Supporting Information

Electrochemical Recognition of Alkylimidazolium-mediated Ultrafast Charge Transfer on the Graphene Surfaces

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Experimental Section

1. Chemical and reagents

1-ethyl-3- methylimidazolium bromide ([emim]Br, 99%) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Graphite powder (99.95%), Anion exchange resin (Ambersep 900 OH), NH₃·H₂O (\geq 25% w/w), glucose (\geq 99.5%), BrCH₂COOH(98%), NaOH(\geq 98%), H₂SO₄(98%, AR), H₂O₂ (30%, AR), HCl(37.5%, AR), Na₂HPO₄ (AR), and NaH₂PO₄ (AR) were purchased from aladdin reagent com. (Shanghai, China). All reagents were used as received without further purification.

2. Preparation of GO-COOH

GO-n nanosheets were prepared by a modified Hummers method. In a 250 mL flask cooled to about 5 °C through refrigerator system, typically, the given volume of water was mixed with the concentrated H₂SO₄ (40 mL) with magnetic stirring at 300 rpm for 10 min, then graphite powder (1.0 g) and NaNO₃ (0.5 g) were added with stirring for 0.5 h, and finally KMnO₄ (3.0 g) was slowly added with continual stirring for another 1 h. Next, the reaction mixture was heated to 35 °C through an oil bath and intensively stirred for 2 h. After the temperature of oil bath was increased to 98 °C, H₂O (64 mL) was dropwise added into the reaction system, and further the temperature was held for 1h. When the system temperature was naturally cooled below 60 °C, H₂O₂ (15 mL, 30 %) was added dropwise until no gas bubble was observed. Afterward, the reaction mixture was centrifuged at 8000 rpm, and the precipitate was redispersed in water for 5 times to remove the any possible acid and metal salts. The resulting product was subjected to ultrasonic dispersion for 1.5 h, and GO-n nanosheets were obtained by centrifugation at 3000 rpm for 15 min to remove the unexfoliated particles.

The carboxyl-functionalized GO-n (GO-n-COOH) was prepared through the conjugation of $BrCH_2COOH$ on GO nanosheets in the presence of alkali. Typically, $BrCH_2COOH$ (0.5g) and NaOH (0.6g) were dissolved in 20mL aqueous GO-n suspension (1 mg·mL⁻¹), and sonicated for 3 h to graft the acetic acid segments on the

nanosheets. The resulting GO-n-COOH suspension was neutralized by aqueous HCl solution (5 wt.%), and collected by centrifugation at 8000 rpm and redispersion in water repeatedly for several times.

3. Preparation of RGO-COO[C₂mim]

1-ethyl-3-methylimidazolium hydroxide ($[C_2mim]OH$) was prepared by the standard anion exchange procedures for $[C_2mim]Br$. Typically, anion exchange resin (Ambersep OH⁻¹ form) was fully rinsed through water, and compactly filled into a chromatographic column with 3 cm diameter. Then, aqueous $[C_2mim]Br$ solution (1.5 wt.%) was transfer to the resin column, and statically cultured more than 8 h for OH⁻¹ ion-exchange, and the aqueous $[C_2mim][OH]$ solution was collected from the effluent in about one drop per min. Br⁻ ions in the effluent was monitored by aqueous AgNO₃ solution (5 wt.%) containing HNO₃, and no precipitate of AgBr was observed.

RGO-n-COO[C₂mim] was prepared by the acid-base reaction of [C₂mim]OH with GO-n-COOH, and subsequently following an reduction. In a typical procedure, 10 mL GO-n-COOH suspension (1 mg·mL⁻¹) was mixed with 20 mL [C₂mim][OH] solution (10 mg·mL⁻¹), and intensively stirred at room temperature for 12 h. In succession, glucose (160mg) was added into the reaction system, and the reduction was performed at 95 °C for 15 min. Finally, RGO-n-COO[C₂mim] was purified by centrifuging at 8000 rpm and water rinsing repeatedly for three cycles. Following the similar reduction processes, the reduced GO-n-COOH (RGO-n-COOH) was prepared for comparison with RGO-n-COO[C₂mim]. 160mg of glucose was added into 10 mL GO-n-COOH suspension (1 mg·mL⁻¹), then 80 ul NH₃·H₂O (\geq 25%w/w) was mixed into the reaction systems and stirred at room temperature for 1.5 h, subsequently the reductions were performed at 95 °C for another 1.5 h. Finally, the products were purified by centrifuging at 8000 rpm and water rinsing repeatedly for three times.

4. Characterizations and Electrochemical Measurements

The Fourier transform infrared (FT-IR) spectral data were collected on a Nicolet 6700 spectrophotometer. The UV-Visible (UV-vis) spectra were measured on a TU-1810 UV-vis spectrophotometer. The analysis of X-ray photoelectron

spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific Inc.) using Al K α X-ray source (10 mA, 15 kV). The analysis of energy-dispersive X-ray spectroscopy (EDS) was carried out on a field emission scanning electron microscopy (FESEM, SU8010, Hitachi).

Glassy carbon electrode (GCE) was carefully pretreated using the standard procedures. GCE was burnished with 1.0, 0.3, and 0.05 μ m alumina slurries in turns, sonicated for 2min in deionized water and ethanol repeatedly for three times, and dried under N₂. Then, 6 μ L homogeneous RGO-COO[C₂mim] suspension (1 mg·mL⁻¹) was coated on the freshly treated GCE surface, and naturally dried at the room temperature. The resulting modified electrode was denoted as RGO-COO[C₂mim]/GCE. The RGO-COOH-modified GCE was prepared in a similar manner for comparison.

All electrochemical measurements of RGO-COO[C₂mim]- or RGO-COOHmodified GCE were performed on a CHI660E electrochemical workstation (Chenhua Instruments Co. Ltd. Shanghai, China) installed a conventional three- electrode setup. The modified GCE (CHI104, 3 mm diameter) was employed as the working electrode, a platinum wire as the counter electrode, a saturated calomel electrode as the reference electrode, and N₂-saturated phosphate buffer solution (PBS, 0.1M, pH=4) containing 10 mM NaNO₂ as the supporting electrolyte. The cyclic voltammetry (CV) was performed from 0 V to 1V at scan rate of 50 mV/s. The differential pulse voltammetry (DPV) was conducted with the increment potential of 0.004 V, pulse amplitude of 0.05 V, pulse width of 0.06 s, sample width of 0.0167 s, pulse period of 0.2s, and quiet time of 2s.



Figure S1. FTIR spectra. Although the changes of O-H deformation at 1379 cm⁻¹ and stretching at 3393 cm⁻¹ are hardly observed from the FTIR spectra of GO-2 and GO-2-COOH (Figure 1A), the introduction of acetic groups causes the decrease in relatively intensities of epoxy and alkoxy C-O stretching at 1062 cm⁻¹ and 1240 cm⁻¹.¹ The band of C=O stretching appears at 1731 cm⁻¹ in GO-2, however, represents the widened one centered at 1615 cm⁻¹ in GO-2-COOH because the interactions among carboxyl groups promote the band to red-shift and merge with aromatic C=C stretching at 1623 cm⁻¹. Simultaneously, the C-H symmetric and asymmetric stretching at 2851 and 2924 cm⁻¹ also indicate the occurrence of acetic groups combined covalently on GO-2.² When [C₂mim]OH is anchored on GO-2-COOH and then the reduced procedures are followed, the FTIR spectrum of the resulting RGO-2-COO[C₂mim] displays fine multiple vibrations in the spectral range of 800~1800 cm⁻¹ resulting mainly from [C₂mim]⁺, and relatively narrowed O-H stretching at 3415 cm⁻¹.



Figure S2. (A) UV-vis absorption spectra of GO-2, GO-2-COOH, and RGO-2-COO[C₂mim]. The formation of functionalized RGO can further confirmed by UV-vis absorption spectrum. The characteristic absorption band at 228 nm in GO-2 is ascribed to the π - π^* transitions of aromatic C=C bond, and red-shifts to 258 nm in RGO-2-COO[C₂mim], implying the restoration of the frame of sp² carbon atoms after glucose reduction. A band grows up at 196 nm GO-2-COOH due to acetic groups, and red-shifts to 211 nm in RGO-2-COO[C₂mim], indicating the conjugation of carboxyl groups and [C₂mim]⁺. (B) UV-vis absorption spectra of GO-n, GO-n-COOH, and RGO-n-COO[C₂mim] (n = 0, 1, 3). All other samples exhibit the similar spectral changes.



Figure S3. (A) XPS survey spectra, (B) Stacked histograms of chemical constitutions.Composites: $RGO-0-COO[C_2mim]$ (a), $RGO-1-COO[C_2mim]$ (b),RGO-2-COO[C_2mim](c), and RGO-3-COO[C_2mim](d).



Figure S4. High-resolution XPS spectra of C 1s for RGO-0-COO[C_2 mim] (a), RGO-1-COO[C_2 mim] (b), RGO-2-COO[C_2 mim] (c), and RGO-3-COO[C_2 mim] (d).



Figure S5. CVs on RGO-2-COO[C₂mim]-modified GCE at 50 mV s⁻¹ in N₂-saturated PBS containing 10 mM NaNO₂ with different pH from 3 to 6. The pH exerts significant effects on the faradaic peak current density (j_{pa}) and the anodic peak potential (E_{pa}) in phosphate buffer solution (PBS) containing 10 mM NaNO₂. Because the pK_a of HNO₂ is 3.30, the low j_{pa} and high E_{pa} could result from the protonation that converts NO₂⁻ into HNO₂ at pH less than 4, whereas the decrease in j_{pa} is ascribed to the interactions of OH⁻ with [C₂mim]⁺ to depress the electrocatalytic activity at pH more than 4. Resultantly, the N₂-saturated PBS of pH=4 with the maximum j_{pa} and minimum E_{pa} is chosen as the medium for electrochemical measurements in the oxidation reaction of NO₂⁻.



Figure S6. (A) CVs on RGO-2-COO[C_2 mim]-modified GCE at different scan rates (10-100 mV s⁻¹) and on RGO-2-COOH-modified GCE at 50 mV s⁻¹ (black curve).



Figure S7. (A) DPVs of NaNO₂ solutions. (B) Peak current on RGO-2-COO[C_2 mim]-modified GCE as the function of NaNO₂ concentration.



Figure S8. UV-vis absorption spectrum of $[C_2mim]Br$ aqueous solution (40µM) containing different concentration (µM) of NaNO₂ (A) and NaNO₃ (B).



Figure S9. UV-vis absorption spectrum of $[C_2mim]$ Br aqueous solution of 40 μ M (black line) respectively containing 1 mM NaCl (blue line), 10 mM NaCl (green line), 1 mM NaNO₂ (violet line), 10 mM NaNO₂ (red line).



Figure S10. CVs on RGO-2-COO[C₂mim]/GCE in N₂-saturated PBS containing 10 mM NaNO₂ and different concentrations of NaNO₃ (mM): 0 (black line), 50 (blue line), 100 (red line).



Figure S11. CVs on RGO-n-COOH-modified GCE at 50 mV s⁻¹ in N₂-saturated PBS (pH=4) containing 10 mM NaNO₂. Composites: RGO-0-COOH (violet line), RGO-1-COOH (blue line), RGO-2-COOH (red line), RGO-3-COOH (black line).



Figure S12. Tafel plot of RGO-0-COO[C_2 mim] (a), RGO-1-COO[C_2 mim] (b), RGO-2-COO[C_2 mim] (c), RGO-3-COO[C_2 mim] (d).



Figure S13. CVs at different scan rates (5-50 mV s⁻¹) for RGO-0-COO[C₂mim] (A), RGO-1-COO[C₂mim] (B), RGO-2-COO[C₂mim] (C), RGO-3-COO[C₂mim] (D) in N₂-saturated PBS (pH=4) containing 10 mM NaNO₂ over the region of 0.1-0.2 V.



Figure S14. CVs at different scan rates (5-50 mV s⁻¹) for RGO-0-COOH (A), RGO-1-COOH (B), RGO-2-COOH (C), and RGO-3-COOH (D) in N₂-saturated PBS (pH=4) containing 10 mM NaNO₂ over the region of 0.1-0.2 V.



Figure S15. Time dependence of the current density for RGO-0-COO[C₂mim] (a), RGO-1-COO[C₂mim] (b), RGO-2-COO[C₂mim] (c), and RGO-3-COO[C₂mim] (d).

Sample	W _C (wt.%)	W ₀ (wt.%)
GO-0	42.531	57.469
GO-1	41.177	58.823
GO-2	40.392	59.608
GO-3	39.287	60.713

Table S1. Chemical element contents of carbon and oxygen in GO-n.

Electrode material	Techniques	Linear response range	LOD	Ref.
		(µM)	(µM)	
PDDA ^a -Fe ₃ O ₄ /L-cys ^b /MWCNTs ^c	DPV	7.49-3330	0.846	3
CuO nanoparticles	CV	4–3700	0.3	4
MOF-525 ^d thin films	CV	20-800	2.1	5
Cu-NDs ^e /rGO	Amperometry	1.25-13,000	0.4	6
Au NPs ^f /SG ^g	Amperometry	10–3960	0.2	7
Nanowire-derived from Cu electrode	DPV	8–5860	1.35	8
Copper coated bismuth	DPV	13-3000	6	9
Au-Pd/rGO/GCE	Amperometry	0.05-1000	0.02	10
PtNPs ^h /rGO/GCE	Amperometry	0.25-90	0.1	11
Pt nanoclusters/GCE	Amperometry	1.2–900	0.4	12
CoPcF ⁱ MWCNTs /GCE	Amperometry	0.096-340	0.062	13
RGO-2-COO[C ₂ mim]	DPV	2-1300	0.018	this work

Table S2. Electrochemical response of nitrite on different chemically modified electrodes

A: poly(diallyldimethylammonium chloride); b: L-cysteine; c: Multiwalled carbon nanotubes; d: porphyrin metal–organic framework; e: Copper nanodendrites; f: gold nanoparticles; g: sulfonated graphene; h: Pt nanoparticles; i: Tetrakis (3-trifluoromethylphenoxy) phthalocyaninato cobalt(II).

$C_{dl,sub}$ (µF)
0.22
0.27
0.30
0.20

 Table S3. Double-layer capacitances for RGO-n-COOH substrates.

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