Supplementary Information

Innovative Copper-Based Heterogeneous Catalyst for Chan-Lam Cross-Coupling

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Dedicated to King Vratislav II

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Characterization techniques

For evaluate the material properties, following techniques were used: Atomic absorption spectroscopy (**AAS**), High resolution transmission electron microscopy/Energy dispersive X-ray spectroscopy (**HRTEM/EDS**), Transmission electron microscopy/Scanning electron microscopy (**TEM/SEM**) Attenuated total reflection-Fourier transform infrared spectroscopy (**ATR-FTIR**), **Raman** spectroscopy, X-ray photoelectron spectroscopy (**XPS**), X-ray roentgen diffraction (**XRD**), BET surface area analysis (**BET**).

XPS

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Nexsa G2 XPS system (Thermo Fisher Scientific) equipped with a monochromatic Al-Kα source (photon energy 1486.7 eV). All spectra were acquired under a vacuum of 1.2×10^{-7} Pa at room temperature (20 °C). The analyzed area on each sample corresponded to a spot of 200 μm in diameter.

Survey spectra were recorded with a pass energy of 150.00 eV and an energy step of 1.0 eV, while high-resolution spectra were obtained with a pass energy of 30.00 eV and an energy step of 0.1 eV. Charge compensation was applied for all measurements. The spectra were processed using Avantage 6.5.1 software (Thermo Fisher Scientific).

BET

BET isotherm measurements for material characterization were performed using a 3Flex instrument, version 5.02 (Micromeritics). Sample mass: 0.2916 g, Analysis free space: 56.0744 cm^3, Low pressure dose: None, Automatic degas: No, Comments: cca. 30 BET points + 14 points up to 0.965 P/P_0, Adsorptive: N_2, Analysis bath temperature: 77.064 K, Thermal correction: No, Ambient free space: 16.2321 cm^3, Equilibration interval: 10 s, Sample density: 1.000 g cm^{-3}

Raman

Raman spectra were acquired using a DXR Raman microscope with a 532 nm laser, full-range grating, and a spectral resolution of 0.5 cm^{-1} FWHM. A 25 μm slit and a 10×/0.25 objective were used. Laser power: 5 mW (GO), 9 mW (rGO and Cu-rGO), Number of exposures: 30 Exposure time: 2 s.

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XRD

X-ray diffraction (XRD) analysis was performed using a D8 ADVANCE diffractometer (Bruker) equipped with a Co Kα radiation source and a LYNXEYE position-sensitive detector, operated in Bragg–Brentano para-focusing geometry.

HRTEM, EDS, TEM, SEM

Scanning Electron Microscopy (SEM) was conducted using a Hitachi SU6600 microscope operating at an accelerating voltage of 15 kV. Energy Dispersive Spectrometry (EDS) data were acquired using a Thermo Noran System 7 with a Si(Li) detector at an accelerating voltage of 15 kV and an acquisition time of 300 s.

For SEM/EDS sample preparation, a small amount of powder was placed in an Eppendorf tube, mixed with purified water, and ultrasonicated for 5 min. The resulting suspension was drop-cast onto a copper grid with a holey carbon film and air-dried.

Transmission Electron Microscopy (TEM) was performed using a JEOL JEM 2010F microscope operated at an accelerating voltage of 160 kV. High-resolution TEM (HRTEM) images were obtained with a TITAN 60–300 microscope equipped with an X-FEG emission gun, operating at 80 kV. This instrument includes a Cs image corrector and a STEM high-angle annular dark-field (HAADF) detector, achieving a point resolution of 0.06 nm in TEM mode.

Elemental mappings were obtained using STEM–EDS with an acquisition time of 20 min. For HRTEM analysis, powder samples were dispersed in ethanol, ultrasonicated for 5 min, and one drop of the suspension was deposited onto a copper grid with a holey carbon film. The samples were dried at room temperature before analysis.

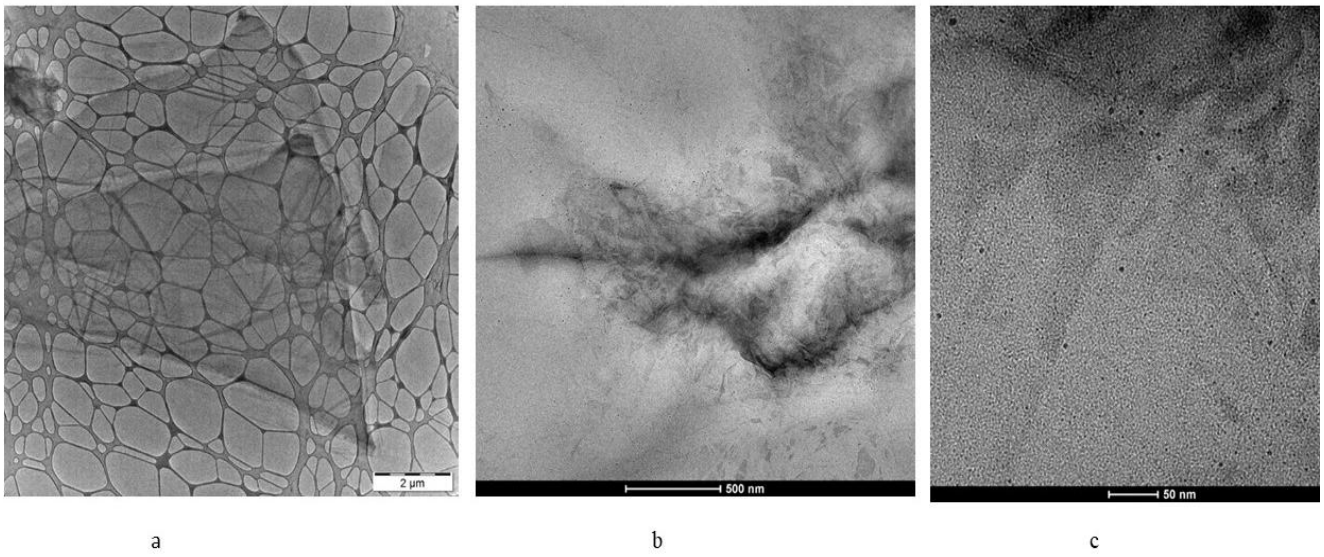


Figure S1: TEM images: (a) graphene oxide, (b) Cu-rGO composite, (c) same composite as (b), magnified view.

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AAS

Atomic absorption spectroscopy (AAS) measurements were performed using a ContrAA 300 atomic absorption spectrometer (Analytik Jena) operated with Aspect CS software.

The instrument was equipped with an optimized high-resolution echelle double monochromator, including a quartz prism pre-monochromator. Wavelength accuracy was maintained through automatic neon wavelength correction. A xenon short-arc lamp operating in UV hot-spot mode was used, featuring automatic hot-spot tracking and simultaneous drift correction. Detection was carried out with a CCD line detector characterized by high quantum efficiency and enhanced UV sensitivity.

Procedure specification: burner: 50 mm, burner high: 1 mm, oxidation agent: acetylene, flow rate: 60 L/h, wavelength: 324.7570 nm, type: absorption, read time: 3.0 s.

ATR-FTIR

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were collected using an iS50 ATR infrared spectrometer (Nicolet). Measurement parameters: Number of scans: 32, resolution:4, data spacing: 1.928 cm^{-1}, detector: DTGS Br, beamsplitter: KBr, source: Polaris™ long-life IR source.

The sample was milled in a mortar to a fine powder, dispersed in 2% nitric acid, and ultrasonicated for 10 minutes. Before measurement, it was filtered and diluted.

General procedure and monitoring of the catalytic experiment

General procedure: A nitrogen nucleophile (0.526 mmol; 1 equiv.), arylboronic acid (1.16 mmol; 2.2 equiv.), and triethylamine (Et_3N; 146 µL; 1.99 mmol; 2 equiv.) were dissolved in 1 mL of methanol (MeOH). After the addition of the Cu/rGO catalyst (20.2 mg; 0.05 equiv.), the resulting suspension was stirred for 24 hours at 30 °C[1].

The reaction mixture was then filtered through diatomaceous earth (Celite) and washed with MeOH. The filtrate was concentrated under reduced pressure and further purified by column chromatography on a silica gel column (40–63 µm particle size).

To monitor the reaction progress and analyse the products, were used TLC and UPLC-MS.

Thin-layer chromatography (TLC) was performed using pre-coated silica gel plates. Detection was carried out under UV light (at 250 or 366 nm), followed by visualization using solutions of $KMnO_4$, ninhydrin, or PMA (phosphomolybdic acid).

UPLC-MS analysis was performed using a system composed of an Acquity UPLC chromatograph equipped with a PDA and MS detector (Waters). A C18 column X-Select HSS T3 (2.5 µm, 3.0 mm × 50 mm, with a guard column, Waters) was used at 30 °C with a flow rate of 600 µL/min. The mobile phases (MP) were: (A) 0.01 M ammonium acetate in H_2O, (B) acetonitrile (ACN). Elution was carried out using a gradient program, linearly programmed according to the specific method

[1] 30 °C was chosen as a temperature close to ambient, yet precisely standardized.

(normal, slow, etc.). The ESI source operated at a capillary voltage of 3 kV, with a desolvation temperature of 350 °C and a source temperature of 120 °C.