Supplementary Information (SI) for Chemical Science.

Graphene-based membrane reactor architecture for electrocatalytic hydrogenation reaction

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Materials and Methods

General

The interlayer distances between the nanosheets in the GO-stacked membranes were studied using X-ray diffraction (XRD, MiniFlex 600, Rigaku, Tokyo, Japan) with CuKα radiation ($\lambda = 0.154$ nm, $U = 40$ kV, and $I = 15$ mA) in the 2θ range 5°– 60°. The oxygen functional groups on the surfaces were analyzed using X-ray photoelectron spectroscopy (XPS, Theta Probe, Thermo Fisher Scientific, Waltham, MA, USA), and the morphologies of the GO nanosheets were observed using atomic force microscopy (Nanocute, Hitachi, Tokyo, Japan). The microstructures of the membranes with catalyst layers were analyzed using scanning electron microscopy (SEM, SU8000, Hitachi). The surface functional groups of the catalyst were studied using Fourier transform infrared spectrometer (FTIR 4100, JASCO). The products were analyzed by gas chromatography with mass spectroscopy (GC-MS) (QP2010 SE).

GO synthesis

Graphene oxide (GO) nanosheets were synthesized using the Tour`s method with modifications.[1] Expanded graphite (3.0 g, median diameter: 15–50 μm, Ito Graphite, Kuwana, Japan) and $KMnO_4$ (18 g) (Wako Pure Chemical Industries, Ltd.) were mixed in a mixture of H_2SO_4 and H_3PO_4 (9:1 in volume ratio, 360 mL). The mixture was stirred at 50 °C for 12 h. The oxidized graphite was cooled to room temperature (25 °C), followed by the addition of H_2O_2 (6 mL). The solid products recovered via centrifugation were washed several times with HCl and distilled water. They were then dispersed in distilled water and ultrasonicated for 5 h to yield GO nanosheets via exfoliation. The obtained GO nanosheets were collected via centrifugation at 10000 rpm for 10 min and then redispersed in distilled water for further use.

Catalyst synthesis

The catalyst was prepared via reported method.[2] In brief, the nanodiamond (Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan)) support was synthesized by thermally annealing fresh nanodiamond powder at 1100 °C under an argon atmosphere (100 mL/min) for 4 hours. The 0.2 wt% Pt@Graphene catalyst was prepared through a deposition-precipitation method using $H_2PtCl_6\cdot 6H_2O$ as a precursor. Initially, 200 mg of the nanodiamond was dispersed in 25 mL of deionized water in a 100 mL round-bottom flask and ultrasonicated for 30 minutes to achieve a homogeneous suspension. The suspension was then stirred under reflux conditions at 100 °C in an oil bath for 30 minutes. Sodium formate (NaCOOH) was added at a molar ratio of NaCOOH/Pt = 933:1, and the mixture was stirred for another 30 minutes. Subsequently, an $H_2PtCl_6\cdot 6H_2O$ solution was introduced dropwise into the suspension while stirring at 100 °C for 1 hour. The resulting product was cooled, filtered, washed with deionized water, dried at 60 °C for 12 hours, and reduced in a 5 vol% H_2/Ar atmosphere at 200 °C for 2 hours. The dispersion of the Pt atoms was examined via high-annular dark-field scanning transmission electron microscopy (HAADF STEM) (Figures S4 and S5), the XPS figures S6 and S7 and XRD figure S8.

Membrane fabrication

GO membranes (60–260 μm thick and 12 mm in diameter) were fabricated via vacuum filtration using a GO suspension (5 mg/mL). $Ce(SO_4)_2.4H_2O$ (0.005 mol, 99.9

%, Wako Pure Chemical Industries, Ltd.) was dissolved in the GO suspension to dope the membrane with Ce. The membrane thickness was controlled by varying the volume of the GO suspension used. Catalyst layers were then applied to both sides of the CeGO membranes by spray-coating Pt@graphene dispersed in isopropanol.

Proton transfer number determination and mixed conductivity studies

The proton transfer number of the GO membrane was determined using concentration cell measurements. A membrane with Pt@graphene layers on both sides was fixed in a glass cell. Pt meshes were attached to both sides of the membrane and connected to an electrometer (Keithley 2100, Keithley Instruments, Cleveland, OH, USA). A continuous flow of H_2 (5 %) in Ar was introduced at one side of the membrane, whereas H_2 at different concentrations (1–5 %) in Ar was introduced at the other side. The flow rates were set at 100 mL/min. The change in the open-circuit potential between the Pt/C electrodes is calculated according to the Nernst equation:

$$E_{cell} = \frac{tRT}{nF} ln \frac{p'_{H2}}{p''_{H2}},$$

Where t (-), R (J K^{-1} mol^{-1}), T (K), F (C/mol), and n (mol) are the proton transport number, gas constant, absolute temperature, Faraday constant, and number of electrons transferred, respectively. The partial pressure indicating H_2 concentration is represented as $p'_{H2}$and p''_{H2} at one side and the other side, respectively. Further, $n = 2$ for the equilibrium reaction of H_2 and protons ($2H^+ + 2e^- \leftrightarrows H_2$), and t is calculated using the slope of the plot of E as a function of ln (p'_{H2}/p''_{H2}).

The proton conductivities of the GO membranes were determined using electrochemical impedance spectroscopy. An electrical impedance analyzer (1260, Solartron Analytical, Farnborough, UK) was used at a voltage and frequency range of 10 mV and 1–10^6 Hz, respectively. The electrical conductivity was derived by measuring the I-V curves using a potentiostat (Interface 1000, Gamry Instruments, Warminster, PA, USA). Conductivity is defined according to the equation $\sigma = L/RA$, where σ (S cm^{-1}), L (cm), R (Ω), and A (cm^2) are the proton or electrical conductivity, membrane thickness, measured bulk resistance of the membrane, and electrode area, respectively.

General procedure for the electrochemical hydrogenation reaction using membrane reactor

The membrane reactor, hydrogenation chamber, and hydrogen supply plate were fabricated from polytetrafluoroethylene (PTFE), as illustrated in Figure S3. Additional components included carbon electrodes, a silicon gasket, carbon paper, a PTFE gasket serving as a separator, and a CeGO membrane. The reactant (alkyne or alkene) was dissolved in isopropanol and loaded into the cathodic chamber. Electrochemical hydrogenation was conducted at room temperature under gentle stirring conditions (500 rpm), with a continuous supply of hydrogen gas (5.0 mL/min) to the anode chamber. The reaction was performed in galvanostatic mode using a constant current density of

100 mA/cm², applied with a potentiostat/galvanostat (Gamry 1010B, Philadelphia, Pennsylvania, USA). Upon completion, the reaction mixture was diluted with ethyl acetate (Wako Pure Chemical Industry, Ltd., Japan), and the product composition was analyzed via gas chromatography-mass spectrometry (GC-MS, Shimadzu Corporation).

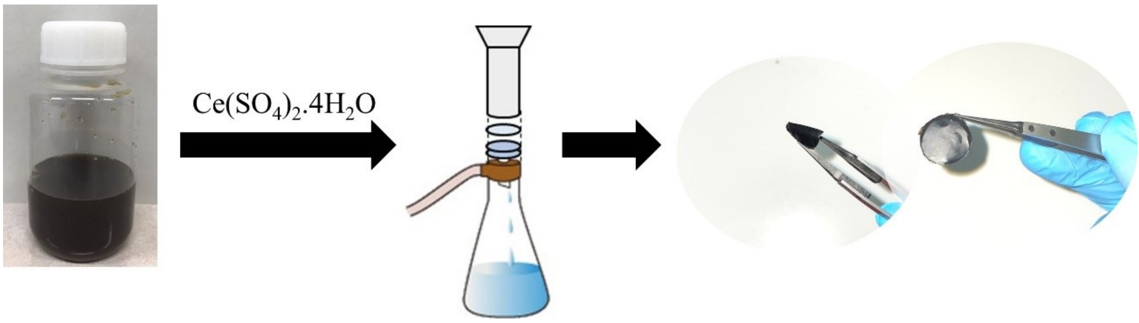

Figure S1: The CeGO membranes were fabricated via vacuum aspiration. A homogeneous mixture of GO and cerium sulfate was prepared by stirring, followed by vacuum filtration to obtain the membranes.

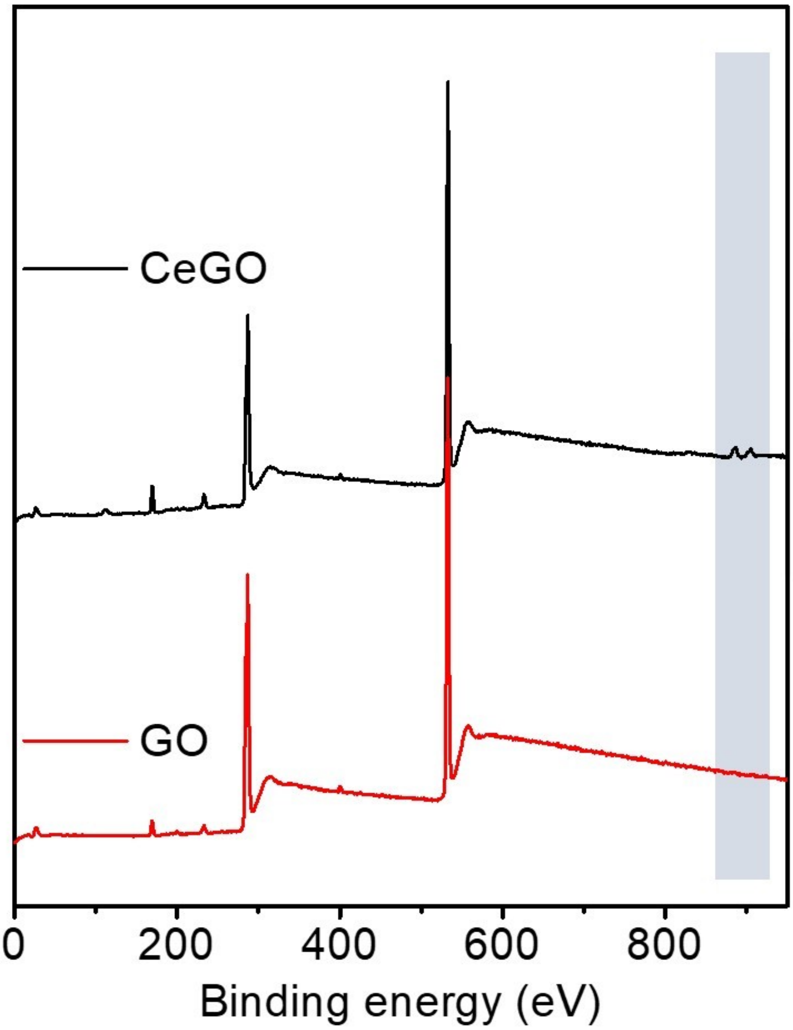

Figure S2: High resolution XPS analysis of CeGO and GO.

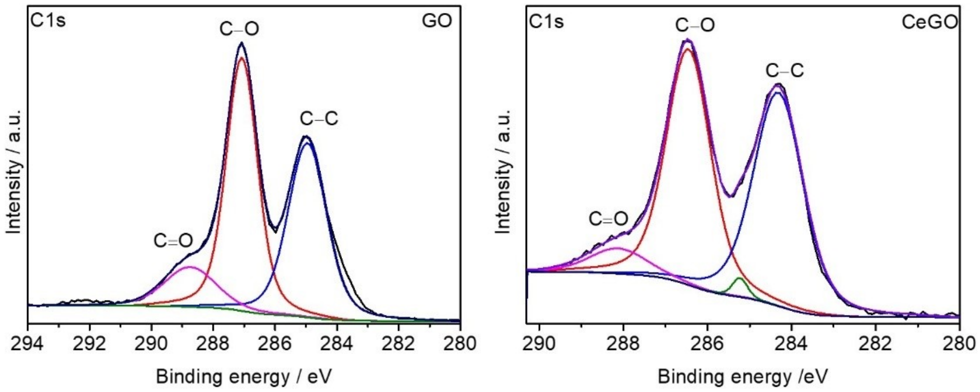

Figure S3: XPS spectra of right side C1s of GO and left side C1s of CeGO

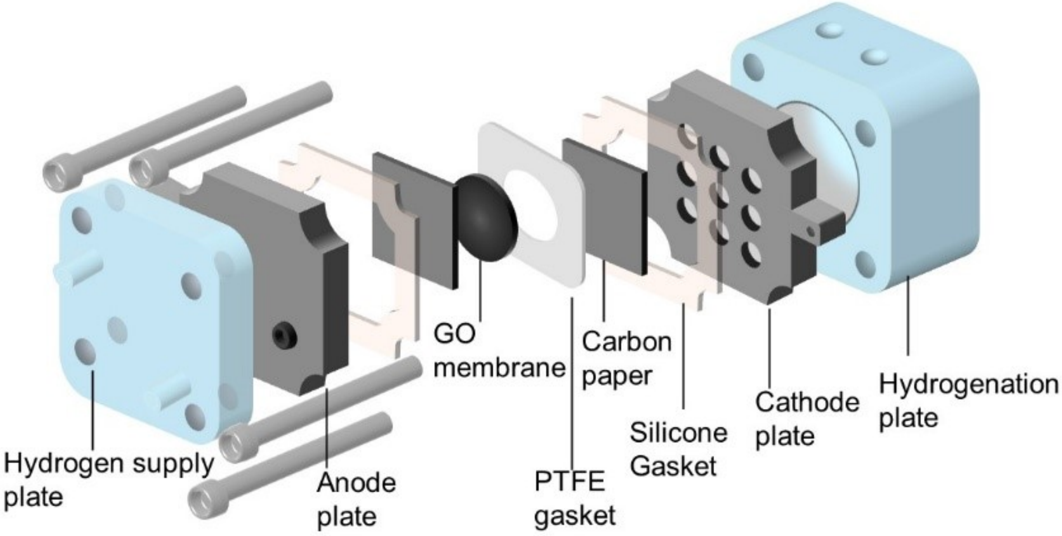

Figure S4: Expanded view of Graphene based membrane reactor for the unsaturated hydrocarbon hydrogenation to the saturated hydrocarbon.

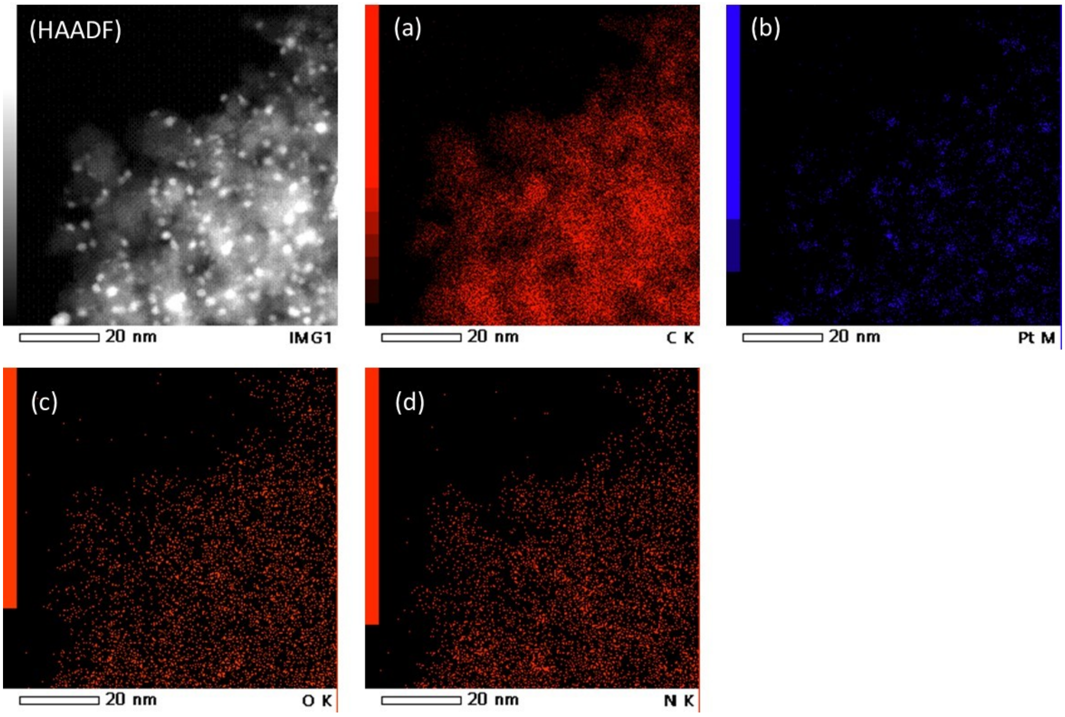

Figure S5: HAADF-STEM mapping images of (a)carbon, (b) platinum, (c) oxygen and (d) nitrogen.

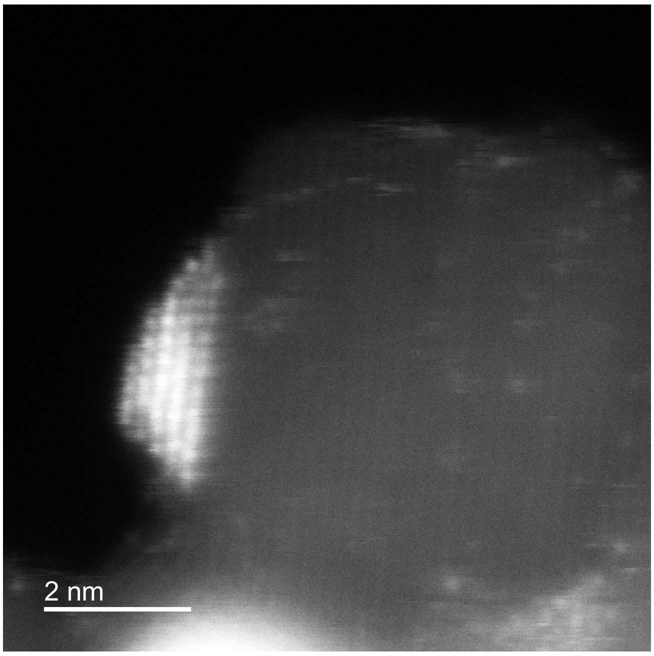

Figure S6: HAADF-STEM image of Pt@Graphene

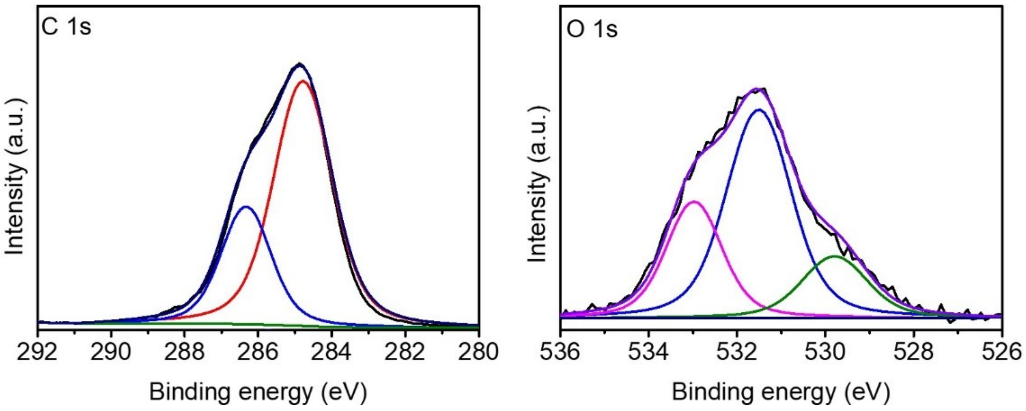

Figure S7: C1s and O1s XPS spectra of the Pt@graphene.

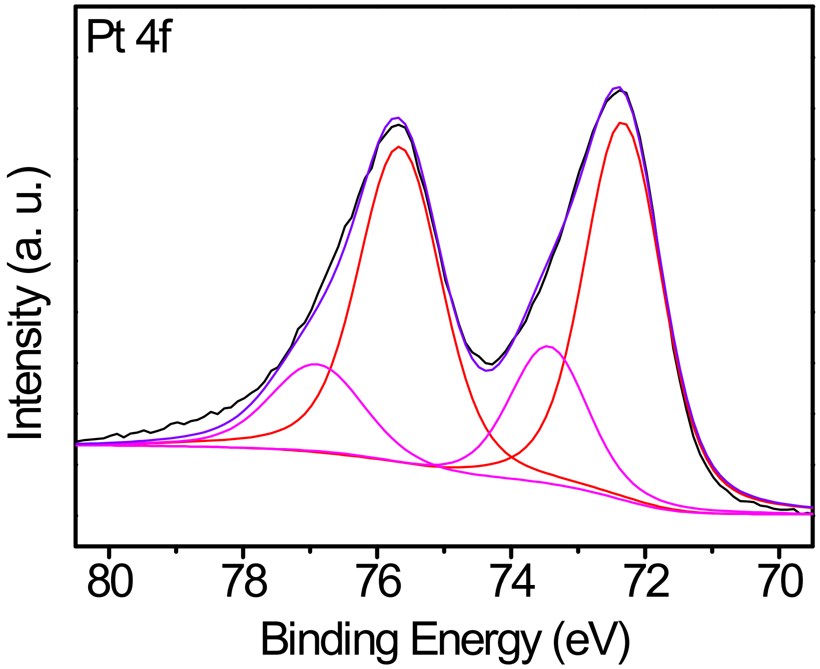

Figure S8: Pt 4f XPS spectrum of the Pt@graphene.

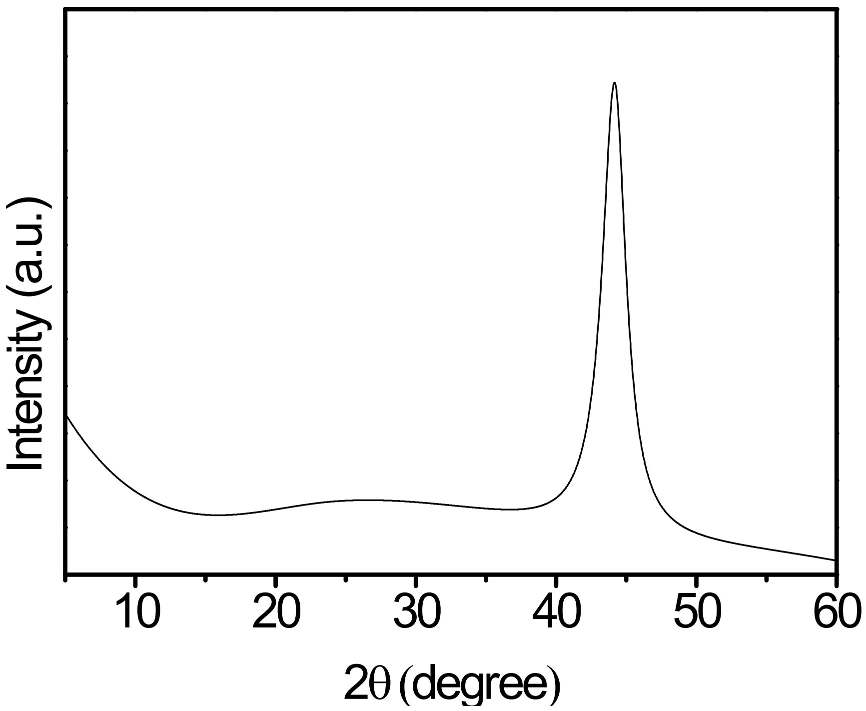

Figure S9: XRD pattern of Pt@Graphene as catalyst. It represents that the diamond phase could be observed in catalyst, there is no signal of Pt in XRD.

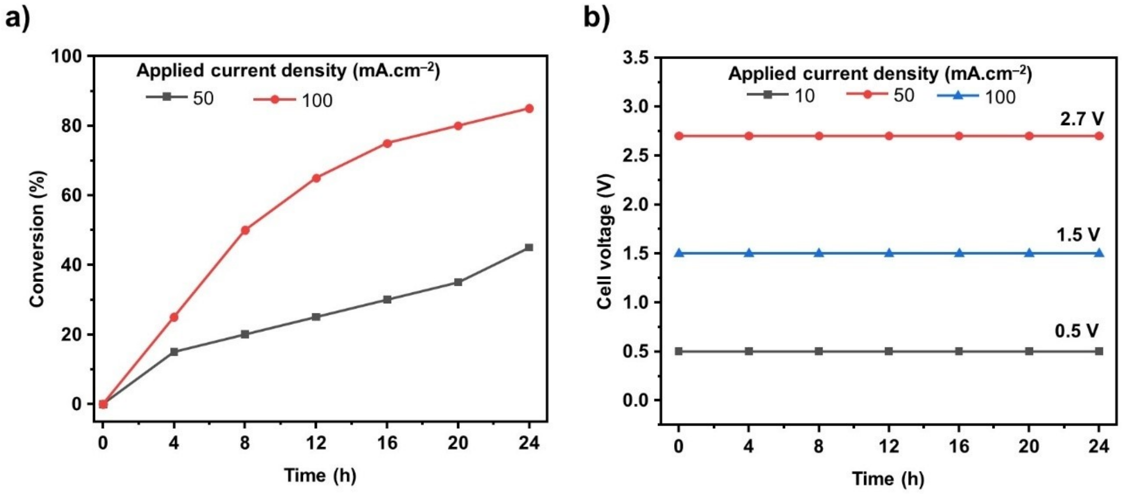

Figure S10: Influence of applied current/voltage and reaction time on the hydrogenation efficancy of phenylacetylene (a) Hydrogenation of phenylacetylene at 50 mA.cm^{-2} and 100macm^{-2} (b) Time dependent cell voltage at different applied current dencities raning from 10 to 100mA.cm^{-2} over 24hrs.

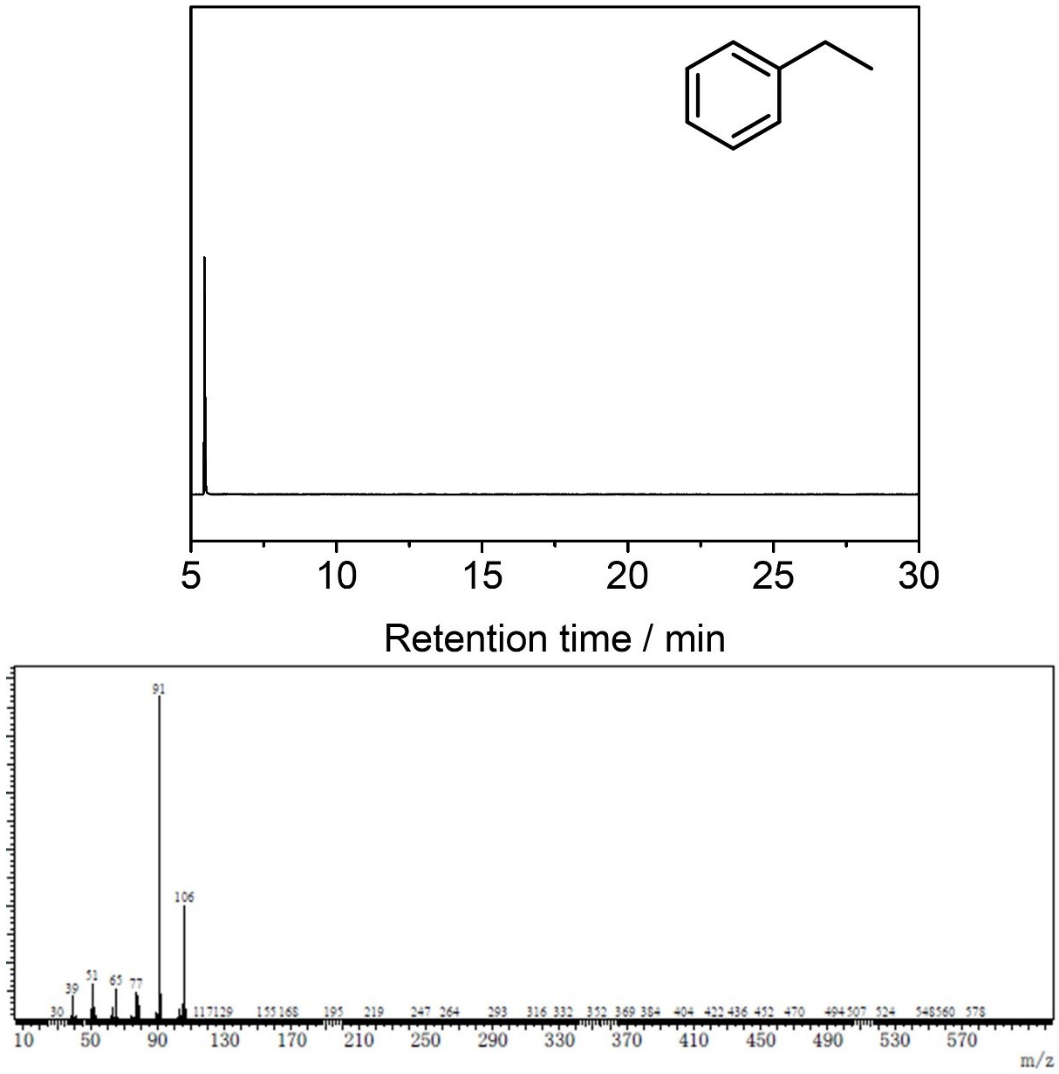

Figure S11: GC-MS results of the ethylbenzne using CeGO membrane. Full conversion and excellent selectivity can be achived.

Reaction conditions: 28 °C, 100 mA cm^{-2}, Pt@graphene as an electrocatalyst, 0.5 mmol of the starting materials, solvent IPA, time 24 hrs, H_2, 5mL/min.

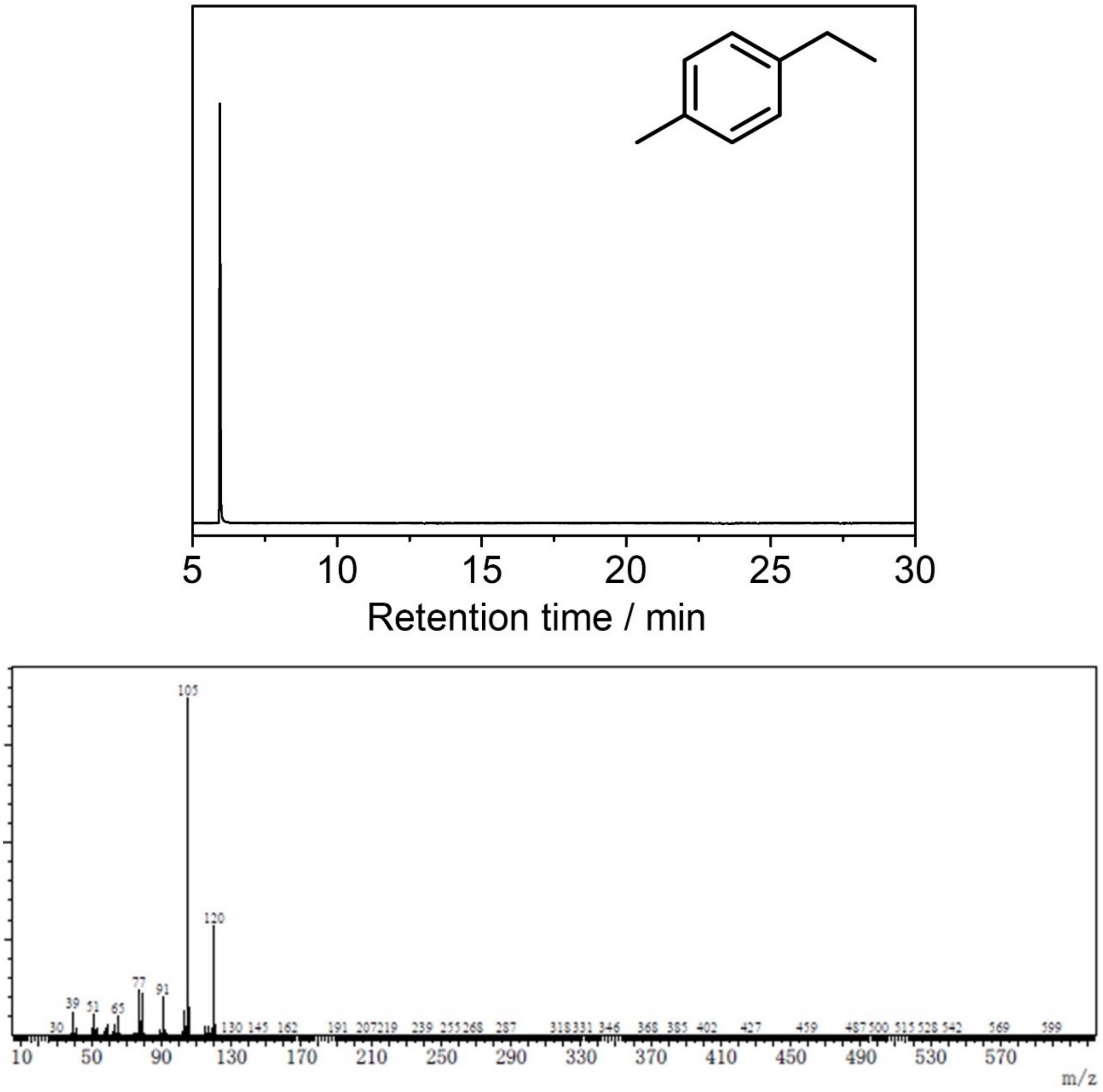

Figure S12: GC-MS results of the 1-ethyl-4-methylbenzne using CeGO membrane. Full conversion and excellent selectivity can be achived.

Reaction conditions: 28 °C, 100 mA cm^{-2}, Pt@graphene as an electrocatalyst, 0.5 mmol of the starting materials, solvent IPA, time 24 hrs, H_2, 5mL/min.

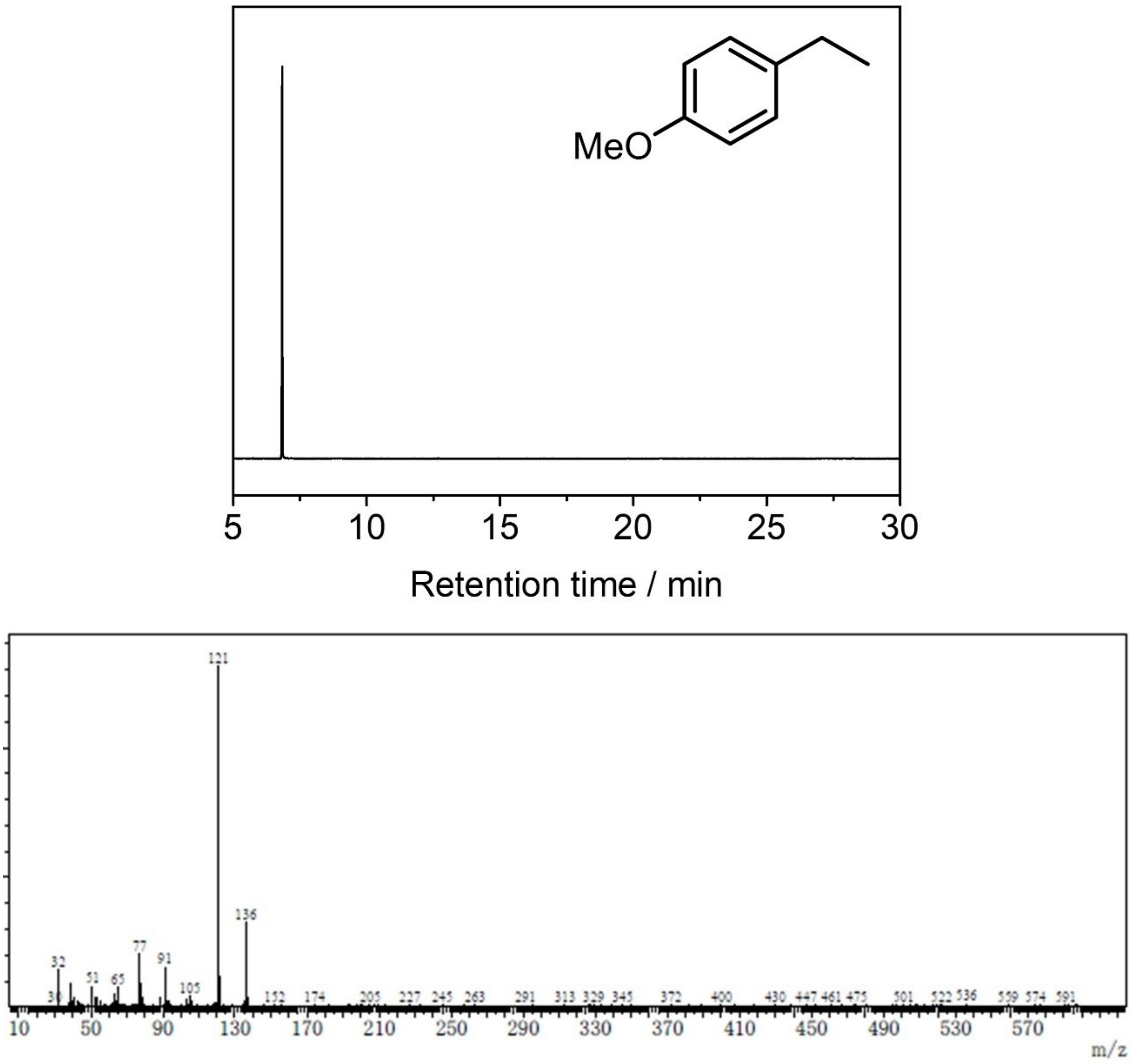

Figure S13: GC-MS results of the 1-ethyl-4-methoxybenzne using CeGO membrane. Full conversion and excellent selectivity can be achived.

Reaction conditions: 28 °C, 100 mA cm^{-2}, Pt@graphene as an electrocatalyst, 0.5 mmol of the starting materials, solvent IPA, time 24 hrs, H_2, 5mL/min.

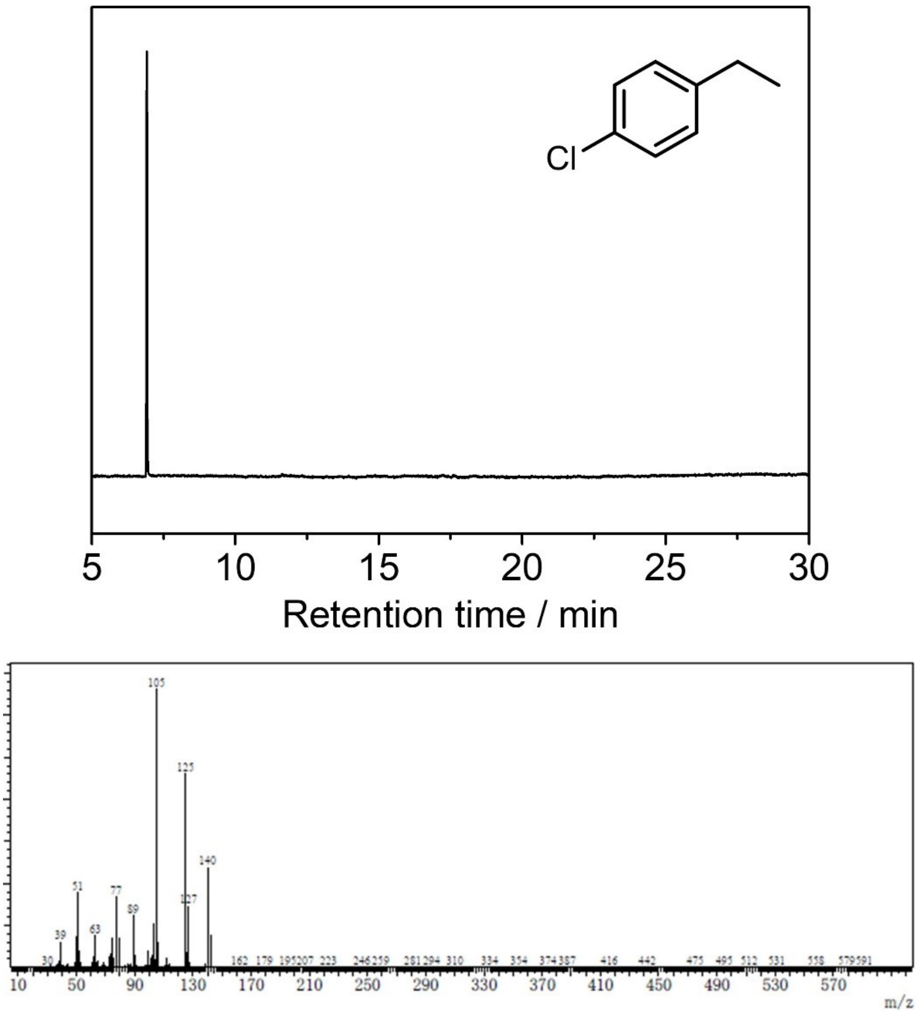

Figure S14: GC-MS results of the 1-chloro-4-ethylbenzne using CeGO membrane. Full conversion and excellent selectivity can be achived.

Reaction conditions: 28 °C, 100 mA cm^{-2}, Pt@graphene as an electrocatalyst, 0.5 mmol of the starting materials, solvent IPA, time 24 hrs, H_2, 5mL/min.

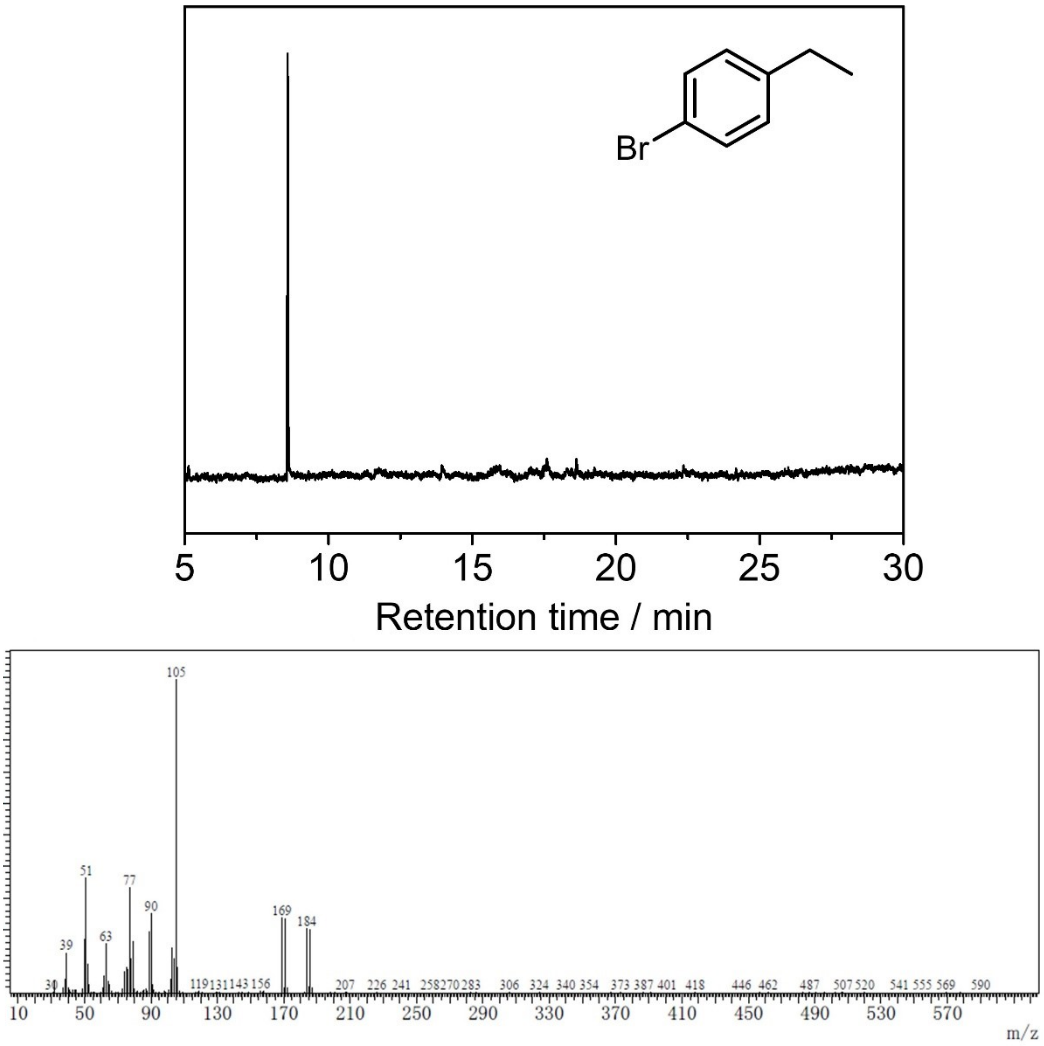

Figure S15: GC-MS results of the 1-Bromo-4-ethylbenzne using CeGO membrane. Full conversion and excellent selectivity can be achived.

Reaction conditions: 28 °C, 100 mA cm^{-2}, Pt@graphene as an electrocatalyst, 0.5 mmol of the starting materials, solvent IPA, time 24 hrs, H_2, 5mL/min.

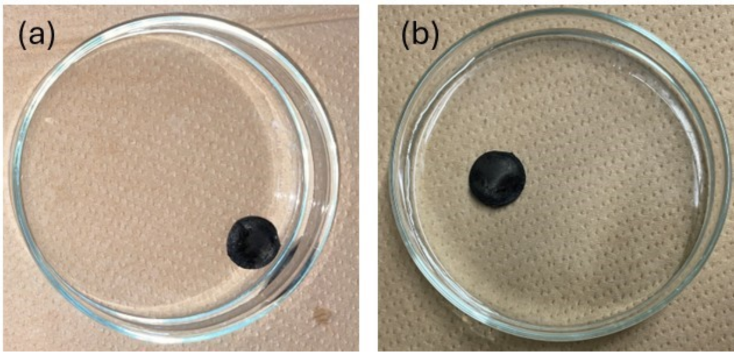

Figure S16: long term stability test, (a) Photograph taken after 5 minutes (b) photograph taken after 14 days

References

1 D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806–4814.

2 Z. Jia, M. Peng, X. Cai, Y. Chen, X. Chen, F. Huang, L. Zhao, J. Diao, N. Wang, D. Xiao, X. Wen, Z. Jiang, H. Liu and D. Ma, *ACS Catal.*, 2022, **12**, 9602–9610.