

## Nitrogen-doped graphene stabilized copper nanoparticles for Huisgen [3+2] cycloaddition “click” chemistry

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### **Materials**

All chemicals and solvents, which were used for the synthesis were purchased from Sigma-Aldrich and used as received unless otherwise stated.

### **Instrumental**

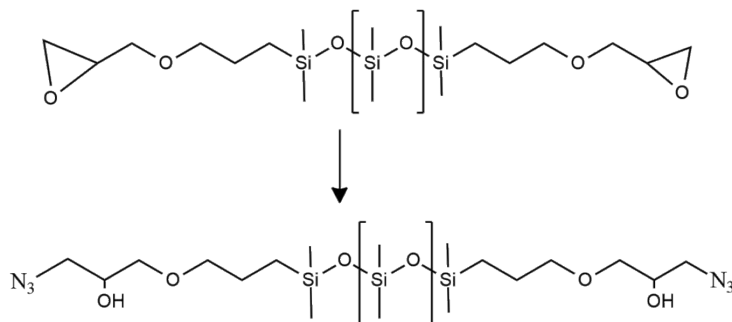
The high-resolution transmission electron microscopy (HRTEM) analyses were performed on a FEI Titan<sup>3</sup> 80-300 electron microscope with a c<sub>s</sub>-image aberration corrector (FEI Company) at 300 kV acceleration voltage. XPS analysis was performed using a XPS PHI Versa Probe 5000 spectrometer. The pressure in the analysis chamber was typically 1.1<sup>-9</sup> Torr. The XPS measurements were performed using a monochromatic AlK α radiation at 1486.6 eV. An neutralizer with a Ar gun was used during the XPS analysis to compensate charging effects. All NMR spectra were recorded on a Varian spectrometer (Gemini 400) at 400 MHz at 27 °C. DSC measurements were performed on a differential scanning calorimeter 204F1/ASC Phoenix from Netzsch. Crucibles and lids made of aluminum were used. Measurements were performed in a temperature range from -20 to 250 °C using heating rates of 5 K/min. As purge gas a flow of dry nitrogen (20 mL/min) was used for all experiments. C, H, N and O content analysis of the samples was performed using CHN PE 2400 Series II from Perkin Elmer. For evaluation of data the Proteus Thermal Analysis Software (Version 5.2.1) and OriginPro7 was used.

### **Synthesis of NRG0-Cu(I)**

GO (100 mg) was dispersed in water (30 mL) by ultrasonication. Subsequently, Copper acetate(II) (20 mg, 0,11 mmol) was added and the mixture was vigorously sonicated for 5 min, the mixture was stirred at room temperature overnight. After several washings with water and acetone the  $\text{Cu}^{2+}$ -GO was dried in vacuum oven at 40 degree C. 100 mg  $\text{Cu}^{2+}$ -GO was sonicated in ethanol resulting a uniform suspension (thick suspension). 200 mg of Melamine (2:1 ratio of N precursor to GO) is added to the above suspension and sonicated (~ 15 minute) further to obtain a uniform suspension. Ethanol from the resulting suspension was evaporated slowly at room temperature under constant stirring to obtain a powder residue. Residue has to be grinded and then dried. The dried powder is heat treated in a tubular furnace under Ar atmosphere. The temperature of the furnace was raised from room temperature to 600 °C with a heating rate of 20 °C/minute, followed by holding the temperature at 600 °C for 10 minutes. The furnace is cooled down to room temperature under Ar atmosphere. The resulting samples was washed with DI water and dried.

### **Synthesis of azide functionalized poly dimethylsiloxane**

A solution of sodium azide (1.93 g, 9.1mmol) in distilled water (3.4 mL) was added to a solution of epoxy-terminated PDMS ( $M_n=800$ ) (DP ~7, 2 g, 2.5 mmol) in propan-2-ol (13 mL). Then the solution was adjusted to pH 6 with glacial acetic acid. The reaction mixture was stirred at 50°C up to the complete disappearance of the starting material, followed by TLC (toluene/ethyl acetate). After dilution with diethyl ether and successive washings with saturated  $\text{NaHCO}_3$  and water, the organic layer was dried on  $\text{Na}_2\text{SO}_4$  to obtain azide functionalized PDMS as a yellowish oil.



### **Synthesis of alkyne functionalized PDMS**

The synthesis was carried out under a dry atmosphere of nitrogen. A three-necked round-bottom flask equipped with mechanical stirrer, reflux condenser and rubber septum was heated under vacuum and flushed with nitrogen several times. Hydroxyl terminated PDMS ( $M_n=550$ ) (DP~9 ,0.4 mmol, 220.0 mg), sodium hydroxide (6.0 eq, 2.4 mmol, 96 mg) and TBAB (0.04 eq, 0.01 mmol, 51 mg) were dissolved in distilled water (1.0 mL). Afterwards, propargyl bromide (6.0 eq, 2.4 mmol, 280 mg, 80.0 wt % solution in toluene) was added dropwise over a period of one hour

and then the temperature was increased to 60 °C and the reaction mixture was heated for 41 h at 60 °C. After the reaction has finished (TLC control, CHCl<sub>3</sub>) the reaction mixture was cooled down to room temperature. Afterwards, the solution was diluted with DCM (150.0 mL) and centrifuged (three times, 10 °C, 5000 rpm, 5 min) to separate the formed salt. The combined organic phases were extracted with distilled water (five times, 500.0 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was removed in vacuo and the crude product was purified by column chromatography (SiO<sub>2</sub>, 230–400 mesh, Merck (Darmstadt, Germany), CHCl<sub>3</sub>, R<sub>f</sub> = 0.62, blue stain) to obtain alkyne functionalized PDMS as a light-yellow liquid in a yield of 75%.

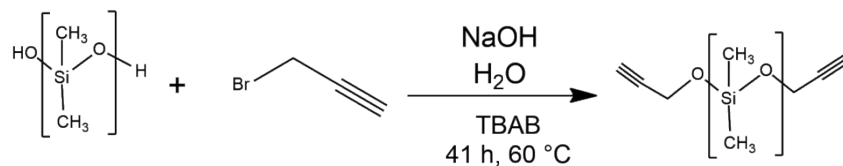


Table S1: Elemental analysis of GO, TRGO/Cu(I), and NRGO/Cu(I)

Sample	C %	H %	N %	O %
GO	76.27	2.16	-	21.57
TRGO/Cu(I)	91.06	1.18	-	7.76
NRGO/Cu(I)	85.93	0.93	9.28	3.86

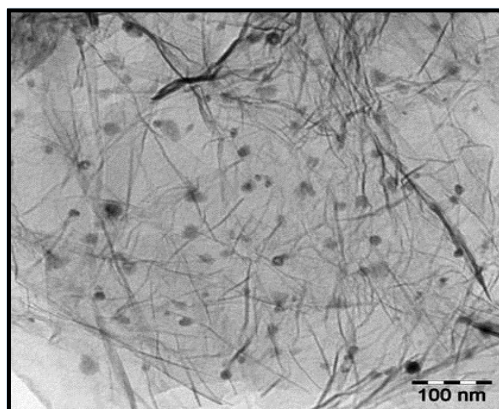


Figure S1: TEM image of TRGO/Cu(I)

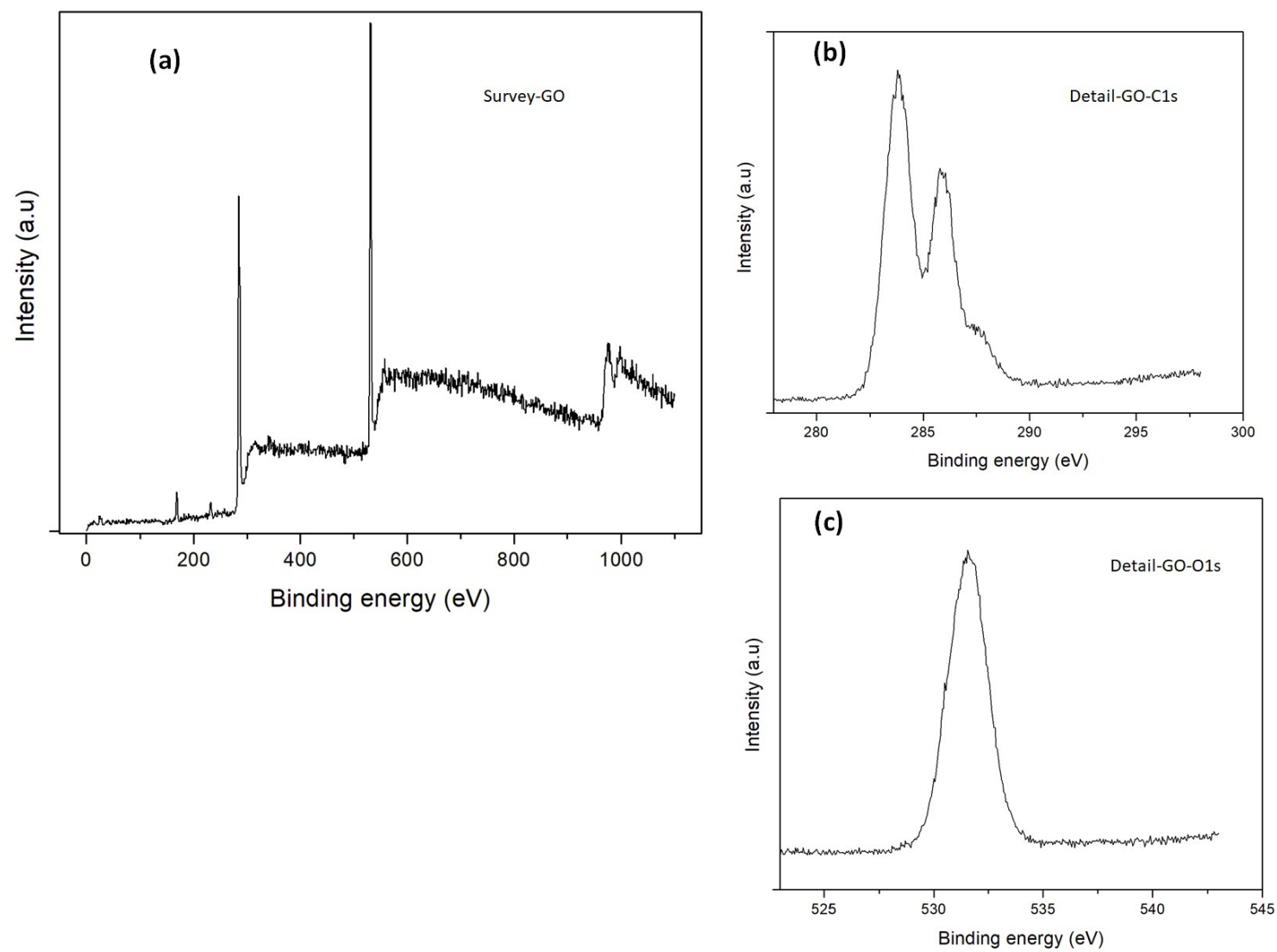


Figure S2: (a) X-ray photoelectron spectroscopy of GO. (b) High resolution XPS of element C, and (c) High resolution XPS of element O.

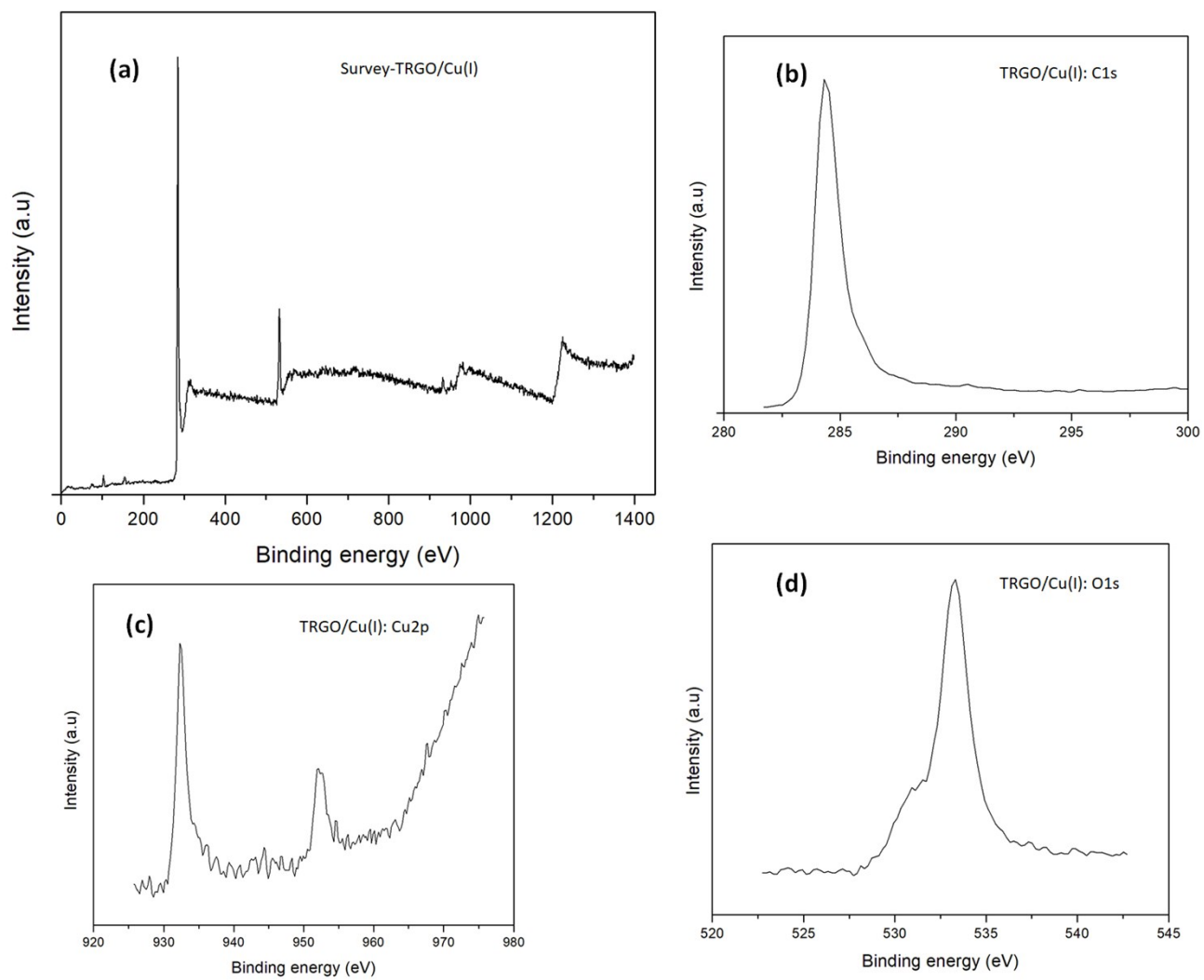


Figure S3: (a) X-ray photoelectron spectroscopy of TRGO/Cu(I). (b) High resolution XPS of element C. (c) High resolution XPS of element Cu. (d) High resolution XPS of element O.

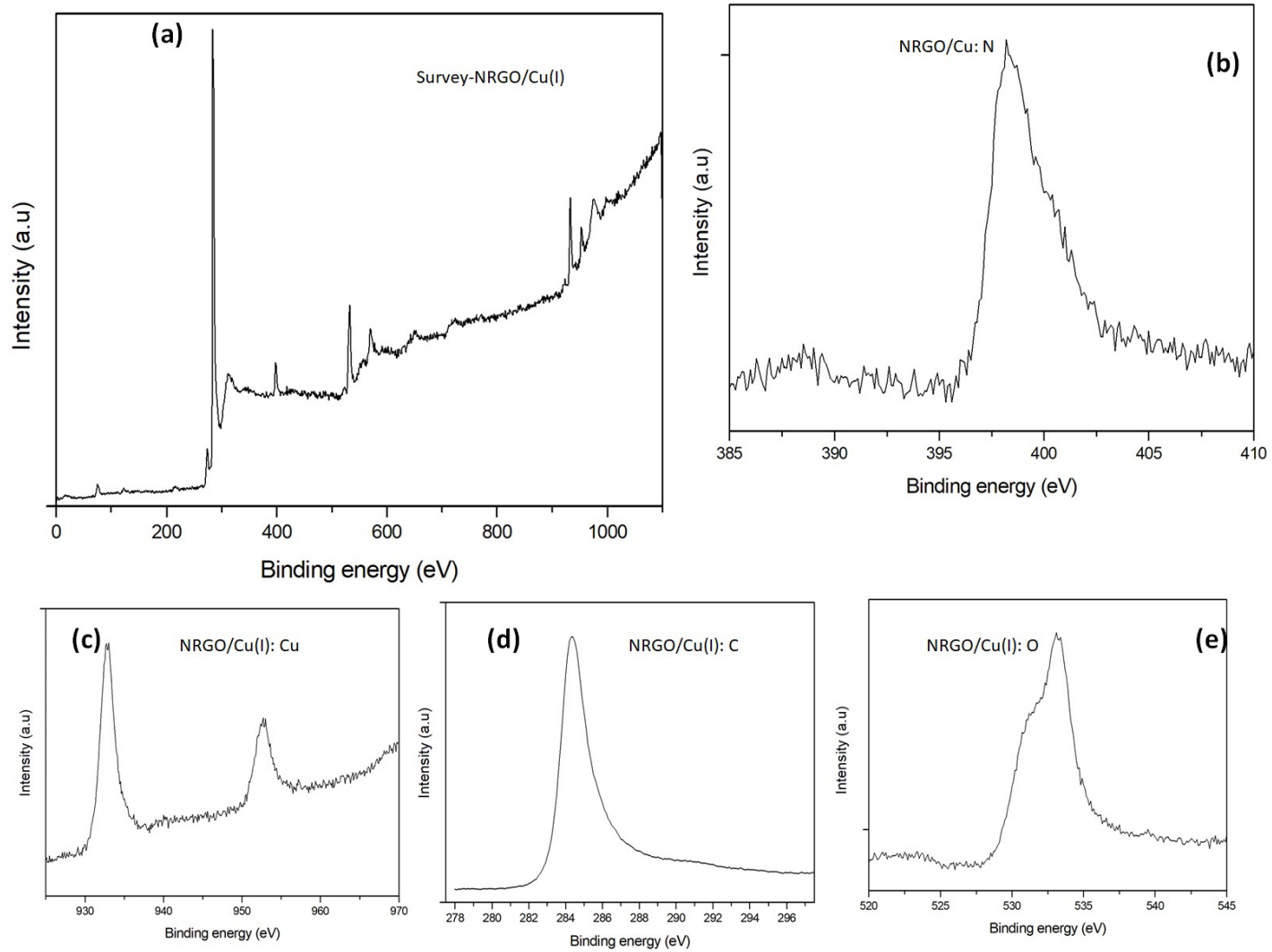


Figure S4: (a) X-ray photoelectron spectroscopy of NRGO/Cu(I). (b) High resolution XPS of element N. (c) High resolution XPS of element Cu. (d) High resolution XPS of element C. (e) High resolution XPS of element O.

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PDMS-N3

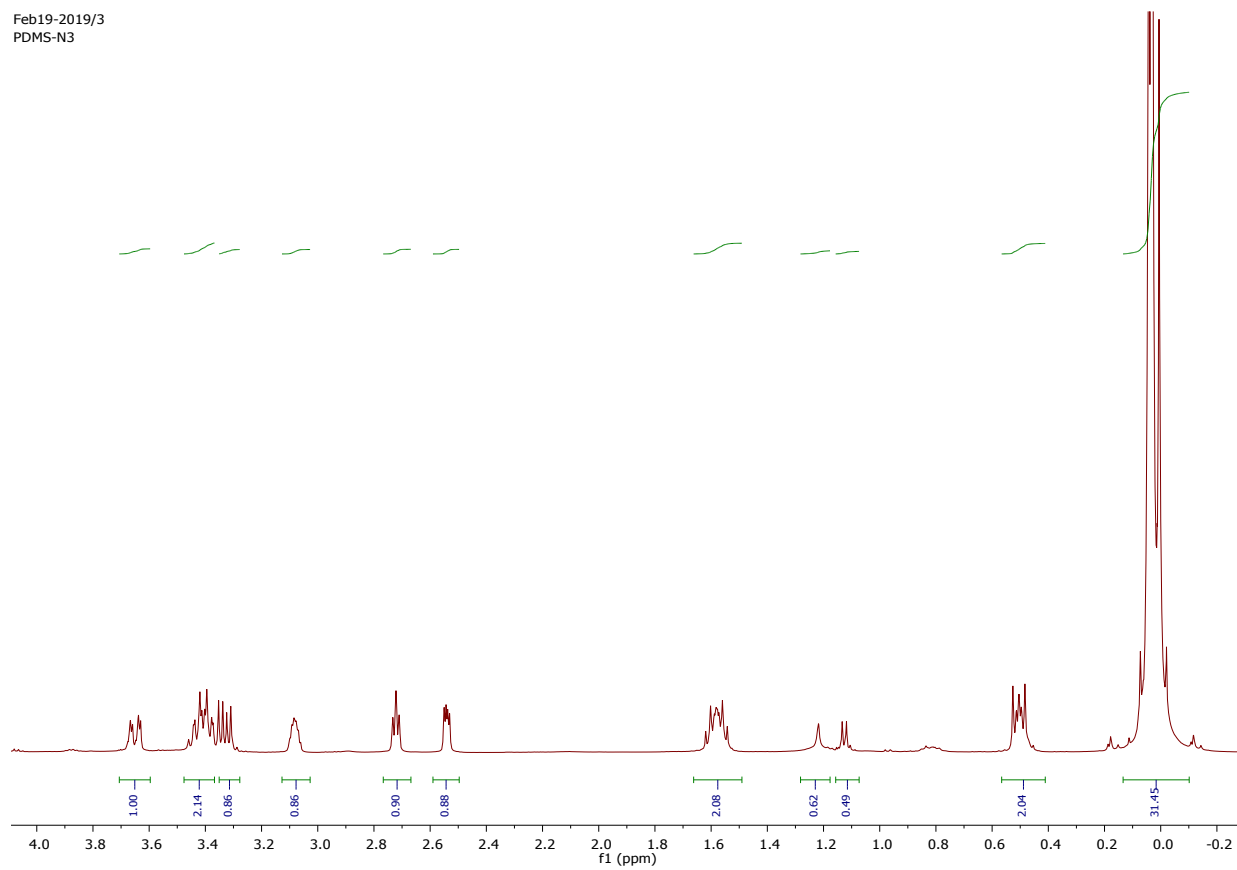


Figure S5: <sup>1</sup>H-NMR spectrum of PDMS-N<sub>3</sub>

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pdms-n3

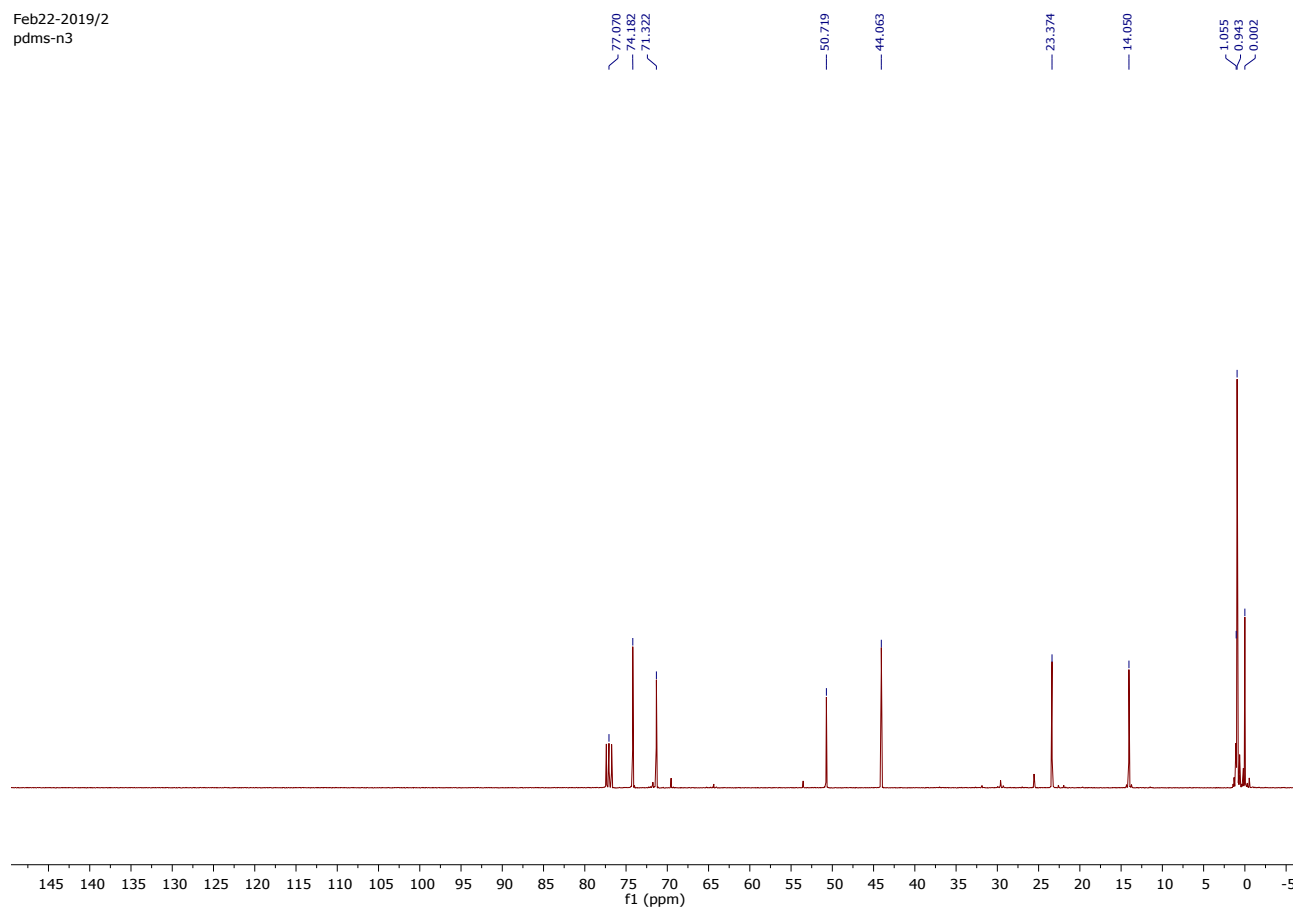


Figure S6:  $^{13}\text{C}$ -NMR spectrum of PDMS-N<sub>3</sub>



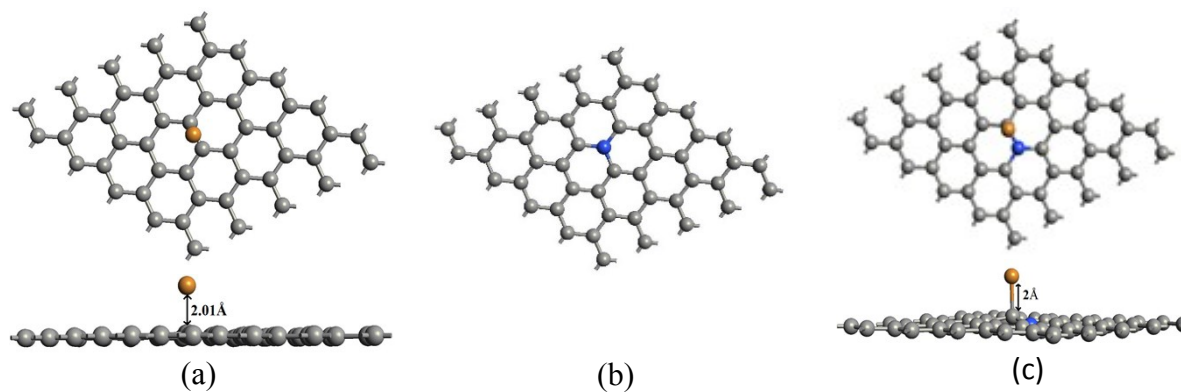


Figure S7. (a) Cu<sup>+</sup> adsorption on pristine graphene, (b) NG, (c) Cu<sup>+</sup> adsorption on NG

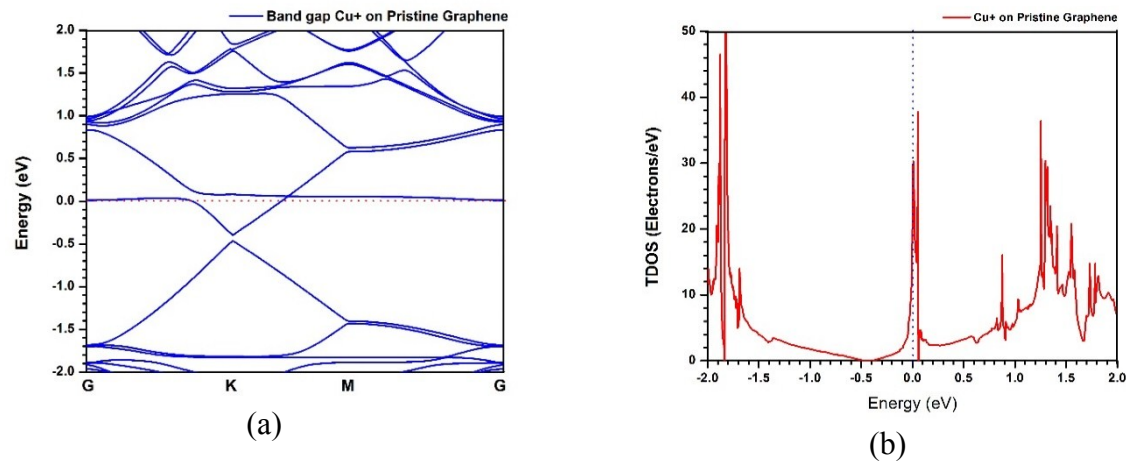
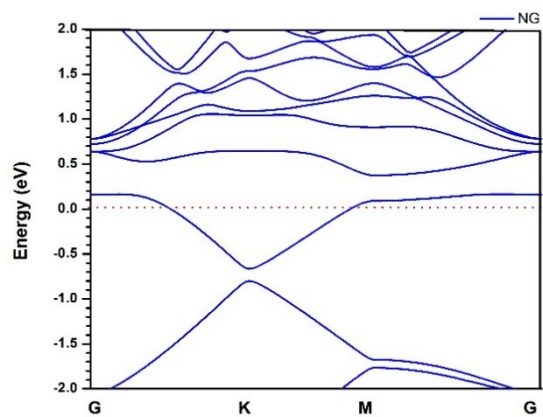
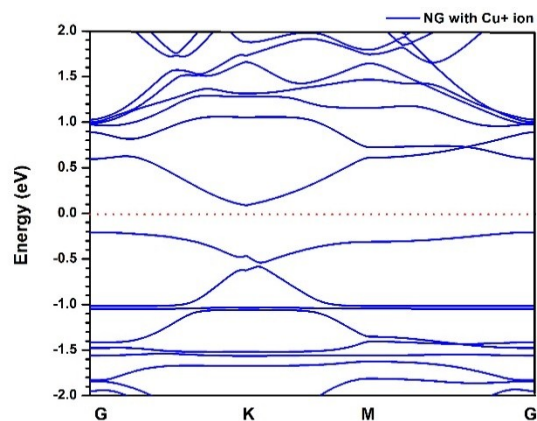


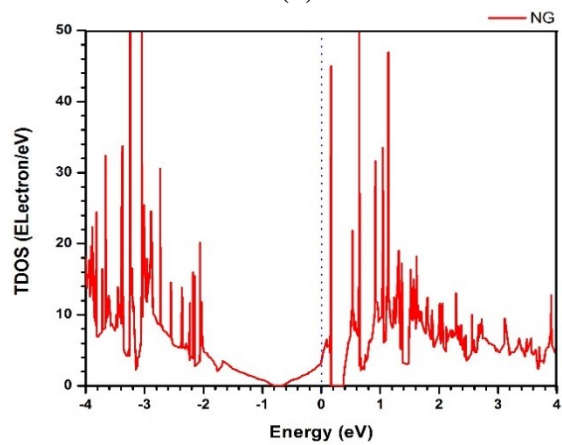
Figure S8: (a) Bandstructure, (b) TDOS of Cu<sup>+</sup> adsorption on pristine graphene.



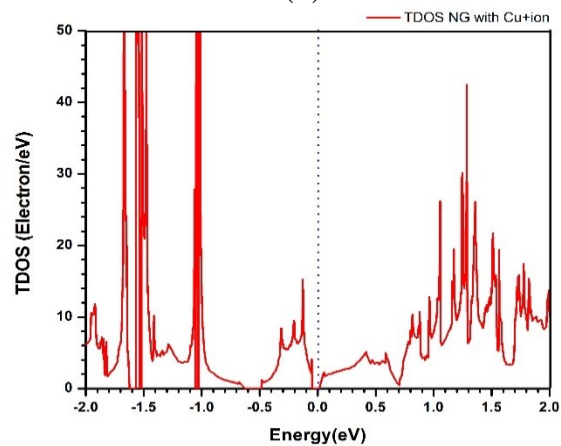
(a)



(b)

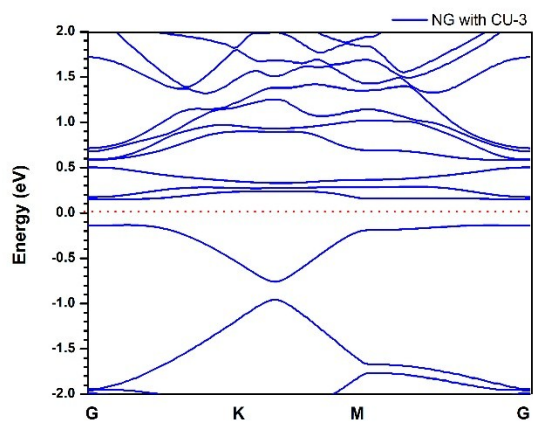


(c)

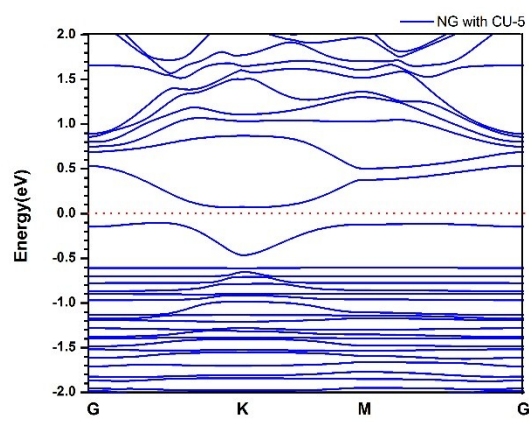


(d)

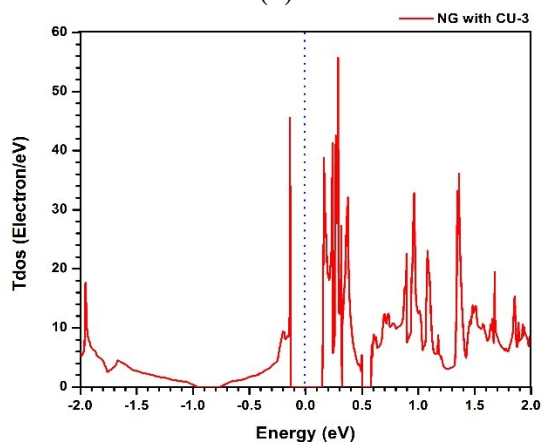
Figure S9: Bandstructure of (a) NG ,(b) NG with Cu<sup>+</sup>, Density of states of (c) NG ,(d) NG with Cu<sup>+</sup>



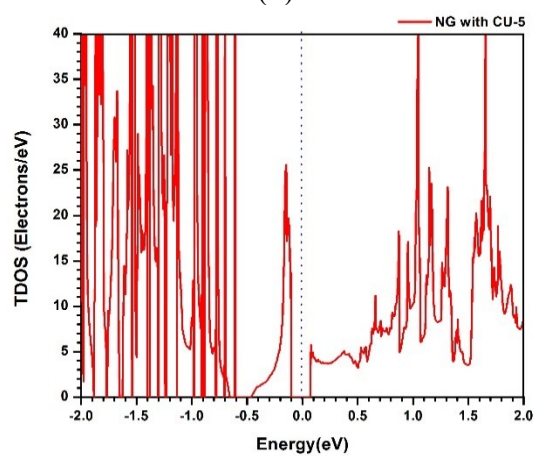
(a)



(b)



(c)



(d)

Figure S10: Band structure of (a) NG with CU-3, (b) NG with CU-5 and density of states of (a) NG with CU-3, (b) NG with CU-5.

Table S2: Comparison of band gap with increasing size of Cu<sup>+</sup> ion cluster.

System	Band Gap (eV)
NG with Cu <sup>+</sup> ion	0.29
NG with CU-3	0.28
NG with CU-5	0.17