Photo-organometallic, Nanoparticle Nucleation on Graphene for Cascaded Doping

Songwei Che, Sanjay K. Behura, and Vikas Berry*  
Department of Chemical Engineering, University of Illinois at Chicago, 945 W. Taylor Street, Chicago, Illinois 60607, United States

ABSTRACT: Controlling the doping levels in graphene by modifying the electric potential of interfaced nanostructures is important to understand “cascaded-doping”-based applications of graphene. However, graphene does not have active sites for nanoparticle attachment, and covalently adding functional groups on graphene disrupts its planar sp2-hybridization, affecting its cascaded doping. Here we show a hexahepto (η6) photo-organometallic chemistry to interface nanoparticles on graphene while retaining the sp2-hybridized state of carbon atoms. For testing cascaded doping with ethanol interaction, transition metal oxide nanoparticles (TMONs) (Cr2O3/CrO3, MoO3, and WO3) are attached on graphene. Here, the transition metal forms six σ-bonds and π-back-bonds with the benzenoid rings of graphene, while its opposite face binds to three carbonyl groups, which enable nucleation and growth of TMONs. With a radius size ranging from 50 to 100 nm, the TMONs downshift the Fermi level of graphene (≈250 mV; p-doping) via interfacial charge transfer. This is consistent with the blue shift of graphene’s G and 2D Raman modes with a hole density of 3.78 × 1012 cm−2. With susceptibility to ethanol, Cr2O3 nanoparticles on graphene enable cascaded doping from ethanol that adsorbs on Cr2O3, leading to doping of graphene to increase the electrical resistance of the TMONs–graphene hybrid. This nanoparticle-on-graphene construct can have several applications in gas/vapor sensing, electrochemical catalysis, and high-energy-density supercapacitors.

KEYWORDS: graphene, surface functionalization, cascaded doping, metal oxide nanoparticles, photochemistry

With a unique linear electronic band dispersion and massless Dirac fermions, graphene, a two-dimensional (2D) monolayer of sp2 carbon atoms with hexagonal crystal structure, is an excellent platform for studying fundamental physics and for advanced applications. Further, graphene’s large surface area (2600 m2/g), high transparency (97.7%), flexibility, and superior electrical (106 S/m) and thermal (2600–5300 W/mK) conductivities make it a promising candidate for optoelectronics,1,2 nanoelectronics,3 electrochemical energy storage4 (batteries and capacitors), and sensors.5,6 Low-dimensional transition metal oxides (WO3, Fe3O4, MnO2, NiO, and Co3O4) are an important class of nanostructures that exhibit extensive applications that leverage several properties including structural,7 magnetic,8 optical,9 and chemiresistive.10 For example, tungsten trioxide (WO3) is sensitive and selective to the detection of various gases (NOx,11,12 O2,13 H2S14) and vapors.15,16 Molybdenum trioxide’s (MoO3)’s high chemical stability, high lithium storage capacity, and high specific capacity make it a promising electrode material for lithium ion batteries.17–19 MoO3 nanoparticle’s (NP) strong affinity to hydrogen sulfide (H2S) enables its composite with reduced graphene oxide (rGO) to exhibit high selectivity to H2S among other analytes including ethanol, carbon monoxide, and nitric oxide.20 Chromium oxide has different oxidation states (CrO3, Cr2O7, CrO2) and its magnetic properties vary with different crystallography, stoichiometry, and nanoparticle size.21–23 In this work, we combine the unique properties of TMONs with graphene in a hybrid composite system without disrupting graphene’s lattice planarity.

However, pristine graphene has no molecular sites for efficient attachment of nucleating particles. Most chemistries to interface transition metal oxide nanoparticles (TMONs) on graphene employ graphene oxide (GO) and rGO, in which the oxy-groups (e.g., carboxyl, hydroxyl, epoxy)24 on GO and rGO offer active sites for attachments of NPs. These covalent-functionalized forms of graphene convert sp2-hybridized carbon atoms to sp3 hybridization, resulting in orders of magnitude loss in charge carrier mobility, thus limiting their applications in sensing, electrochemical catalysis, and nanoelectronics. The main techniques to synthesize graphene–TMONs nanocomposites include solvothermal and hydrothermal methods. In such a process, high temperature (120–200 °C) and high pressure are used to grow TMONs on graphene nanomaterials (nanosheets or nanoplates) by adding toxic reducing reactants (e.g., ethylene glycol, hydrazine).25–28

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Nevertheless, in chemically functionalized graphene, some organometallic chemistries can modify graphene with negligible change in graphene’s crystallographic planarity. In the \(\eta^6\)-functionalized graphene, transition metal (e.g., chromium) tricarbonyl moieties coordinate to six carbon atoms of the benzenoid rings on graphene. Sarkar and co-workers have synthesized high-mobility hexahapto-functionalized graphene under refluxing conditions (40–140 °C, 6–48 h) using variable chromium carbonyl complexes. Moreover, a vapor-phase route has been developed to form a \((\eta^6\text{-graphene})\text{Cr(CO)}_6\) complex by dissociating \(\text{Cr(CO)}_6\) inside a tube furnace (130 °C, 40 min). Also, a photochemical method could effectively organometallic-functionalize carbon materials (e.g., single-walled carbon nanotubes). Three-dimensional cross-linked graphene nanoplatelets (GNPs) are synthesized under irradiation of UV light in which bis-hexahapto bonds work as bridges to interconnect GNPs and electrical conductivity is enhanced correspondingly. The same photoactivated reactions are also performed on single-layer graphene to synthesize a \((\eta^6\text{-graphene})\text{Cr}_6\text{L}_{12}\) complex, leading to enhanced conductivity.

In such a method, UVC light (wavelength \(\lambda = 254\) nm) is employed to provide dissociation energy of metal–CO bonds to further form \((\eta^6\text{-graphene})\text{Cr(CO)}_3\) in very short times (10–110 s). However, interfacing TMONs on monolayer graphene via a one-step, photochemical and organometallic route has not been shown, which is performed under mild conditions (low temperature, low vacuum), avoiding toxic reducing chemicals.

In this work, TMONs are incorporated on large-scale monolayer graphene produced by chemical vapor deposition (CVD) by a one-step, photo-organometallic route. By combination of thermal (temperature) and light energy (LED white light, wavelength \(\lambda = 450–475\) nm), \(\eta^6\)-functionalized graphene is synthesized. Simultaneously TMONs are formed, nucleated, and attached on such hexahapto-modified graphene. Raman spectroscopy is used to characterize the TMONs–graphene composite, showing slight enhancement (less than 10%) in the intensity of the D-peak with a blue shift in both G- and 2D-bands. \(\text{Via field emission scanning electron microscopy (FESEM), chromium oxide nanoparticles (Cr}_x\text{O}_y\), consisting of Cr}_3\text{O}_3 \text{ and Cr}_2\text{O}_3\), molybdenum oxide (MoO}_3\), and tungsten oxide (W}_2\text{O}_3\) nanoparticles with different shapes and sizes are observed on the graphene surface, respectively. Moreover, variable valence phases formed in TMONs are studied by X-ray photoelectron spectroscopy (XPS). Further, the electronic transport measurements on back-gated graphene transistors suggest that the electrical conductivity is enhanced, while the mobility is reduced as the Fermi level is lowered by 250 mV postattachment of Cr}_2\text{O}_3 nanoparticles. In the ethanol sensing test, the resistance of Cr}_2\text{O}_3 \text{ NPs incorporated graphene is increased, resulting from the absorption of ethanol gas. A cascaded-doping mechanism is proposed to explain the enhanced resistance when Cr}_2\text{O}_3 \text{ NPs incorporated graphene interfaces with ethanol. This represents that electrons transfer from ethanol to Cr}_2\text{O}_3 \text{ NPs, followed by the transport of electrons from Cr}_2\text{O}_3 \text{ NPs to graphene.}

The Chemical Mechanism. The photochemistry developed here to bind TMONs on graphene involves two simultaneous processes, as shown in Figure 1. First, graphene is chemically functionalized with \(\text{TM(CO)}_6\) via the \(\eta^6\)-chemistry to form \((\eta^6\text{-graphene})\text{TM(CO)}_3\), providing molecular anchors for NP nucleation and growth. Second, by absorbing energy from high-energy UV or visible photons, the \(\text{TM(CO)}_6\) molecules dissociate into TM radicals that react with dissolved O\(_2\) to form transition metal oxide radicals and NPs. The radicals nucleate and grow, and the NPs deposit on the \((\eta^6\text{-graphene})\text{TM(CO)}_3\) sites on graphene.

For the \(\eta^6\) reaction, it is known that the C≡O groups from the metal carbonyl complexes can be substituted by other ligands, such as tetrahydrofuran (THF). It is also reported that a mild photochemical route can synthesize arene tricarbonyl chromium(0) at room temperature with a medium-pressure mercury lamp. In our process, three C≡O groups from \(\text{TM(CO)}_6\) are dissociated under irradiation to form \(\text{TM(CO)}_3\) groups that graft on the benzenoid rings of graphene with carbon monoxide as a byproduct, as shown in the following reaction (eq 1). As shown in Figure 1b, right inset, \(\text{TM(CO)}_3\) moieties bind with six carbon atoms of benzenoid rings on graphene via coordination bonds. The metal atoms are located on the top center of the benzenoid rings, while on the other side of the metal atoms carbon and oxygen atoms from carbonyl groups are parallel with the graphene sheets. To some extent, the interaction of graphene to \(\text{Cr(CO)}_3\) moieties is similar to that in \((\eta^6\text{-arene})\text{Cr(CO)}_3\), in which the carbon atoms from the benzene ring are located at the same distance from chromium atoms with the same angle between carbon atoms (120 ± 0.01°). Also, a DFT simulation on organometallic hexahapto-functionalized graphene confirms that in \((\eta^6\text{-graphene})\text{Cr(CO)}_3\) the bonding lengths between carbon atoms of graphene’s benzenoid ring and Cr are almost the same at 2.247 Å. This indicates that the graphene’s sp\(^2\) hybrid state and planarity are preserved after \(\eta^6\) chemistry.
For the second process, the absorbed photons break the bonding between transition metals and carbonyls (TM−CO). Then the photodissociated transition metal radicals react with O$_2$ to form TMONs, as represented in the chemical reaction shown in eq 2.

$$2\text{TM(CO)}_6 + \text{O}_2 \rightarrow 2\text{TMONs} + 12\text{CO}$$  \hspace{1cm} (2)

The key source of oxygen is the small volume of water dissolved in nondehydrated THF.\textsuperscript{41} Due to its high photoactivity, transition metal carbonyl complexes (e.g., Fe$_2$(CO)$_9$, Ni(CO)$_4$, Mo(CO)$_6$)\textsuperscript{43} are widely used as precursors to synthesize metal nanoparticles via the photolysis route. For example, Mo nanoparticles are prepared using Kr−F laser (wavelength: 248 nm) pulse photolysis of Mo(CO)$_6$ vapor mixed with argon. At room temperature, the mean diameters of Mo nanoparticles are variable in the range of 3−13 nm, depending on the numbers of excimer Kr−F laser pulses.\textsuperscript{44}

Further, it is observed that a large quantity of MoO$_3$ nanoparticles are attached on the graphene surface (Figure S2) compared with pristine graphene (Figure S3), while very few nanoparticles are found on silicon dioxide-coated Si (SiO$_2$/Si) (possibly on defect sites). This confirms that the η$^6$-binding sites on graphene are essential for the nucleation/growth and incorporation of TMONs.

RESULTS AND DISCUSSION

Confocal Raman vibrational spectroscopy is a versatile tool to investigate the surface doping effect in graphene.\textsuperscript{45,46} Figure 2a and b show the G-band (from 1581 to 1592 cm$^{-1}$) before (a) and after (d) the attachment of Cr$_2$O$_3$ NPs; (b, e) 2D-band position (ranging from 2670 to 2682 cm$^{-1}$) before (b) and after (e) the attachment of Cr$_2$O$_3$ NPs; (c, f) Raman images of D-to-G peak intensity ratio ($I_D/I_G$) of graphene (c) and after (f) incorporation of Cr$_2$O$_3$ NPs. (g) G-band Raman spectra of pristine graphene (blue line) and graphene with attachment of Cr$_2$O$_3$ NPs (red line); (h) Raman peak shift of the 2D band before (blue line) and after the incorporation of Cr$_2$O$_3$ NPs on graphene (red line); (i) Raman spectra of graphene and Cr$_2$O$_3$ NPs decorated graphene by averaging the circled area in the Raman maps.
Cr(CO)₃ in η⁶ chemistry is electron-withdrawing (the electrons transfer from graphene to Cr(CO)₃), which corresponds to the hole-doping in graphene. Moreover, the transition metal oxide has a high work function (ΦTMO > 5 eV), while that of graphene (ΦG) is 4.48 eV. Since ΦTMO > ΦG, the Fermi level shifts downward by moving electrons to TMONs from graphene, which is consistent with the results of electrical measurements shown later. Further, the I_D/I_G intensity ratio becomes 0.061 after the attachments of CrO₃ nanoparticles (I_D/I_G ≈ 0.056, before attachment) (Figure 1c, f, and i), indicating that the attachment of TMONs on the graphene surface does not disrupt graphene’s trigonal-planar sp² lattice structure. This result corroborates the non-destructive η⁶ chemistry. The attachment of CrO₃ NPs on graphene is sensitive to the process temperature, as observed in the FESEM images (Figure 3a–c). The density of NPs increased with process temperature (0 to 50 °C), which is attributed to the η⁶ chemistry and NP formation being endothermic. Sarkar and co-workers have functionalized single-layer graphene by using chromium hexacarbonyl (Cr(CO)₆) as reactant in refluxing conditions (140 °C). Also, a vapor-phase η⁶-functionalization of graphene has been achieved at 130 °C under low vacuum. Moreover, Cr, Mo, W, and other transition metal nanoparticles (Fe, Ru, Os) have been stably synthesized in ionic liquids by thermal decomposition (90–250 °C, 6–12 h) and photolysis (UV, 15 min), in which the mono-, di-, and trinuclear metal carbonyl precursors are completely decomposed by absorbing the supplied thermal and photonic energy. It is also suggested that a faster decomposition and growth occur in photolysis. Figure 3d and e show the density of shaped nanostructures on the graphene surface consisting of five or six CrO₃ NPs that are around 100 nm in diameter. This bracelet-like arrangement of CrO₃ NPs on the graphene surface (25 °C) is attributed to magnetic moment-directed self-assembly. CrO₃ NPs are antiferromagnetic, with the presence of a net magnetic moment at its surface, corresponding to imbalanced spin numbers below the Neel temperature. Therefore, it is speculated that the magnetic moments are induced in the mixture of antiferromagnetic CrO₃ nanoparticles, in which internal structural defects and surface spins are unbalanced. As a result, the formation of the bracelet-shaped NPs can be directed by the magnetic moments of CrO₃ NPs, while the dipolar interactions compete with nondirectional van der Waals interactions at short range. Further, the bracelet-shaped NPs are not observed at 50 °C, consistent with the disappearance of magnetic moments when the temperature exceeds the Neel temperature (T_N = 308 K for the bulk Cr₂O₃ and decreases with reducing the particle size). To confirm the attachment of TMONs on graphene and comprehend its binding mechanism, XPS (Kratos AXIS-165) characterization was performed. In Figure 3f, the core level Cr 2p-peaks under high-resolution scan (dotted line) is fitted by the Lorentzian–Gaussian equation (solid line). The Cr peaks centered at 576.55 eV (2p₃/2) and 586.38 eV (2p₁/2) are assigned to Cr(II), while the peaks at higher binding energy (578.75 eV for 2p₃/2 and 588.35 for 2p₁/2) correspond to Cr(VI). This indicates that the chromium oxide nanoparticles are formed as a mixture of Cr₂O₃ and CrO₃. Further, the energy dispersive spectroscopy (EDS) analysis in Figure S5 shows the chromium adsorption peaks located in the range of 0–1 keV and 5–6 keV, confirming the presence of Cr₂O₃ nanoparticles on the graphene surface. In addition to temperature, the effects of irradiation time and light source on nanoparticles’ morphology are also investigated. In Figure S6, it is observed that the density of NPs incorporated on the graphene surface is increased quickly between 1 and 3 h and then slowly between 3 and 5 h. Since the η⁶-functionalization acts as active sites for the attachment of NPs on the graphene surface and the formation energy of (η⁶-benzene)Cr(CO)₃ (ΔH(benzene-Cr(CO)₃) = −341.6 kJ/mol) is larger than the dissociation energy of Cr-CO (D(Cr-CO) ≈ −35.8 kJ/mol), it indicates that during 1–3 h the rate of the η⁶ reaction limits the density of NPs attached on the graphene sheets. Moreover, during 3–5 h a large quantity of nanoparticles grows larger (see Figure S6e and f). UVC light (wavelength λ = 200–280 nm) offers higher energy than LED white light, so that both the size and density

Figure 3. FESEM and XPS characterization of Cr₂O₃/NPs-decorated graphene: (a–c) FESEM images of graphene with the attachment of Cr₂O₃ NPs at 0 °C (a), 25 °C (b), and 50 °C (c). (d and e) AFM images of bracelet-shape Cr₂O₃ NPs incorporated on graphene (e) obtained by scanning the square-region in (d). (f) High-resolution XPS spectra of Cr 2p-peaks.
of NPs are higher than those under LED white light (see Figure S7). In order to control the size of NPs more conveniently, LED white light is used in this work.

The nanostructured composites of MoO₃ and WO₃ combined with other materials (e.g., rGO, carbon nanotube, and silicon) have been widely used in the application areas of gas sensing, batteries, supercapacitors, photocatalysis, and the environment. Therefore, by using analogous reactants under the same conditions, we attached MoO₃ and WO₃ nanoparticles on graphene. As shown in Figure 4a and c, the density of the TMONs on graphene generally follows WO₃ > CrₓO₃ > MoO₃ NPs. Like CrₓO₃ NPs, the attachments of MoO₃ and WO₃ were also confirmed by XPS. In Figure 4b, the Mo 3d-peaks are fitted by using the Lorentzian–Gaussian equation and observed at 235.5 eV (3d₃/₂) and 232.3 eV (3d₅/₂), assigned to Mo(VI). The W(VI) 4d₃/₂ and W(VI) 4d₅/₂ peaks are located at 259.8 and 247.3 eV, respectively, as shown in Figure 4d. The C 1s peak (Figure S4) is deconvoluted into three components in both pristine graphene and TMONs-decorated graphene, including sp² C–C (284.2 eV), C–O (285.6 eV), and C≡O (288.0 ± 0.1 eV). The C–O peak is attributed to the poly(methyl methacrylate) (PMMA) residue from the transfer process or adventitious carbon. The η⁶-chemistry occurs on graphene’s basal surface, which acts as an active site for TMON nucleation and attachment. Moreover, the Raman

Figure 4. FESEM and XPS characterization of MoO₃- and WO₃NPs-decorated graphene: FESEM topography images of (a) MoO₃NPs@G and (c) WO₃NPs@G. High-resolution XPS spectra of (b) Mo 3d-peaks and (d) W 4d-peaks.

Figure 5. Electronic transport measurements of graphene field-effect transistor (FET) devices: (a) Schematic of a graphene back-gated FET device with Ti/Au as electrode contacts. (b) Profiles of conductance versus back-gate voltage (V_{BG}) of pristine graphene (black line) and CrₓO₃ NPs-decorated graphene (red line) at T = 20 K with V_{DS} = 10 mV. (c) I_{DS} versus V_{DS} (source–drain voltage) at T = 20 K obtained on graphene devices before and after incorporation of CrₓO₃ NPs. The inset shows an optical image of the graphene channel used for electrical studies (scale bar = 10 μm).
spectra in Figures S9 and S10 show that blue shifts of G- and 2D-bands resulting in MoO3NPs@G and WO3NPs@G. In order to investigate the influence of CrO3 NPs on graphene’s electrical properties, the charge-carrier transport characterization was performed on graphene back-gated field-effect transistor (FET) devices. After graphene sheets were transferred onto 300 nm SiO2-coated Si substrates, the devices were fabricated by metallization and photolithography process steps. Figure 5a is a schematic diagram of the back-gated graphene FET device, with Ti/Au (10 nm/60 nm) as contact electrodes and a graphene channel of 5 μm × 3 μm (length × width) (inset of Figure 5c) (device fabrication details are outlined in the Materials and Methods section). Figure 5b displays a plot of conductance as a function of back-gate voltage (VBG) at 20 K. After the incorporation of CrO3 NPs on graphene, the Dirac voltage (VDirac) shifts to 50 V from 0 V, which indicates heavy p-doping of graphene with CrO3 NPs and also a change in the Fermi level. The Fermi level can be tuned by the interfacial interactions between the metal oxide nanoparticles and graphene and/or by a different work function of NPs. As mentioned earlier, the work function of graphene is relatively smaller than that of CrO3 NPs. This will lead to electron transfer from graphene to NPs, causing the Fermi energy to reduce by 250 meV following the equation77

\[ E_F^p(CrO_3) = E_F(G) + kT \ln \left( \frac{I_F}{I_{FG}} \right) \]

where \( E_F(G) \) is the Fermi level of graphene, \( I_F \) is the carrier density induced by incorporation of NPs (estimated to be 3.78 × 10^{12} \text{ cm}^{-2} \text{ from the equation}88 \[ n = C_d \left( \frac{V_{G}}{V_{BG}} \right)^2 \]

is the dielectric capacitance, \( V_{DG} \) is the Dirac point of CrO3NPs-decorated graphene, \( C_d \) is the Dirac point of pristine graphene, and \( e \) is the electron charge). Further, the field-effect mobility (\( \mu_{FET} \)) is calculated using the Drude formula87

\[ \mu_{FET} = \frac{e}{c} \left( \frac{d\sigma}{dV_G} \right) \left( \frac{L}{W} \right) \]

where \( \sigma \) is the conductance, \( V_{BG} \) is the back-gating voltage, and \( L \) and \( W \) are the length and width of the graphene channel, respectively. \( \mu_{FET} \) is estimated to be 2220 and 115 \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1} \text{ for graphene and CrO3NPs@G devices, respectively}. \text{ Since the attachment of CrO3 NPs on graphene will introduce potential barriers causing short-range and long-range scattering sites, the carrier mobility is reduced by an order of magnitude.79 } \]

The transition metal oxide nanostructures are widely used to combine with carbon materials (e.g., carbon nanotubes (CNTs), rGO) to improve the gas-sensing performance. For these nanohybrid material systems, electron transfer occurs at the interface of transition metal oxide nanostructures and carbon materials. Moreover, while the nanohybrids are exposed to gas molecules, the formed cascaded-based doping will alter both the Fermi level and resistivity of carbon materials. Lu et al.80 coated CNTs with tin oxide (SnO2) nanocrystals to detect NO2, CO, and H2. They proposed that the CNT’s Fermi level shifted toward the valence band and the conductivity was enhanced correspondingly when exposed to NO2 gas, due to the cascaded-electron transfer from CNT toward SnO2 at the interface and then toward absorbent NO2 molecules. Wang and co-workers81 find when the prepared WO3 nanorods/sulfonated rGO (S-rGO) nanocomposites interface with NO2 molecules, NO2’s continuous electron capture at the surface of WO3 shifts the Fermi level of WO3 lower than that in S-rGO, so that electrons transfer from S-rGO to WO3, leading to enhanced conductivity of WO3/S-rGO nanocomposites. Here, by leveraging the affinity of CrO3 NPs to ethanol, an ethanol-detection device construct was tested by measuring the resistance with changing ethanol concentration around the sensor chip. The ethanol gas flow is introduced by connecting a bubbler system, where nitrogen gas (with a purity of 99.9%) acts as a carrier. To investigate the reproducibility of CrO3NPs@G devices at room temperature,82 as shown in eq 3 and Figure 6b. Second, the cascaded-electron transfer is carried out when CrO3NPs are attached on graphene.

Figure 6. Molecular sensing of TMON-incorporated ƞ-crystalline graphene: (a) Ethanol gas absorption behavior of CrO3NPs@G devices at room temperature (300 K). (b) Electronic band diagram of CrO3NPs@G by absorbing O2 on the surface. \( E_F^p(CrO_3) \) and \( E_F(G) \) are Fermi level of CrO3 and graphene before interfacing with each other, respectively. (c) Schematic diagram of proposed cascaded-doping mechanism while CrO3NPs@G are exposed to ethanol. \( E_F^p(G) \) is the Fermi level of doped graphene by CrO3 NPs. \( \Phi_{C} \) represents the work function of CrO3. Interface 1 is the surface when ethanol is attached on the CrO3 NP surface. Interface 2 is formed when CrO3 NPs are attached on graphene.
devices interface with ethanol. The adsorbed (reducing) ethanol molecules on the Cr$_2$O$_3$ surface catalytically react with O$_2^-$ (also adsorbed) to form H$_2$O and CO$_2$, releasing electrons to Cr$_2$O$_3$.\cite{83,84} (interface 1), shown in eq 4. After accepting electrons, Cr$_2$O$_3$'s Fermi level is moved upward, which is even higher than that of graphene ($E_F$(Cr$_2$O$_3$) > $E_F$(G), shown in Figure 6c). As a result, the difference of Fermi levels pushes electrons into graphene from Cr$_2$O$_3$ (interface 2). The electron addition into the valence band reduces the density of the majority charge carrier (holes) in graphene, resulting in an upshift of graphene's Fermi level and an increase in its resistivity. The mechanism involves electron transfer from ethanol to graphene through two interfaces and is therefore denoted as cascaded doping. Consistently, it is shown in Figure S11 that the absorbance of ethanol on pristine graphene results in reduced resistance due to ethanol's donor characteristics.

$$\text{O}_2 \text{(gas)} + e^- \rightleftharpoons \text{O}_2^{-} \text{(ads)} \quad (3)$$

$$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2^{-} \text{(ads)} \rightarrow 3\text{H}_2\text{O} + 2\text{CO}_2 + 3e^- \quad (4)$$

CONCLUSIONS
A unique photo-organometallic route is reported to anchor transition metal oxide nanoparticles (Cr$_2$O$_3$, WO$_3$, and MoO$_3$) of 50–100 nm radius on graphene without distorting graphene's sp$^2$-hybridization. The thermal energy plays a vital role in controlling the deposition density and morphology of nanoparticles on graphene's surface. Further, room-temperature, magnetic-moment-directed self-assembly of Cr$_2$O$_3$ nanoparticles into a bracelet structure on graphene was also achieved. The XPS high-resolution spectroscopy confirms that there are two valence phases of chromium (III and VI) formed in Cr$_2$O$_3$ nanoparticles and one (VI) in MoO$_3$ and WO$_3$ nanoparticles. Low-temperature electronic transport measurements on FET devices of Cr$_2$O$_3$ nanoparticles deposited on graphene show p-doping (hole density = 3.78 × 10$^{12}$ cm$^{-2}$) with 250 mV lower Fermi level, which is also consistent with a blue shift in both G and 2D Raman vibrational bands. The electrical conductivity is enhanced due to the increase of nanoparticle-interfaced graphene. The absorption of ethanol gas on the surface of Cr$_2$O$_3$ NPs incorporated graphene enhances the resistance via the proposed cascaded-doping mechanism, while it results in a decrease of resistance on pristine graphene devices.

MATERIALS AND METHODS
TMONs Attachment. Transferred CVD graphene on a 300 nm SiO$_2$/Si chip is exposed to 15 mL of 50 mM transition metal hexacarbonyl (TM(CO)$_6$, TM = Mo, Cr, and W)/THF/dibutyl ether solution (THF:dibutyl ether = 1:2). THF is used to dissolve the sublimated solid. By connecting to a vacuum pump and with LED white light (wavelength $\lambda = 450-475$ nm) irradiating on the solution, the reaction occurs under vacuum. After 3 h, the chip is washed with acetone and isopropyl alcohol (IPA) to remove those unattached nanoparticles, followed by being dried with N$_2$ gas. A schematic of the experimental setup is shown in Figure 1a.

Raman Spectroscopy and Mapping. The confocal Raman microscope (Raman-AFM, WITec alpha 300 RA, laser wavelength of 532 nm) is used to obtain the Raman spectroscopy and spatial Raman mapping. The laser spot size is 721 nm by using a 100× objective lens (numerical aperture = 0.90). All the Raman maps had a pixel size of 0.08 μm for both x- and y-directions. Before and after the attachments of Cr$_2$O$_3$ NPs, the transferred graphene on SiO$_2$/Si with a region of 4 × 4 μm$^2$ was scanned to obtain the G-peak (from 1581 to 1592 cm$^{-1}$) and 2D-band (from 2670 to 2682 cm$^{-1}$) position mappings and the intensity ratio between the D-band and G-band ($I_D/I_G$).

Device Fabrication and Electronic Transport Measurements. The electrical contacts (Ti/Au, 10 nm/60 nm) were deposited on transferred graphene chips via electron beam evaporation (Temescal FC2000). The LOR 3A was spin-coated onto a sample at 3000 rpm for 35 s, followed by hard baking at 175 °C for 5 min. Then the positive photoresist (1811) was deposited onto the samples at 3000 rpm for 35 s. The samples were baked on the hot plate at 115 °C for 1 min. Photolithography (Laser Pattern Generator, Microtech LW405) was used to define contact pattern. The graphene channel with a length of 5 μm and width of 3 μm (as shown in Figure 5c) was obtained via oxygen reactive ion etching (RIE, Oxford) to remove the unwanted graphene. Subsequently, the photoresists were removed by exposing the samples to 1165 remover. After annealing under vacuum at 200 °C to remove residuals, the back-gated graphene transistors were measured with a source meter (Keithley 2612) in a variable-temperature probe station (ARS cryostat). The measurements are performed under vacuum (∼10$^{-5}$ Pa).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.9b05484.

Raman mapping of D-band intensity, AFM and Raman characterization on MoO$_3$-deposited graphene, FESEM image of pristine graphene, XPS of carbon 1s peaks in graphene and TMONs@G, EDS of Cr$_2$O$_3$ NPs deposited on graphene, FESEM images of Cr$_2$O$_3$ NPs deposited on graphene at 50 °C for variable irradiation time, FESEM images of Cr$_2$O$_3$ NPs deposited on graphene at 25 °C using UVC light and LED white light, FESEM images of Cr$_2$O$_3$ NPs deposited on graphene for annealing test, Raman characterization of MoO$_3$ deposited on graphene, Raman characterization of WO$_3$ deposited on graphene, ethanol-sensing effect of pristine graphene (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: vikash@uic.edu.

ORCID
Sanjay K. Behura: 0000-0001-7339-9997
Vikas Berry: 0000-0002-1102-1996

Notes
The authors declare no competing financial interest.

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