Supporting Information

for

Bio-inspired Multinuclear Copper Complexes Covalently Immobilized on Reduced Graphene Oxide as Efficient Electrocatalysts for the Oxygen Reduction Reaction**

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1. Catalysts preparation

1.1 rGO-TADPyCu catalyst composite preparation

Graphene oxide (GO) was obtained by harsh oxidation of the graphite powder (SP-1 graphite, purchased from Bay Carbon Corporation) according to the modified Hummers method.[S1] The purified GO (18.0 mg) and 6-((triisopropylsilyl)ethynyl) pyridin-3-amine[S2](1.5 g, 5.46 mmol) were dispersed in 45 mL of CH_3CN under sonication, and isoamyl nitrite (1.0 mL, 7.44 mmol) was then added. The solution was stirred at 80 °C for 24 h under N_2 atmosphere. After cooling to room temperature, the solution was centrifuged, and the resultant sediment was washed with *N*, *N*-dimethylformamide (DMF, ×3), and deionized water (×3). The resulting GO-pyridin-ethynyl precursor was then dispersed in 45 mL of DMF by sonication. Tetrabutylammonium fluoride (1.0 M in THF, 0.1 mL, 0.1 mmol) was added to the solution at 0 °C under N_2 atmosphere, and the solution was warmed up to RT and further stirred for 3 h. Then $CuSO_4 \cdot 5H_2O$ (6.0 mg, 0.024 mmol), sodium ascorbate (25 mg, 0.12 mmol), and 2-azidopyridine[S3] (75 mg, 0.62 mmol) were added to the solution, and the mixture was stirred at 50 °C for 36 h under N_2 atmosphere. The resulting GO-TADPy product was collected by centrifugation and then thoroughly washed with DMF (×3), 50 mM EDTA aqueous solution (×3), deionized water (×3), and ethanol (×3), respectively.

Caution: Azide compounds are potentially explosive and must be handled with care in a small amount.

The obtained GO-TADPy was then reduced under hydrazine atmosphere. GO-TADPy (10 mg) was dispersed in 5 mL of ethanol by sonication for 3 h in order to get small pieces of GO-TADPy. After centrifugation, the sediment was dried under vacuum overnight. The resultant solid was kept in a small open glass vial, and the vial was then put into a stainless autoclave. A hydrazine hydrate solution (80%, 5 mL) was added to the autoclave. Be careful to keep the solid non-contact with the hydrazine solution. Then, close the autoclave tightly and put it in an oven, followed by heating at 150 °C for 24 h. After cooling to RT, the reduced product rGO-TADPy was taken out and thoroughly washed with deionized water and ethanol.

Lastly, the rGO-TADPyCu catalyst was prepared by mixing the above rGO-TADPy with

$CuCl_2$. The reduced rGO-TADPy (10 mg) was dispersed in 20 mL of CH_3CN by sonication for 30 min, to which $CuCl_2$ (20 mg) was added. The solution was further stirred at RT for 24 h. The final product was obtained by centrifugation, and it was washed with deionized water (×3) and methanol (×3).

1.2 Control catalyst (rGO/TAPyCu) preparation.

Preparation of 2-((4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)methyl)pyridine (TAPy): To a solution of 2-azidopyridine (0.75 g, 6.25 mmol) and ethynylbenzene (0.65 g, 6.37 mmol) in DMF (10 mL), $CuSO_4 \cdot 5H_2O$ (60 mg, 0.24 mmol) and sodium ascorbate (260 mg, 1.24 mmol) was added to the above mixture. Then the solution was heated to 50 °C for 36 h. Reaction was monitored by TLC. After completion of the reaction, the reaction solution was poured into 150 mL of water. The resultant precipitates were filtrated and washed with deionized water (×3), small amount of ethanol, and dried under vacuum. The crude product thus obtained was purified by column chromatography with CH_2Cl_2/petroleum ether (V:V = 3:1) as eluent to afford a yellow solid (0.45 g, Yield, 28%). **^{1}H NMR** (DMSO-d_6, 400 MHz) δ: 9.39 (s, 1H), 8.66–8.64 (m, 1H), 8.21–8.14 (m, 2H), 8.06–8.04 (m, 2H), 7.61–7.57 (m, 1H), 7.52–7.48 (m, 2H), 7.42–7.38 (m, 1H). **ESI-MS** *m/z* ($[M+1]^+$): calcd. 223.09, found 223.1.

Preparation of TAPyCu: The above prepared **TAPy** (0.40 g, 1.8 mmol) and $CuCl_2 \cdot 2H_2O$ (0.31 g, 1.8 mmol) were mixed in 40 mL of CH_3CN. The solution was stirred at RT for 24 h. The resultant precipitates were filtrated and washed with CH_3CN (×3), and dried under vacuum. Yield: 0.36 g, 69%. **HR ESI-MS** *m/z* ($[M-Cl]^+$): calcd. for $C_{26}H_{20}ClCuN_8$: 542.0795, found: 542.0769 (Figure S4).

Preparation of rGO/TAPyCu: The composite was prepared by mixing reduced graphene oxide (13.2 mg) with **TAPyCu** (0.5 mg) in CH_3CN, and the suspension solution was stirred for 16 h at RT. The rGO/TAPyCu was obtained by centrifugation and dried under vacuum.

1.3 Control catalyst (rGO/TADPyCu) preparation.

Preparation of 2,2'-(1H-1,2,3-triazole-1,4-diyl)dipyridine (TADPy): TADPy was obtained by a click reaction according to the reported literature.[S4] **^{1}H NMR** ($CDCl_3$, 500 MHz) δ: 9.21 (s, 1H), 8.66 (d, 1H), 8.55 (d, 1H), 8.25 (d, 2H), 7.95 (dt, 1H,), 7.83 (dt, 1H), 7.37 (m, 1H), 7.29

(m,1H). ESI-MS *m/z* $[M+H]^+$: calcd. for $[C_{12}H_{10}N_5]^+$: 224.09; found: 224.1.

Preparation of TADPyCu: The above prepared TADPy (0.448 g, 2.0 mmol) and $CuCl_2{\cdot}2H_2O$ (0.376 g, 2.2 mmol) were mixed in 40 mL of CH_3CN. The solution was stirred at RT for 24 h. The resultant precipitates were filtrated and washed with CH_3CN (×3), and dried under vacuum. Yield: 0.40 g, 58%. **MALDI-MS** *m/z* ($[M+MeOH]^+$): calcd. for $C_{25}H_{22}Cl_2Cu_2N_{10}O$: 674.0, found:674.4 .

Preparation of rGO/TADPyCu: The composite was prepared by mixing reduced graphene oxide (13.2 mg) with TADPyCu (0.5 mg) in CH_3CN, and the suspension solution was stirred for 16 h at RT. The rGO/TADPyCu was obtained by centrifugation and dried under vacuum.

2. Catalyst characterization

The morphology of the rGO-TADPyCu composite was examined TEM (JEOL JEM-2011) operating at 100 kV. AFM images were obtained with a Veeco/DI atomic force microscope, and XPS data were collected on a Thermo Escalab 250 XPS instrument with a monochromatic Al Kα X-ray source ($h\nu$ =1486.6 eV). All binding energies were referenced to the C1s peak (284.6 eV) arising from adventitious carbon. Raman spectra were collected on a confocal microscopy Raman spectrometer (Renishaw, RM-1000) with a laser excitation wavelength of 532 nm. FTIR spectra were recorded on a Shimadzu Fourier transform infrared spectrometer (IRPrestige-21). ^{1}H NMR spectra were recorded on Bruker AV400 spectrometer (400 MHz). ESI mass spectra were performed on Solarix70 FT-MS mass spectrometer. MALDI mass spectra were taken on Thermo Fisher Scientific LTQ FT Ultra mass spectrometer.

3. Preparation of catalyst ink:

Catalyst (7.0 mg, rGO-TADPyCu, rGO/TAPyCu, or rGO) was mixed in a glass vial with 50 μL of a 5 wt% dispersion solution of Nafion (Aldrich) and 450 μL of methanol. The ink was sonicated in a bath sonicator for 3 h. The catalyst ink (8 μL) was applied to the surface of a glassy carbon disk (0.196 cm^2), and the solvent was evaporated at room temperature under air to produce a uniform film with a catalyst loading of ~0.6 mg cm^{-2}.

20 wt% Pt on Vulcan XC-72 (JM HiSPEC 3000) was used as the reference catalyst, and the Pt loading was ~0.2 mg_{Pt} cm^{-2}.

4. Electrochemical measurement

4.1 General: An RRDE (Pine Instruments) with a 5.0 mm diameter glassy carbon disk and Pt ring (geometric area 0.110 cm^{-2}) was used to evaluate catalyst performance on a CH Instrument Model 760D potentiostat in a standard three-electrode cell, with a graphite rod (diameter: 4.0 mm) as the counter electrode. In 0.1 M KOH electrolyte, a Hg/HgO electrode was used as the reference electrode. In 0.1 M phosphate buffer electrolyte, a Ag/AgCl electrode was used as the reference electrode. The glassy carbon disk was polished with a 5.0 μm alumina suspension and then with a 0.3 μm suspension to afford a mirror finish. Then, the electrode was rinsed and sonicated with double distilled water, followed by drying under vacuum. All the potentials in this study were reported with respect to the reversible hydrogen electrode (RHE). All cyclic voltammetry (CV) and RRDE tests were performed at room temperature with a scan rate of 10 mV s^{-1}. The electrolyte was bubbled with O_2 for 30 min prior to each experiment, and O_2 purging was maintained over the electrolyte during electrochemical measurements. Before the test measurement, the electrode was pre-treated by the repeated cycling of the potential between 0.0 and 1.2 V versus RHE at a sweep rate of 100 mVs^{-1} to remove any surface contamination. A 30s potential hold at the open cell potential preceded every polarization experiment. The ring potential was set to 1.3 V versus RHE. The ring collection efficiency (N) in RRDE experiments was 0.16 as measured using 10 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl solution. High purity water (≥ 18.25 MΩ·cm) was used for preparing buffers and aqueous solutions.

4.2 Catalyst electrochemical evaluation

For RDE measurement: Koutecky–Levich plots (J^{-1} vs. $\omega^{-1/2}$) were analyzed at various electrode potentials. The slopes of their best linear fit lines were used to calculate the number of electrons transferred (n) on the basis of the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}}$$

where J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities, $B = 0.62nFC_{O_2}D^{2/3}\upsilon^{-1/6}$, ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed), n is transferred electron number, F is the Faraday constant, C_{O_2} is the concentration of dissolved oxygen in electrolyte, D is the diffusion coefficient of dissolved

oxygen, and υ is the kinematic viscosity of the electrolyte. 0.1 M KOH, $Co_2 = 1.2\times10^{-6}$ mol cm^{-3}, $Do_2 = 1.9\times10^{-5}$ cm^2 S^{-1}, υ = 0.01 cm^2 S^{-1}, F = 96485 Cmol^{-1})

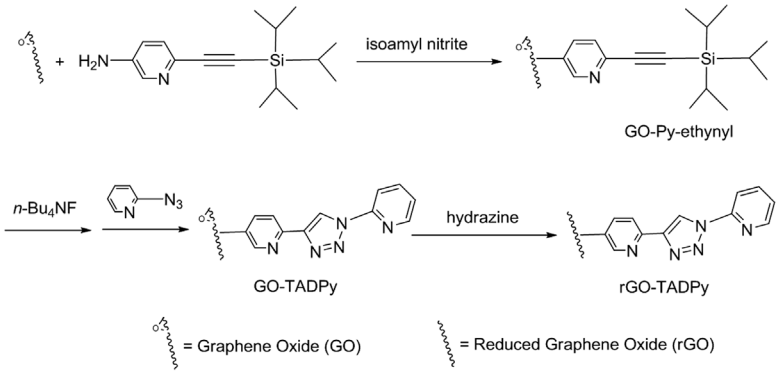
For RRDE measurements: The H_2O_2 yield and the electron transfer number (n) were calculated from RRDE data following the equations:

$$H_2O_2\% = \frac{2\times I_r}{(N\times I_d)+I_r}\times 100$$

$$n = 4\times\frac{I_d}{I_d + I_r/N}$$

where I_r is the ring current, I_d is the disk current, and N is the collection efficiency.

For RHE calibration: The RHE calibration was performed in high purity H_2-saturated (99.999%) electrolyte with a Pt wire as the working electrode. The potential at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. The high purity H_2 (99.999%) was provided from a hydrogen generator by electrolyzing of pure water.



Scheme S1 Schematic route for the preparation of the rGO-TADPy.

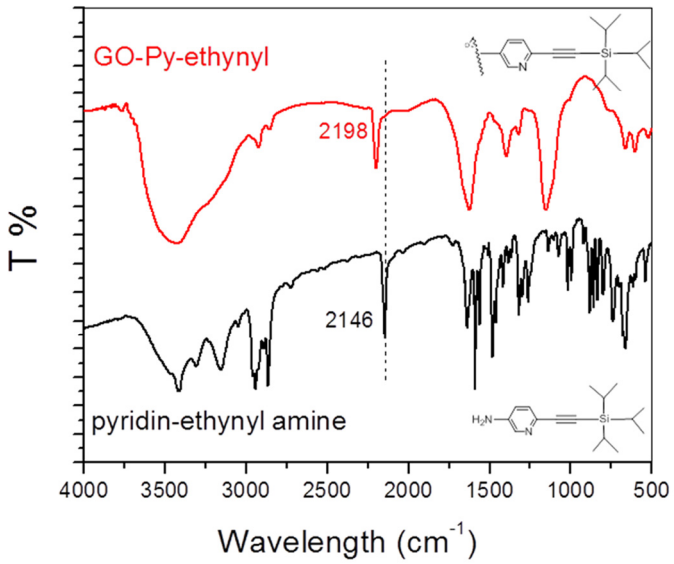


Figure S1 FT-IR spectra of the pyridin-ethynyl-amine reactant (black) and the GO-pyridin-ethynyl product (red).

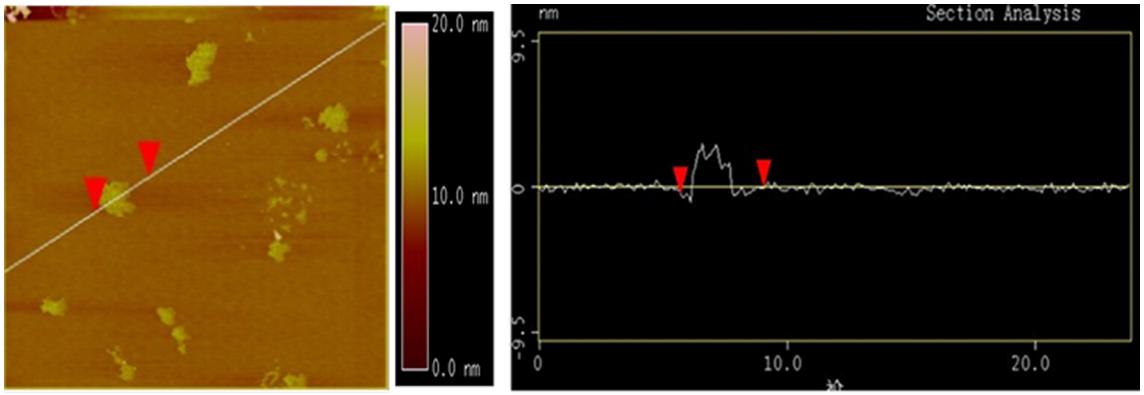


Figure S2 AFM images of rGO-TADPyCu.

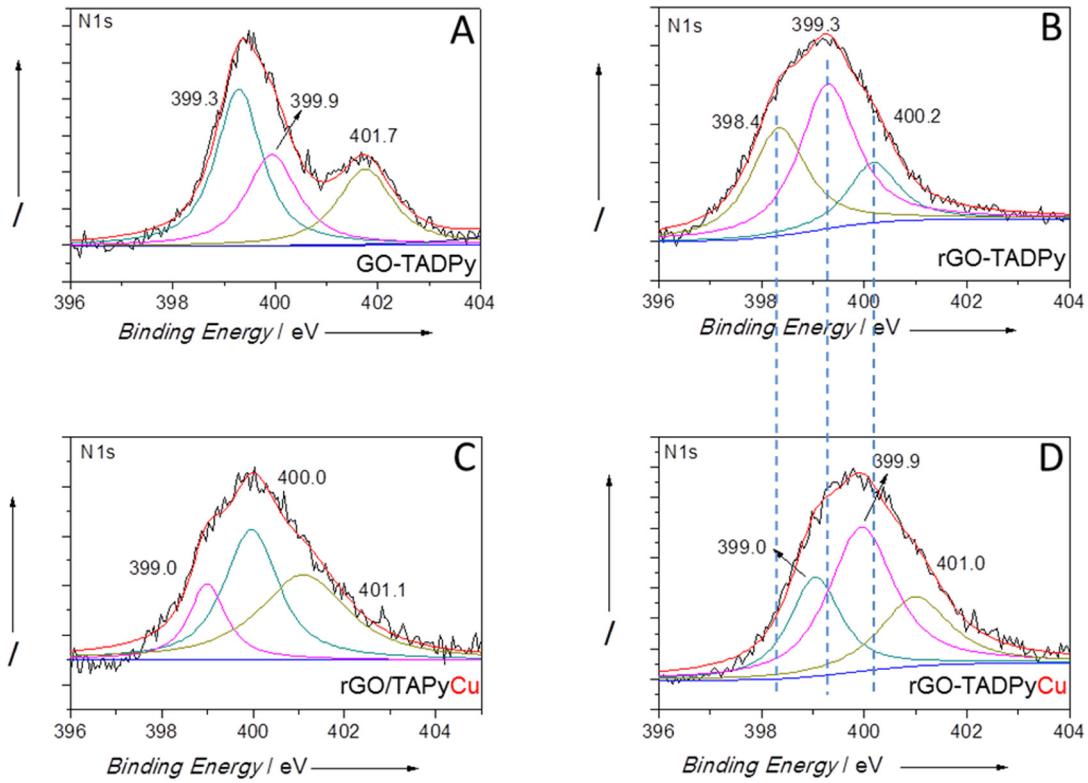


Figure S3 High resolution XP N1s spectra of GO-TADPy (A), rGO-TADPy (B), rGO/TAPyCu (C), and rGO-TADPyCu (D).

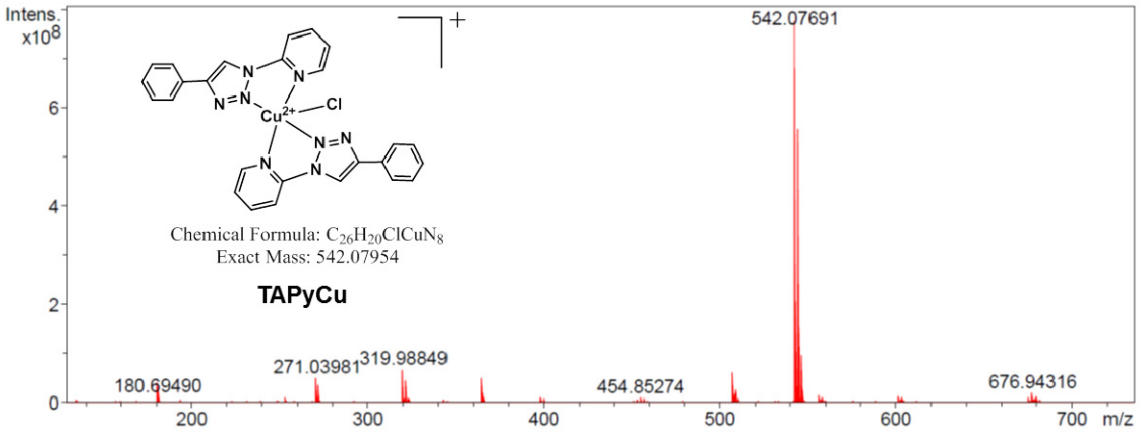


Figure S4 ESI-MS spectrum of TAPyCu.

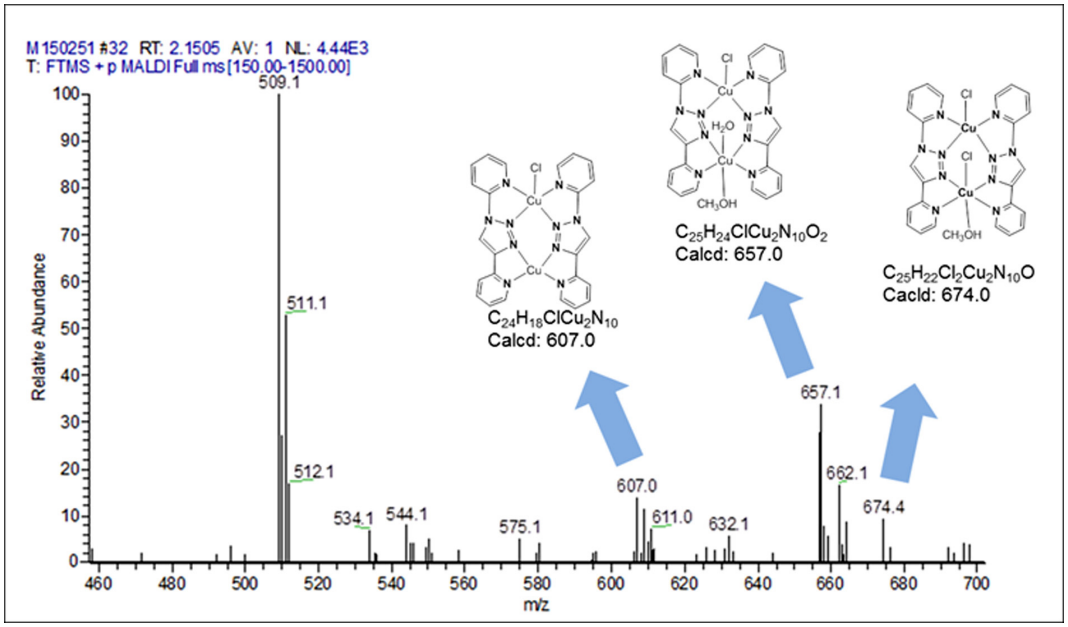


Figure S5 MALDI-MS spectrum of TADPyCu.

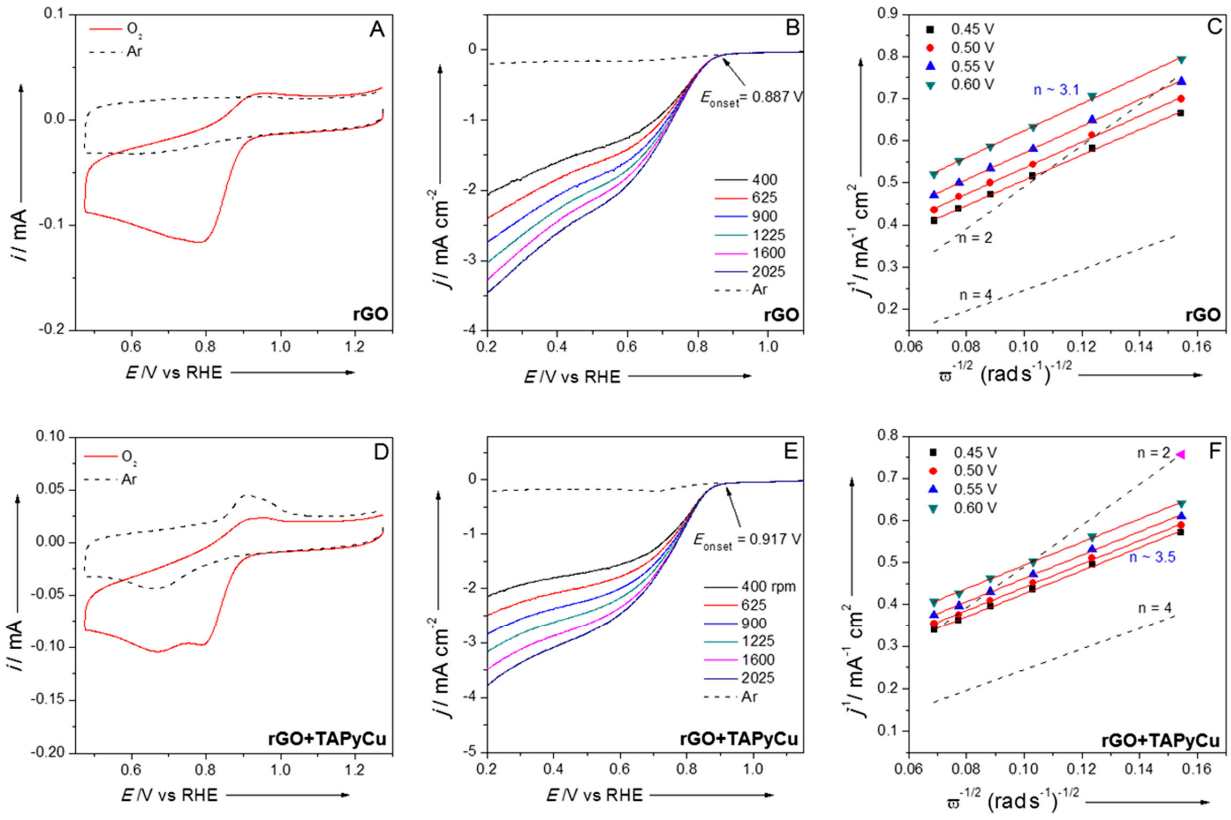


Figure S6 (A) Cyclic voltammograms of rGO in Ar (dotted black) and O_2-saturated (red solid) 0.1 M KOH solution. (B) Rotating-disk voltammograms of rGO (loading 0.6 mg cm^{-2}) in O_2-saturated 0.1 M KOH solution at different rotation rates indicated. The dotted line indicates the background when scanned in Ar-saturated solution. (C) Koutecky–Levich plots at different potentials for rGO. Scan rate, 10 mVs^{-1}. Theoretical $2e^-$ and $4e^-$ reduction processes are shown as dotted lines. (D) Cyclic voltammograms of rGO/TAPyCu in Ar (dotted black) and O_2-saturated (red solid) 0.1 M KOH solution. (E) Rotating-disk voltammograms of rGO/TAPyCu (loading 0.6 mg cm^{-2}) in O_2-saturated 0.1 M KOH solution at different rotation rates indicated. The dotted line indicates the background when scanned in Ar-saturated solution. (F) Koutecky–Levich plots at different potentials for rGO/TAPyCu. Scan rate, 10 mVs^{-1}. Theoretical $2e^-$ and $4e^-$ reduction processes are shown as dotted lines.

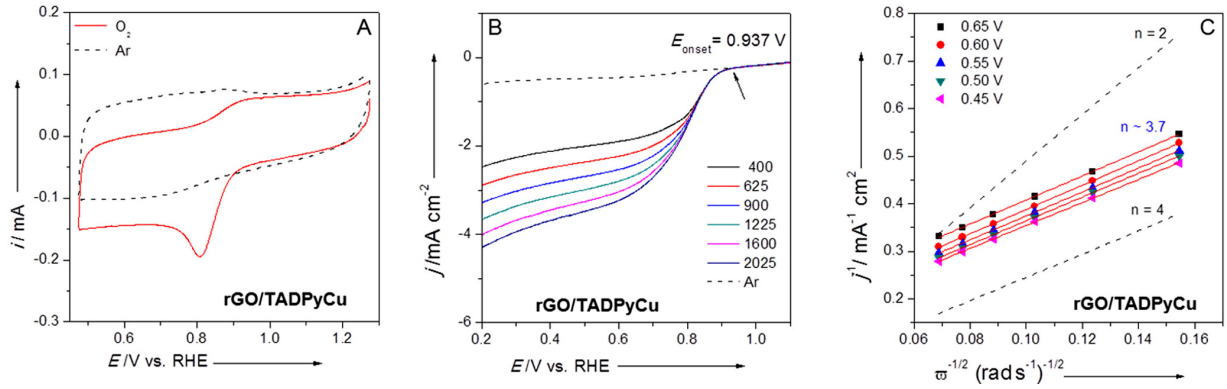


Figure S7 (A) Cyclic voltammograms of rGO/TADPyCu in Ar (dotted black) and O_2-saturated (red solid) 0.1 M KOH solution. (B) Rotating-disk voltammograms of rGO/TADPyCu (loading 0.6 mg cm^{-2}) in O_2-saturated 0.1 M KOH solution at different rotation rates indicated. The dotted line indicates the background when scanned in Ar-saturated solution. (C) Koutecky–Levich plots at different potentials for rGO/TADPyCu. Scan rate, 10 mVs^{-1}. Theoretical $2e^-$ and $4e^-$ reduction processes are shown as dotted lines.

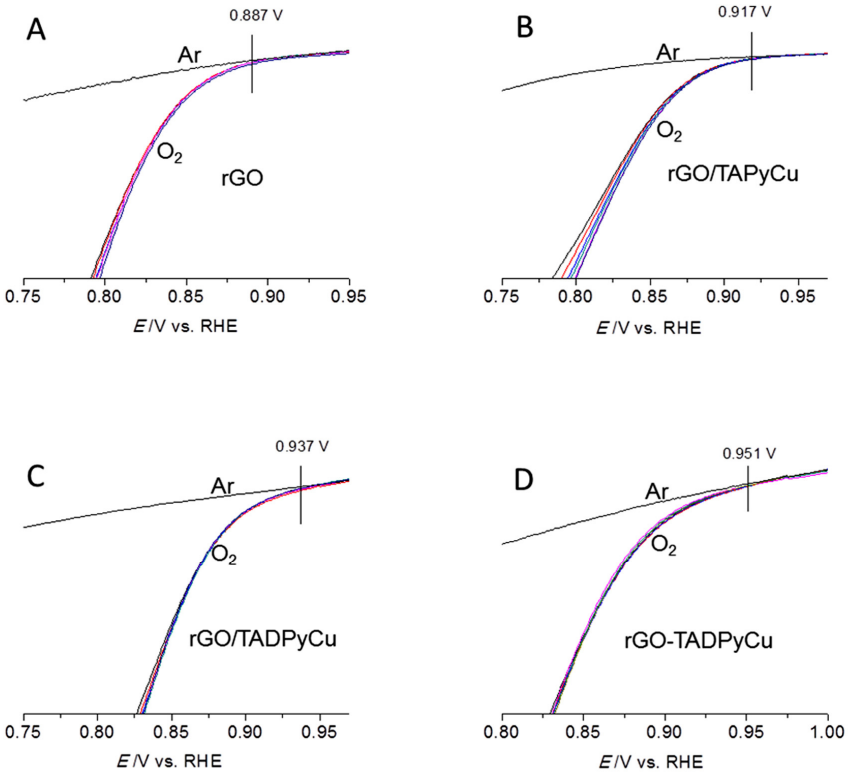


Figure S8 The onset potential for ORR (A) rGO, (B) rGO/TAPyCu, (C) rGO/TADPyCu, (D) rGO-TADPyCu. The E_{onset} is defined here as the potential where the current deviates from that of the background under Ar atmosphere.

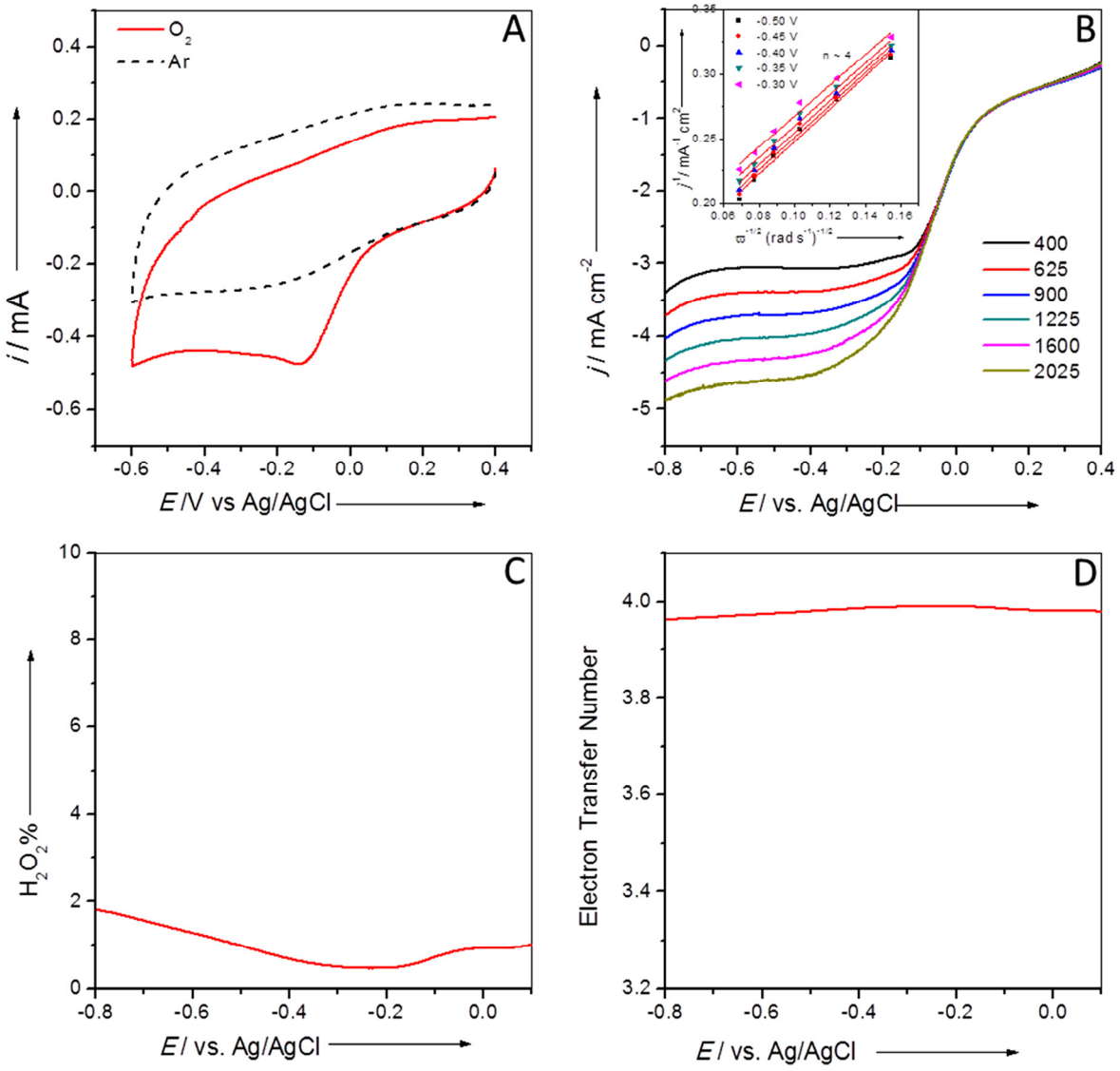


Figure S9 (A) Cyclic voltammograms of rGO-TADPyCu in Ar (dotted black) and O_2-saturated (red solid) 0.1 M phosphate buffer solution (pH 6.4). (B) Rotating-disk voltammograms of rGO-TADPyCu (loading 0.6 mg cm^{-2}) in 0.1 M phosphate buffer solution (pH 6.4) at different rotation rates indicated. The inset shows the corresponding Koutecky–Levich plots at different potentials. Scan rate, 10 mVs^{-1}. (C) Peroxide yield and (D) electron transfer number of the ORR catalyzed by the rGO-TADPyCu catalyst in O_2-saturated 0.1 M phosphate buffer solution (pH 6.4).

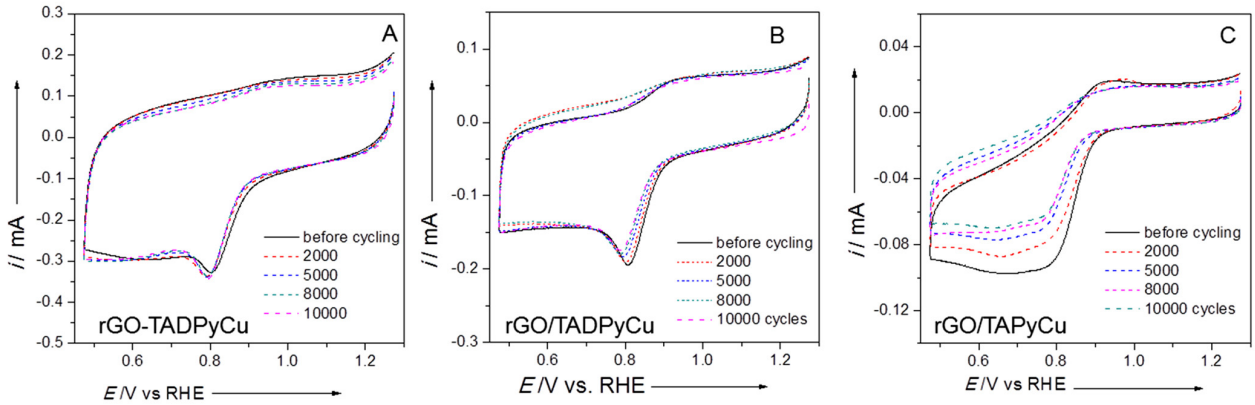


Figure S10 Cyclic voltammograms of rGO-TADPyCu (A), rGO/TADPyCu (B), and rGO/TAPyCu (C) in O_2-saturated 0.1 M KOH solution. The first, 2000th, 5000th, 8000th, and 10000th curves were shown, respectively. Scan rate, 50 mVs^{-1}.

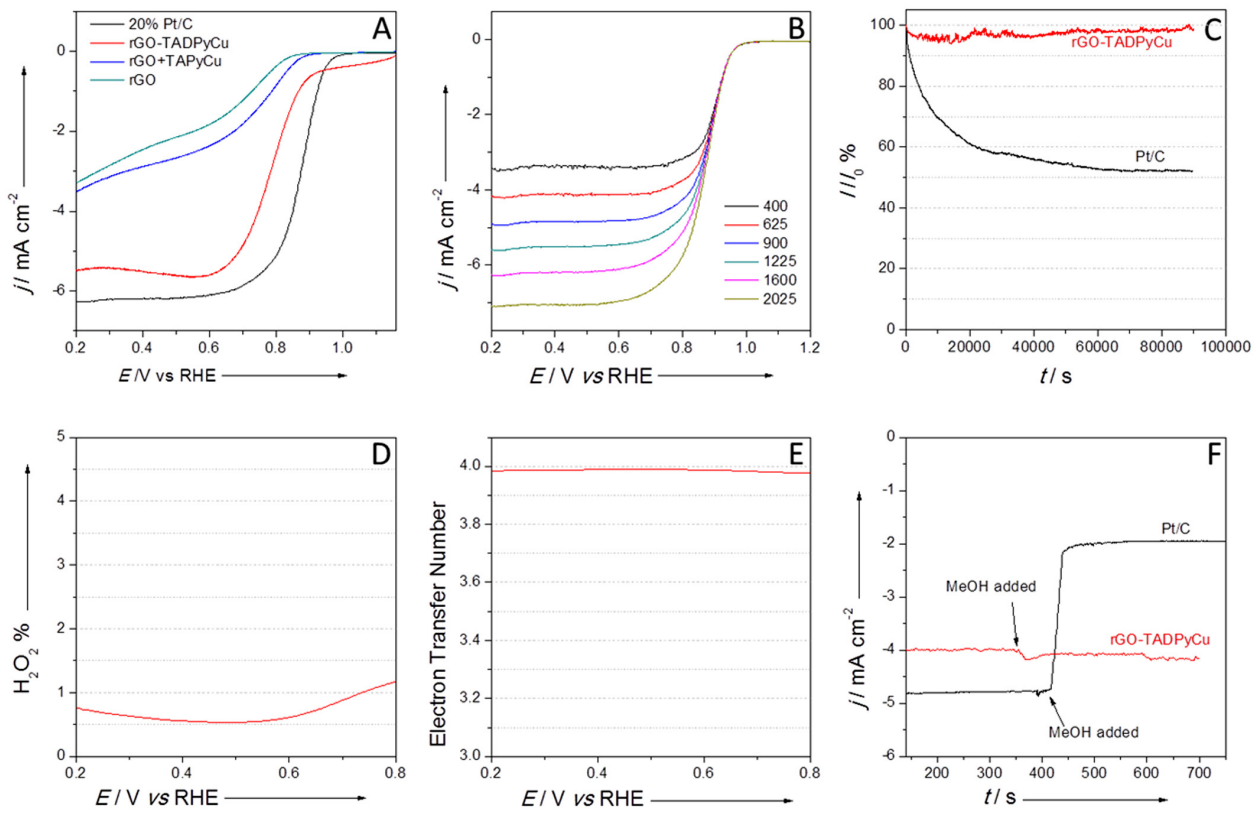


Figure S11 (A) Linear scanning voltammograms of rGO/TAPyCu (blue), rGO-TADPyCu (red), rGO (green) and 20% Pt/C (black) catalysts in O_2-saturated 0.1 M KOH. Electrode rotation speed 1600 rpm; scan rate, 10 mVs^{-1}; loading: NPMCs, 0.6 mg cm^{-2}; 20% Pt/C, 1.0 mg cm^{-2}. (B) Rotating-disk voltammograms of 20% Pt/C (loading 200 μg_{pt} cm^{-2}) in O_2-saturated 0.1 M KOH solution at different rotation rates indicated. (C) Current–time (*i*–*t*) chronoamperometric response of rGO-TADPyCu (red), and 20% Pt/C (black) modified GC electrode at 0.7 V in an O_2-saturated 0.1 M KOH solution. Electrode rotation speed, 900 rpm. Peroxide yield (D) and electron-transfer number (*n*) of 20% Pt/C for ORR in 0.1 M KOH solution. (F) Current–time chronoamperometric response of rGO-TADPyCu (red) and 20% Pt/C (black) upon the addition of 2.0 M methanol in an O_2-saturated 0.1M KOH solution. The arrow indicates the introduction of methanol. Electrode rotation speed, 900 rpm.

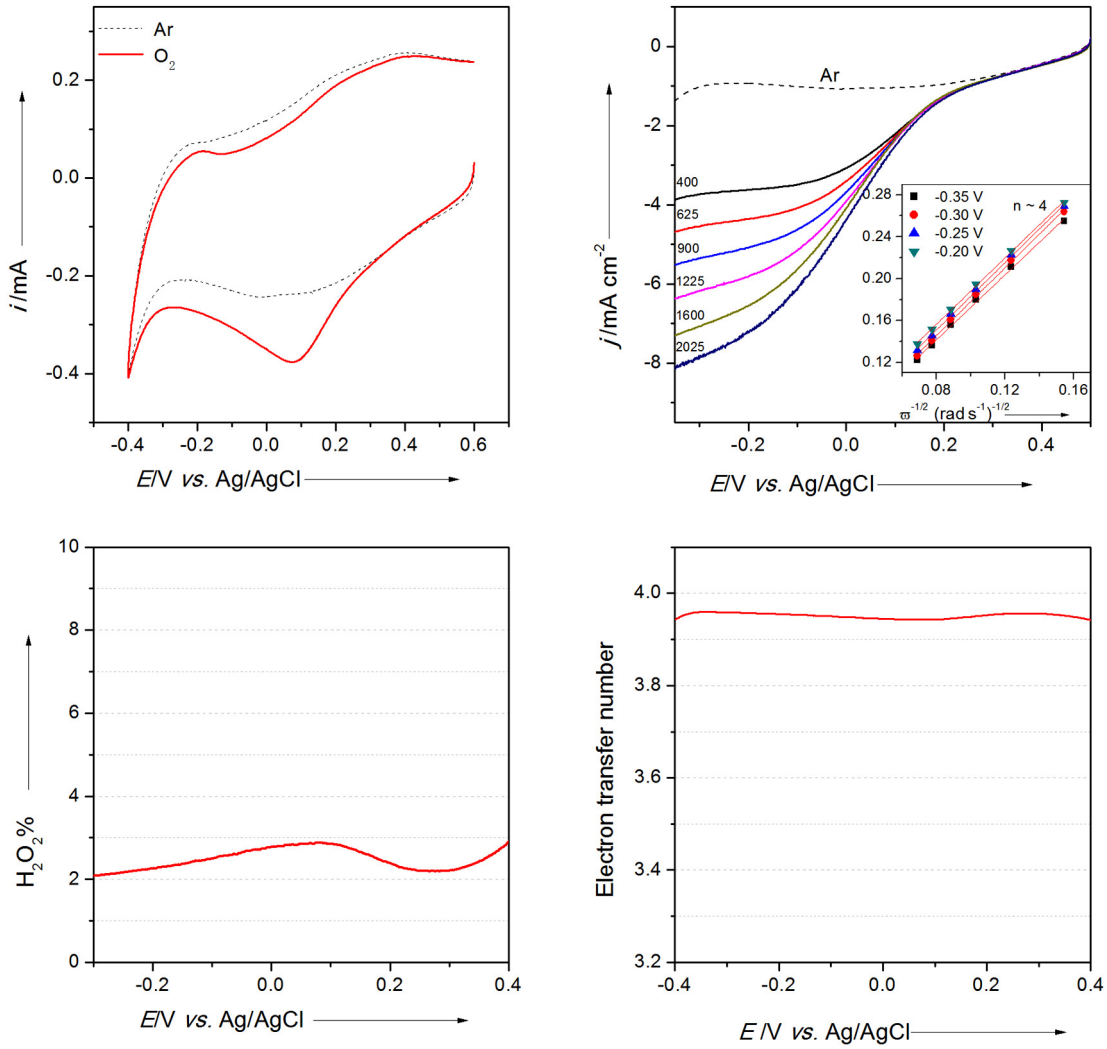


Figure S12 (A) Cyclic voltammograms of rGO-TADPyCu in Ar (dotted black) and O_2-saturated (red solid) 0.1 M $HClO_4$ solution. (B) Rotating-disk voltammograms of rGO-TADPyCu (loading 0.6 mg cm^{-2}) in 0.1 M $HClO_4$ solution at different rotation rates indicated. The inset shows the corresponding Koutecky–Levich plots at different potentials. Scan rate, 10 mVs^{-1}. (C) Peroxide yield and (D) electron transfer number of the ORR catalyzed by the rGO-TADPyCu catalyst in O_2-saturated 0.1 M $HClO_4$ solution.

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[S1] (a) W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339; (b) N. I. Kovtykhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, A. D. Gorchinskiy, *Chem. Mater.* **1999**, *11*, 771.

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