46</sup> chemical or electrochemical experimental doping exhibited a maximum Raman shift of about 10–15 cm<sup>-1</sup> at 633 nm excitation, corresponding to movement of the Fermi level below the second semiconducting CNT transition. We observed very strong suppression of the <sup>S</sup>E<sub>22</sub> in the absorption spectra of annealed MoO<sub>x</sub>-CNT films, indicating that for many tubes in these networks this level of degenerate doping has been reached.<sup>47</sup>

It may be understood from the optical and Raman spectroscopy that before annealing considerable charge transfer from  $MoO_x$  to a CNT adlayer took place. However, annealing the bilayer in an inert environment to temperatures of 450-500 °C conferred great advantage both in terms of film robustness and in a much more significant degree of charge transfer from the CNTs. Heating the bilayer drove the partial oxidation of the CNTs and the partial reduction of  $MoO_3$  much further than did simple deposition of CNTs onto the supported  $MoO_x$  surface. We understand this in terms of the activation of the  $MoO_x$  toward chemical oxidation of nanocarbon, which occurs optimally around 450 °C.

We observed precisely this activation via ultraviolet photoelectron spectroscopy. After deposition of 55 Å of  $MoO_x$  in UHV onto an indium tin oxide substrate its work function (WF) was measured to be 6.82 eV. The  $MoO_x$  film was then exposed to air for one hour. This enormously reduced the surface WF to 5.64 eV, 1.18 eV lower than the initially evaporated  $MoO_x$  film. After the exposure, the  $MoO_x$  film was reintroduced into the UHV measurement chamber with a base pressure of  $8 \times 10^{-11}$  Torr, and gradually annealed. At 375, 410, and 460 °C temperatures the WF were measured to be 6.09, 6.28, and 6.36 eV, respectively. At 460 °C, the WF recovery saturated and did not change further with increasing annealing temperature. The final WF observed at 460 °C was over 6.3 eV, slightly more than 60% of the initial value.

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The most typical work functions of carbon nanotubes are about 4.7 eV but a wide range exists from 4.4 to up to 5.95 eV for certain CNTs.<sup>48</sup> The first van Hove peaks in semiconducting CNTs lie about 0.26–0.8 eV below the Fermi level, and the second about 0.5–1.5 eV below the Fermi level.<sup>49</sup> van Hove transitions in metallic tubes are somewhat less than 1 eV below the Fermi level.<sup>50</sup> The doping data and the UPS data agree very well. The lower work function of about 5.6 eV for air-exposed MoO<sub>x</sub> was sufficient to withdraw charge from <sup>S</sup>E<sub>11</sub> in many of the nanotubes in the network; spontaneous charge transfer from the CNTs still took place. When air-exposed MoO<sub>x</sub> was annealed past about 450 °C in an oxygen-poor environment, it became a much stronger reducing agent and then in many cases was capable of shifting the Fermi level of the CNTs in the network even past <sup>S</sup>E<sub>22</sub> and <sup>M</sup>E<sub>11</sub>.

X-ray photoelectron spectroscopy also provided some insight into the mechanism of interaction between the  $MoO_x$  and the CNTs and into its stability. As shown in Figure 4, despite a small amount of coloration in the  $MoO_x$  film, the  $Mo^{6+}$ oxidation state dominated the Mo 3d spectrum, while the  $Mo^{4+}$  oxidation state was absent before annealing. After annealing, while  $Mo^{6+}$  was still the dominant species,  $Mo^{4+}$ and intermediate oxidation states became visible. This is strong evidence for the chemical reduction of  $MoO_x$ , that is, the receipt of electrons from the CNTs. In addition, no strong evidence of Mo-C bonding was observed in Mo 3d spectrum after annealing.

Also as shown in Figure 4, we observed a shift in the oxygen 1s peak away from the characteristic binding energy of  $MoO_x$  and toward the binding energy of adsorbed oxygen/moisture species or carbon–oxygen bonds. The binding energy of oxygen in  $MoO_3$  is around 530 eV, whereas the binding energy of adsorbed oxygen or carbon–oxygen bonds is around 532–533 eV.<sup>51–53</sup> This substantial shift in the oxygen 1s peak toward higher binding energy species is another piece of evidence for oxygen-associated doping of CNTs at the expense of lattice oxygen in the  $MoO_x$ . We suggest that the stability of the resulting charge transfer has to do with the nonvolatile nature

of the metal oxides and with the permanence of the chemical changes induced by higher temperatures, even when the composite is subject to air or chemical exposure or thermal stress.

One of the great advantages of the  $MoO_x$ -CNT charge transfer system is its stability, particularly its thermal stability. Figure 5 shows the relative impact of various stressors on the sheet resistance of  $MoO_x$ -CNT bilayer films, compared with similar data on CNT films that have been doped with F4-TCNQ, and to alternative dopants in the literature.  $MoO_x$  is the most stable of the strong CNT dopants currently available.



Figure 5. (a) Response of MoO<sub>x</sub>-CNT- and F4-TCNQ-doped CNT samples to different thermal and chemical stressors. The inset shows comparative results calculated from data provided in refs 18, 18, 13, 28, 28, and 23 respectively. (b) Summary figure showing sheet resistances and transmittances of selected transparent conductors for which temporal stability data is available. The blue diamonds indicate performance as fabricated or best performance; the red squares indicate performance after a certain amount of time. Some sheet resistances and transmittances are inferred or calculated from data provided in the references and these are meant to be guidelines only. Green arrow thicknesses are inversely proportional to time (the thinner the arrow, the longer the time), although many real sheet resistances decay nonlinearly as a function of time. The listing is ordered by decreasing dc to optical conductivity ratio. (i) CNT doped with HSO<sub>3</sub>Cl and measured after 48 h;<sup>13</sup> (ii) Cu nanowires fabricated and measured after 650 h;<sup>3</sup> (iii) CNT doped with  $MoO_x$  and measured after 400 h (this work); (iv) PEDOT:PSS films fabricated and measured after 400 h;<sup>4</sup> (v) CNT doped with  $(C_2H_5)_3O^+SbCl_6$  and let sit for 100 h;<sup>13</sup> (vi) undoped CNT, no stability reported <sup>54</sup>; (vii) CNT doped with HNO<sub>3</sub> and SOCl<sub>2</sub> and measured after 400 h;<sup>28</sup> (viii) CNT doped with HNO3 only and measured after 400 h.<sup>28</sup> Also note that with the exception of  $MoO_x$ -doped CNT, most  $R_{sq}$  deterioration rates are substantially accelerated by application of heat.

In ambient conditions over 20 days, sheet resistances changed, on average, less than 10%.  $MoO_x$ -CNT composites had superior chemical stability over F4-TCNQ doped samples subject to every chemical test performed except for 1 h immersion in water. This instability is most likely due to the small but notable solubility of  $MoO_x$  in water.

MoO<sub>x</sub>-CNT composites are particularly valuable transparent conductors for applications that require thermal stability. Unlike previously reported dopants, they maintained low sheet resistances even up to overnight heating in ambient at 300 °C. The sheet resistances of unannealed samples improved subject to temperatures in the range 400–500 °C in an inert environment. After the first annealing, MoO<sub>x</sub>-CNT bilayers could sustain reheating to the same temperature in an inert environment for at least three hours with negligible change in sheet resistances. In air, the thermal stability limit was the temperature at which CNTs themselves oxidize, which is about 390 °C. We attribute the exceptional thermal stability to the nonvolatility of supported MoO<sub>x</sub> below this temperature.

The process of  $MoO_x$ -doping as reported in this work is extensible to other methods of depositing MoO<sub>x</sub>. The most difficult aspect of achieving entirely solution-processed MoO<sub>x</sub>-CNT transparent electrodes is in fabrication of a sufficiently thin and uniform film of  $MoO_x$ . By synthesizing a peroxy poly molybdic acid precursor according to literature<sup>55</sup> and by airbrushing or spin-coating this precursor onto glass substrates prior to CNT deposition and annealing, we were able to achieve highly doped CNT networks with strongly suppressed <sup>S</sup>E<sub>22</sub> van Hove transitions and Raman G-bands above 1608 cm<sup>-1</sup>. We thus fabricated an entirely solution-deposited transparent conductor with sheet resistance of 120  $\Omega/sq$  at 76% transmittance, corresponding to a dc to optical conductivity ratio of 10.5. We believe that with continued optimization of precursor deposition, we can achieve equivalent results with airbrushed and vacuum deposited MoO<sub>x</sub>.

Furthermore, we have also demonstrated that, analogously to carbon nanotubes, thermally activated doping of graphene by  $MoO_x$  confers both better stability and a greater degree of charge transfer than simple  $MoO_x$  evaporation. Recently, Chen et al. demonstrated by photoelectron spectroscopy<sup>39</sup> that  $MoO_x$  can induce a work function increase of 2.4 eV in graphene in vacuum, but that upon even 2 h air exposure, the doped work function decreased by 1.5 eV, indicating a strongly reduced doping effect. We observed this small doping effect of air-exposed  $MoO_x$  on top of single-layer graphene grown by chemical vapor deposition and transferred to an Si/SiO<sub>2</sub> substrate. Before doping, the graphene had an initial sheet resistance of 465  $\Omega$ /sq. After evaporating  $MoO_x$  on the graphene and exposing to air, the sheet resistance of the graphene decreased to 340  $\Omega$ /sq.

We then annealed the  $MoO_x$ -graphene bilayer to induce further charge transfer, in analogy with our process for SWNT. Immediately after annealing, we observed a graphene sheet resistance of 320  $\Omega$ /sq. After 24 h, we observed a sheet resistance of 270  $\Omega$ /sq. The overall improvement of about 42% (a factor of 1.7) is comparable with the initial effects of unstable strong acid doping on graphene films in the literature.<sup>56</sup> Furthermore, rather than being deleterious to the doping effect, substantial exposure to air after annealing improved the final film sheet resistance, probably due to additional doping from air that had desorbed from the  $MoO_x$ -graphene bilayer during annealing. This is testament to the stability of the annealed  $MoO_x$ -graphene composite to ambient environment.



Figure 6. Raman spectra of graphene before (black) and after (red) doping and annealing with MoO<sub>x</sub>.

Figure 6 shows Raman spectra of single-layer graphene on an Si/SiO<sub>2</sub> substrate, taken at 633 nm excitation wavelength, both before and after  $MoO_x$  doping. As in the case of SWNT, the G-band of graphene is known to stiffen with p-type doping. We observe about a 9 cm<sup>-1</sup> center-to-center shift in the Raman G-band of graphene after doping. We also do not observe any substantial D-band intensity increase after doping, implying that the treatment is nondestructive. Interestingly, we consistently observe a small G-band splitting in the doped films, which was not observed in the unannealed films of Chen et al. While we are not certain of the detailed origin of this effect here, it has precedence, originating on occasion when some materials are deposited or adsorbed onto single-layer graphene,<sup>57</sup> when the graphene is subject to strain,<sup>58</sup> or in the presence of local charge inhomogeneity.<sup>59</sup>

In conclusion, we have developed a method of stably and strongly doping CNTs and graphene using  $MOO_x$  as a nontoxic, inexpensive, vacuum- or solution-deposited alternative to strong liquid acids. We have fabricated highly competitive transparent conductors with dc to optical conductivity ratios of as high as 23. We demonstrate that annealing to 450 °C can substantially activate this dopant and encourage the charge transfer from CNTs to  $MoO_x$ , and that because of this activation behavior,  $MoO_x$ -CNT composites exhibit stable sheet conductances even for extended periods under ambient conditions or at elevated temperatures. This represents a substantial step toward practical realization of nanocarbon transparent conductors.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Details of experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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