

Electronic Supplementary Information (ESI) for
Copper nanoparticle decorated three dimensional graphene
with high catalytic activity for Huisgen 1,3-dipolar
cycloaddition

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Preparation of GO

The graphite powder (2.5 g) was first treated with a mixture of 12.5 mL of concentrated H₂SO₄ with 2.5 g K₂S₂O₈ and 2.5 g P₂O₅. The mixture was kept at 80 °C for 6 h. Subsequently, the mixture was cooled to room temperature and diluted with 500 mL DI water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight. The pre-oxidized graphite was then subjected to oxidation by Hummers's method. The pretreated graphite powder was put into cold (0 °C) concentrated H₂SO₄ (125 mL). Then KMnO₄ (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 °C by cooling. The mixture was then stirred at 35 °C for 4 h and then diluted with DI water (250 mL). Because adding water to concentrated sulfuric acid medium releases a large amount of heat, the dilution was carried out in an ice bath to keep the temperature below 50 °C. After adding all of the 250 mL DI water, the mixture was stirred for 2 h, and then an additional 750 mL DI water was added. Shortly thereafter, 20 ml 30% H₂O₂ was added to the mixture and the color of the mixture changed into brilliant yellow and began bubbling. The mixture was filtered and washed with 0.5 M HCl to remove metal ions, followed by 500 mL DI water to remove the acid, and then was dialyzed against DI water. The resulting GO solid was dried in air.^{s1}

Preparation of 3D Graphene

GO dispersion (3 mg/mL, 30 mL) was mixed uniformly with 120 µL of ethylenediamine (EDA) by sonication for 5 min. The resulting stable suspension was transferred into a 50 mL Teflon-lined autoclave and heated for 6 h at 120 °C for the synthesis of the 3D graphene hydrogel. After the subsequent freeze-drying, the 3D graphene was produced.^{s2} The nitrogenloading was determined to be 17.44 wt% by elemental analysis (CHN).

Preparation of 3D Graphene/Cu nanocomposite

The 3D graphene (100 mg) was ultrasonically dissolved in 50 mL of water. After that, CuNO₃·3H₂O (0.5 mmol) was added into the solution, the mixture was ultrasonically treated for 3 h. L-ascorbic acid (5 mmol) was gradually added into the solution and stirred for 24 h. The resulted precipitation was collected, washed with water (5 × 10 ml) and Ethanol (3 × 10), and was exposed to air for 4h. The atomic absorption spectroscopy (AAS) analysis gave the actual Cu contents as 2.97 mmol.g⁻¹ for 3D graphene/Cu nanocomposite.

General procedure for the 1,3-dipolar cycloaddition

A mixture of 3D graphene/Cu nanocomposite (5 mol % of Cu), aryl azide (1.0 mmol) and phenylacetylene (1.0 mmol) in EtOH:H₂O (1:1; 3 mL) was heated at 50 °C for 1 h. After completion of the reaction (TLC), the heterogeneous mixture was cooled to room temperature and the ethyl acetate was added to the flask and the catalyst was separated by centrifugation. The organic layer was dried over MgSO₄ and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. Obtained triazole was purified by recrystallization from EtOAc and *n*-hexane.

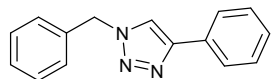
General procedure for the multicomponent 1,3-dipolar cycloaddition

A mixture of 3D graphene/Cu nanocomposite (5 mol % of Cu), alkyl/benzyl halide (1.0 mmol), sodium azide (1.2 mmol), phenylacetylene (1.0 mmol) in EtOH:H₂O (1:1; 3 mL) was heated at 50 °C for 3 h. After completion of the reaction (TLC), the heterogeneous mixture was cooled to room temperature and the ethyl acetate was added to the flask and the catalyst was separated by centrifugation. The products were extracted with ethyl acetate–water mixture. The organic layer was dried over MgSO₄ and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. Obtained triazole was purified by recrystallization from EtOAc and *n*-hexane.

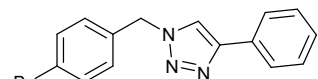
Characterization

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. Raman spectra were recorded on a Bruker SENTERR (2009) with an excitation beam wavelength at 785 nm. Diffraction data were collected on a STOE STADI P with scintillation detector, secondary monochromator and Cu-Kα1 radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy characterization was performed using an electron microscope Philips XL-30 ESEM. Transmission electron microscopy characterization was performed using a transmission microscope Philips CM-30 with an accelerating voltage of 150 kV. The concentration of copper was estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer and inductively coupled plasma optical emission spectrometer

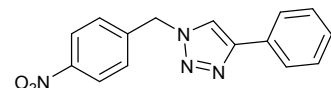
(ICP-OES) Varian Vista PRO Radial. $^1\text{H-NMR}$ spectra were recorded on a BRUKERDRX-300AVANCEspectrometer at 300.13. $^1\text{H-NMR}$ spectra were obtained in $\text{DMSO-}d_6$ using TMS as internal standard. Melting points of products were measured on an Elecrtothermal 9100 apparatus and are uncorrected.



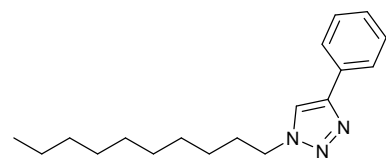
White solid, mp: 130-132 °C (lit.^{s3} mp: 129.0-129.5 °C). $^1\text{H NMR}$: (300 MHz, CDCl_3) δ (ppm): 5.65 (s, 2H), 7.30-7.46 (m, 8H), 7.84-7.97 (s, 2H), 8.66 (s, 1H).



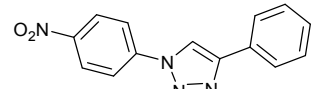
White solid, mp: 147-149 °C (lit.^{s3} 152.0-153.0°C). $^1\text{H NMR}$: (300 MHz, CDCl_3) δ (ppm): 5.65 (s, 2H), 7.33-7.85 (m, 9H), 8.63 (s, 1H).



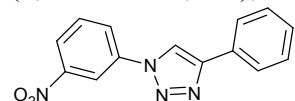
Yellow solid, mp: 152-154 °C (lit.^{s3} mp: 156-157 °C). $^1\text{H NMR}$: (300 MHz, CDCl_3) δ (ppm): 5.85 (s, 2H), 7.31-7.58 (m, 5H), 7.85 (d, $J = 7.2$ Hz, 2H), 8.25 (d, $J = 8.1$ Hz, 2H), 8.70 (s, 1H).



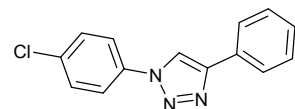
White solid, mp: 80-82 °C (lit.^{s4} mp: 83.6-84.5°C). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 0.84 (s, 3H), 1.22 (s, 14H), 1.85 (s, 2H), 4.38 (t, $J = 6.6$ Hz, 2H), 7.32-7.47 (m, 3H), 7.84 (d, $J = 7.2$ Hz, 2H), 8.59 (s, 1H).



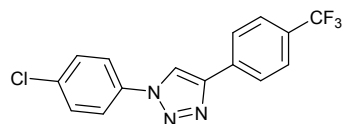
Yellow solid, mp: 245-247 °C (lit.^{s5} mp: 250-252 °C). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.39-7.56 (m, 3H), 7.97 (d, $J = 7.5$ Hz, 2H), 8.27 (d, $J = 9$ Hz, 2H), 8.15 (d, $J = 8.7$ Hz, 2H), 8.55 (s, 1H).



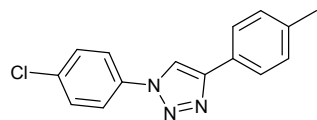
Yellow solid, mp: 203-205 °C (lit.^{s6} mp: 192-194 °C). $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm): 7.36-7.53 (m, 3H), 7.88-7.95 (m, 3H), 8.31-8.45 (m, 2H), 8.76 (s, 1H), 8.53 (s, 1H);



White solid, mp: 228-230 °C (lit.^{s6} mp: 224-226 °C). $^1\text{H NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.40-7.54 (m, 3H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.93-8.02 (m, 4H), 9.34 (s, 1H)



White solid, mp: 194-196 °C. ¹H-NMR (300 MHz, CDCl₃), δ (ppm): 7.74 (d, *J* = 7.5 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 8.16 (d, *J* = 8.1 Hz, 2H), 9.53 (s, 1H)



White solid, mp: 244-246 °C ¹H NMR (300 MHz, CDCl₃) δ (ppm): 2.35 (s, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 8.82 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 9.25 (s, 1H)

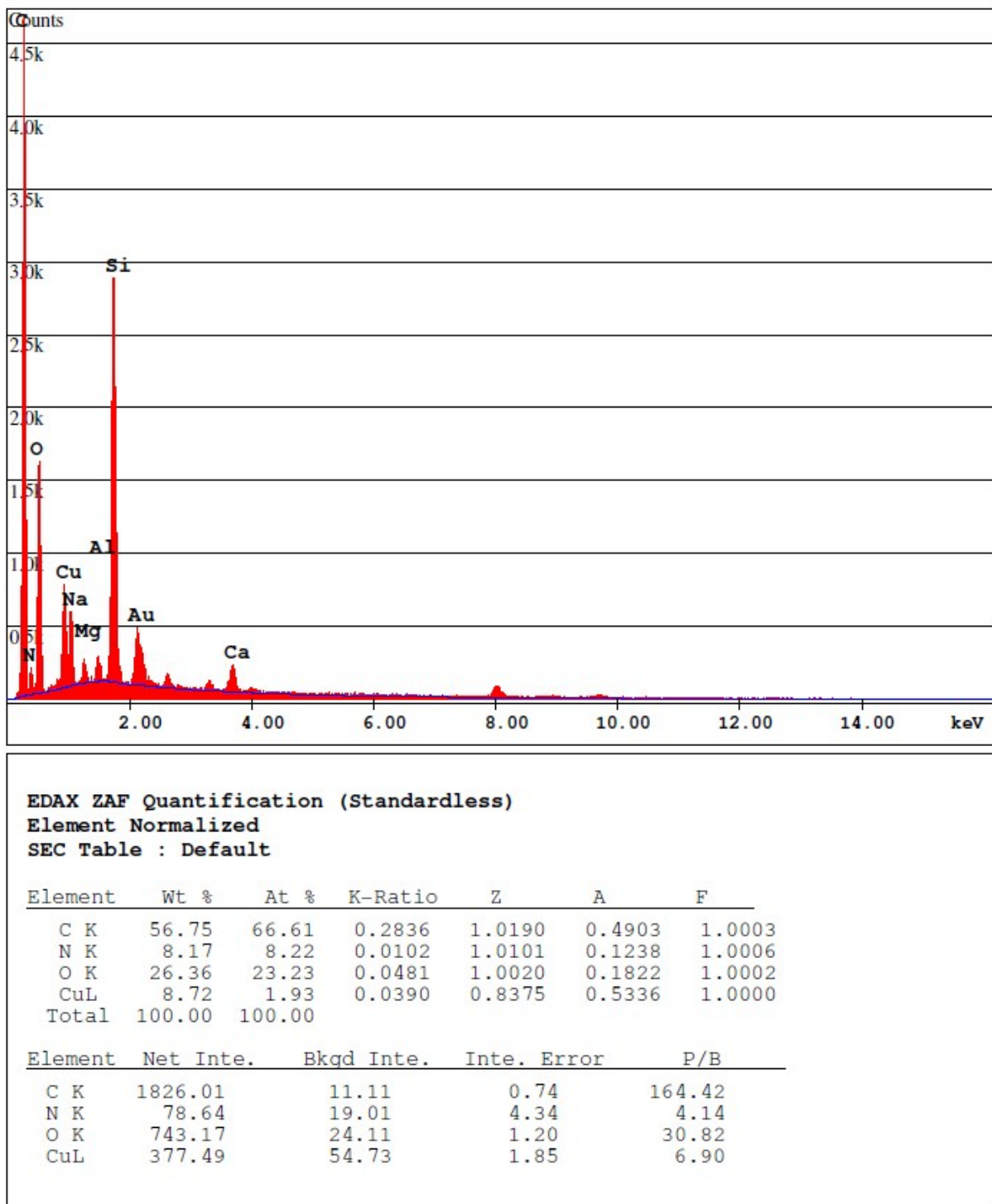


Fig S1. EDS result for 3D graphene/Cu

The peaks of elements Na, Mg, Al, Si and Ca correspond to sample holder of SEM and lamel (Fig S2).

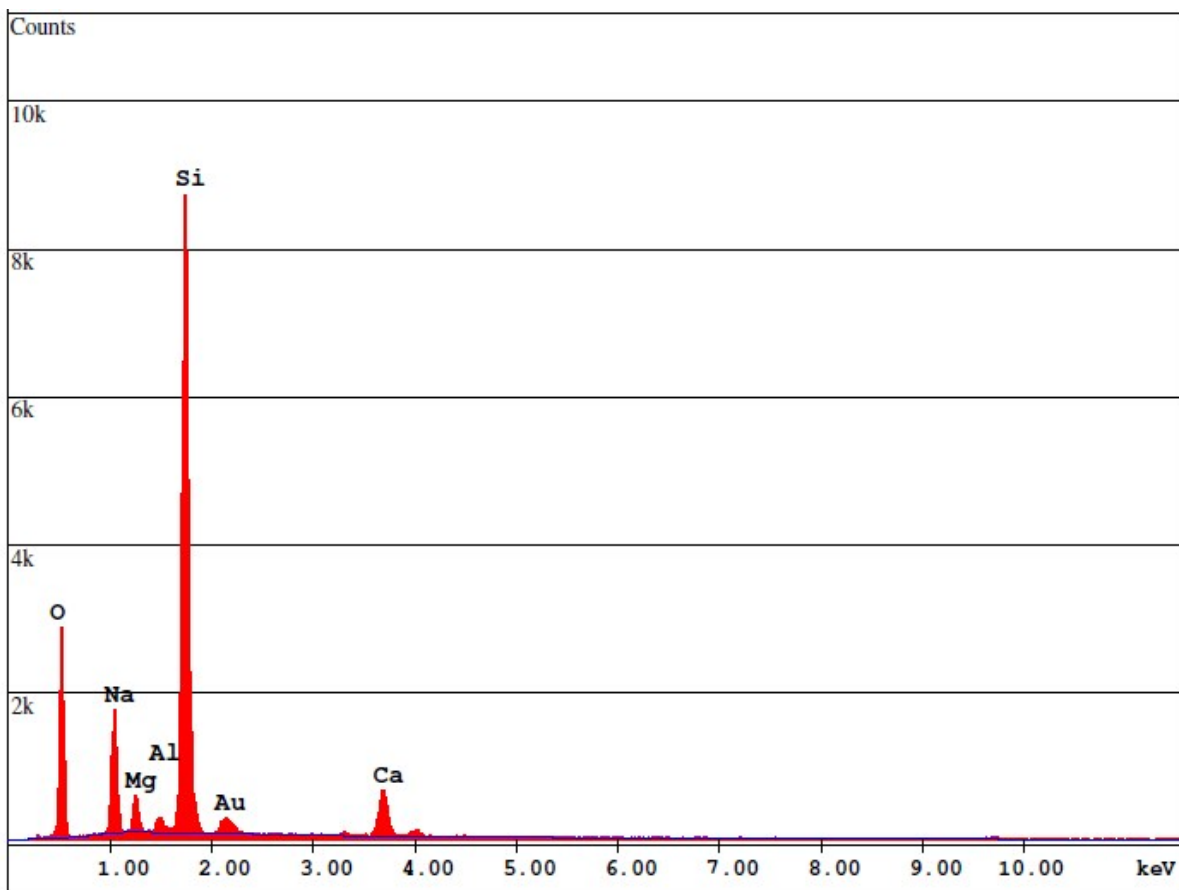


Fig S2. The EDS result for sample holder of SEM and label

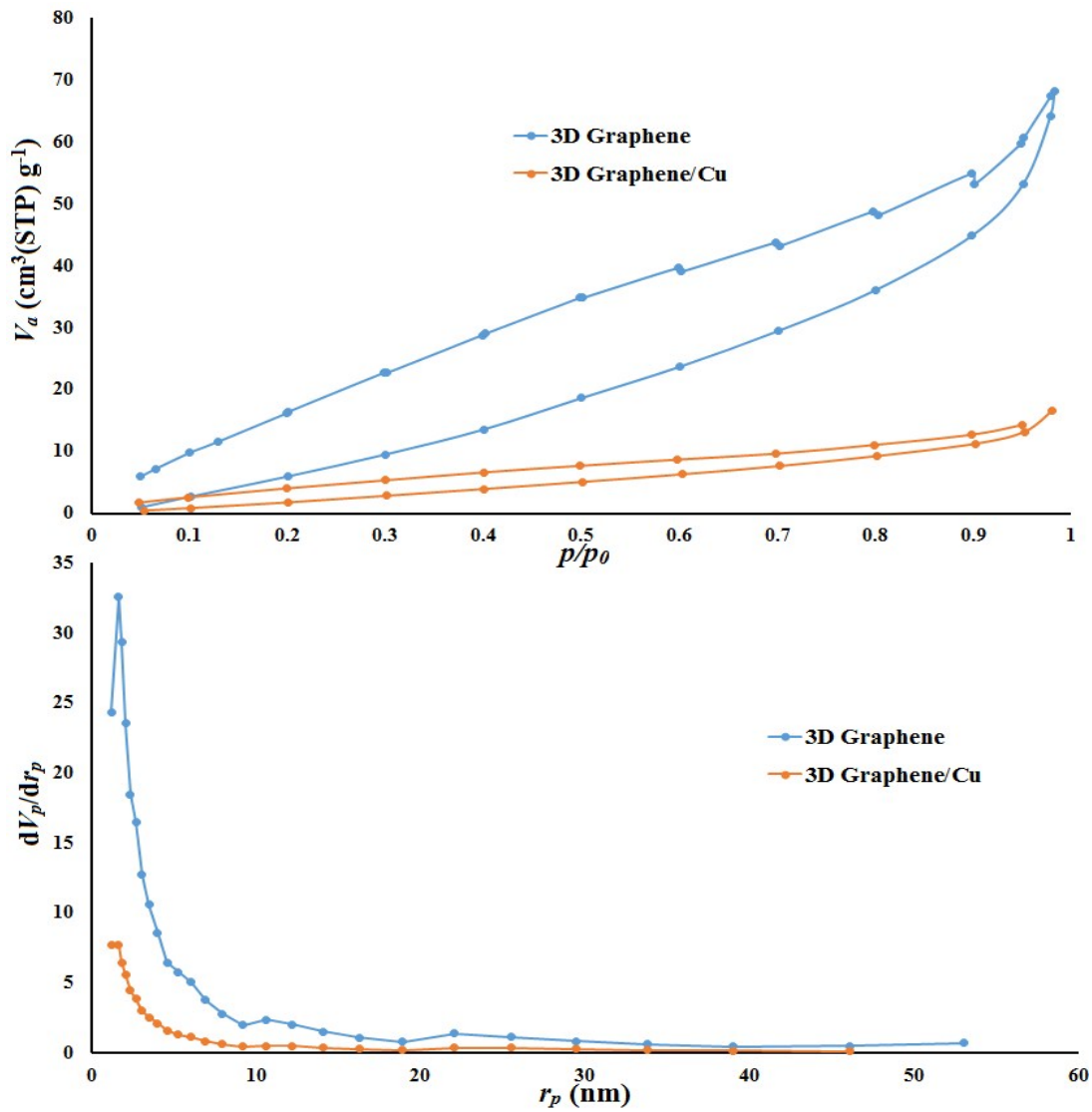


Fig S3. Nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves of the 3D graphene and 3D graphene/Cu composites

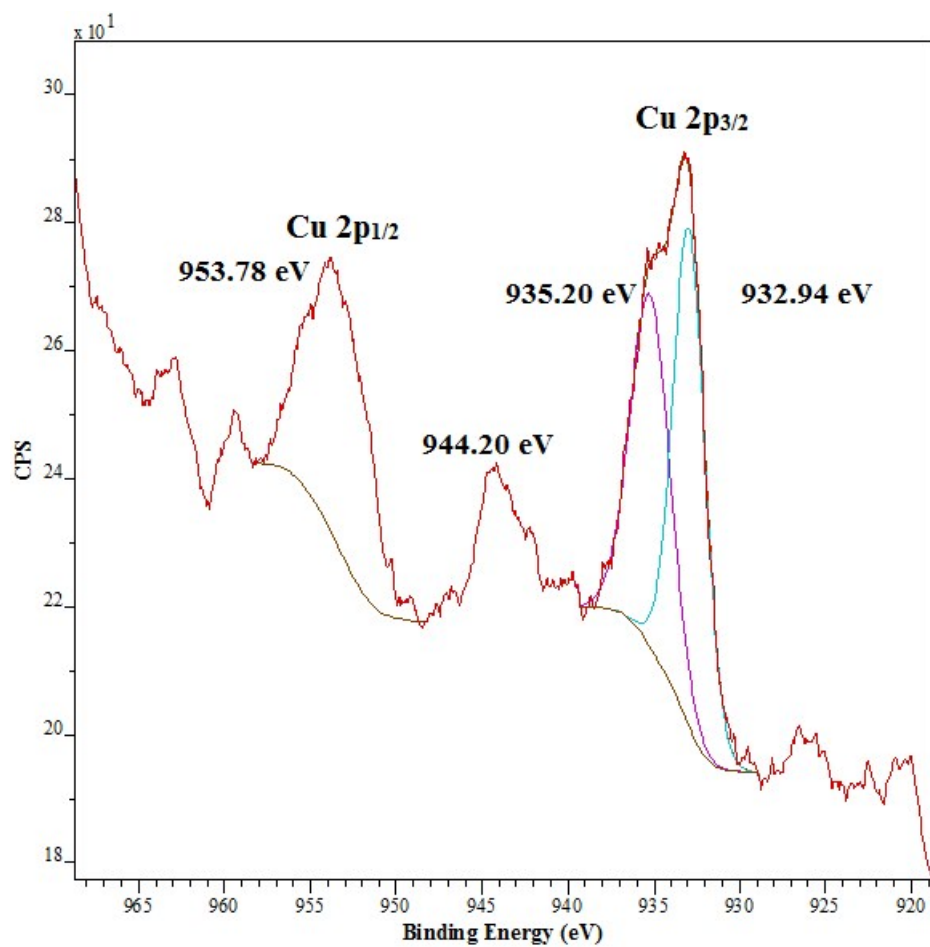


Fig S4. XPS spectrum of the Cu 2p core level region of 3D graphene/Cu nanocomposite

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