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A pH-mediated enhancement of the graphene carbocatalyst activity for the reduction of 4-nitrophenol

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Experimental section

Materials

L(+)-ascorbic acid (GR ACS ISO) was provided by International Laboratory, USA. Fine graphite powder was purchased from Tianheng Technology Co. Ltd. (Hong Kong SAR, China). 4-Nitrophenol (ReagentPlus®, \geq 99%) was provided by Sigma-Adrich. Sodium borohydride (99%) was purchased from Oriental Chem. and Lab. Supplies Ltd. (Hong Kong SAR, China). Ammonia (28.0-30.0% NH₃ basis) was obtained from Sigma-Adrich. All other chemicals were supplied by Sigma-Adrich and used as received.

Preparation of graphene carbocatalysts G1 and G2

GO was synthesized by a modified Hummers method [1, 2]. The typical fabrication of graphene carbocatalysts is given as following procedures. A mixture of DI water (50 mL) and graphite oxide powder (50 mg) was ultrasonically treated (150 W) for 1 h to form a brown colloidal dispersion of GO (1.0 mg/mL). The AA powder (50 mg) was then dissolved into the GO dispersion (50 mL, 1.0 mg/mL), followed by magnetically stirring at 25 °C for 24 h. The resulting reaction mixture was filtered under vacuum using an Anodisc membrane with a 0.22 μ m pore size, successively washed with DI water (10 × 100 mL) and methanol (2 × 100 mL), and finally dried under vacuum at room temperature. The thus-obtained AA-mediated graphene without involving alkaline pH adjustment is referred to as G1. The alkaline pH adjustment was achieved by adding additional 2.5 mL of ammonia to the GO suspension before mixing AA powder, with the same other conditions as those described above. The resulting graphene carbocatalyst involving the pH adjustment is designated as G2.

Catalytic activity measurements

NaBH₄ (14.5 mg) was completely dissolved into a 4NP solution (5 mL, 0.1 mM). The graphene carbocatalyst (2.5 mg) was then added to trigger the catalytic reaction. A digital camera and a UV/vis spectrometer were adopted to monitor the catalytic reaction. Note that graphene carbocatalysts were used as prepared without further sonication treatment, and the catalytic reactions were kept undisturbed at room temperature once the catalytic reaction was triggered. For comparison, the catalytic activities of the control samples were also measured, including graphite, AA and GO.

Characterization

ATR-FTIR spectra were collected by a FTIR spectrometer (PerkinElmer System 2000). UV/vis spectra were captured on a Lambda 18 UV/VIS spectrometer. The powder XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer (Bruker AXS, Karlsruhe, Germany). TGA coupled with DSC was conducted on a Mettler Toledo TGA/SDTA851 under N₂ atmosphere at a heating rate of 10 °C/min.

The surface morphologies were observed by a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F). XPS measurements were performed using a Sengyang SKL-12 photoelectron spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer. BET surface area was evaluated by nitrogen adsorption-desorption measurements at 77 K (liquid nitrogen temperature), using a Micromeritics ASAP 2020 apparatus.



Additional scheme and figures

Scheme S1 Schematic illustration of the preparation procedures for carbocatalyst films G1 and G2.



Fig. S1 Investigation of GO powder, its water dispersion (1.0 mg/mL) and the pH level of the dispersion. a) GO powder under a digital camera. b, c) GO powder under SEM with different magnification scales. d) A photoimage of 1.0 mg/mL water dispersion of GO. e) The pH test result of the GO water dispersion. f) The corresponding pH standard color card.



Fig. S2 A control experiment on the reaction between GO and ammonia without involving the reagent AA (reaction conditions: room temperature for 24 h). a) A photoimage showing the starting water dispersion containing GO (1.0 mg/mL) and ammonia. b) A photoimage showing the dispersion after reaction at room temperature for 24 h. c) A photoimage displaying the final obtained powder (note that a film-like structure could be formed, revealing the importance of AA in the formation of a continuous film). d) Dispersing the powder in water. e-g) SEM images of the powder under different magnification scales.



Fig. S3 The stabilities of the GO powder, G1 film and G2 film in water against shaking. a) GO powder in a vial. b) Slowly adding D.I. water into the vial. c) Shaking the vial containing D.I. water and GO powder. d) A G1 film and D.I. water in a vial. e) Shaking the vial containing the D.I. water and G1 film. f) A G2 film and D.I. water in a vial. g) Shaking the vial containing the D.I. water and G2 film.



Fig. S4 The stabilities of GO powder, a G1 film and a G2 film in water against

NaBH₄ and NaBH₄+4NP. a) GO powder in a vial. b) Adding water into the vial containing GO. c-e) Recording the dispersing (like "dissolving") process of GO powder to some extent resulting from the impact of NaBH₄: (c) adding NaBH₄ at the starting point; (d)-(e) GO powder could be quickly dispersed to some extent. f) Adding 4NP to the vial shown in the panel (e). g) A G1 film in water. h) Adding NaBH₄ to the vial containing the G1 film and water. i) Adding 4NP to the vial shown in the panel (h). j) A G2 film in water. k) Adding NaBH₄ to the vial containing the G2 film and water. l) Adding 4NP to the vial shown in the panel (k).



Fig. S5 a,b) Cross-section SEM images of the G1 (a) and G2 (b) films.



Fig. S6 a) A starting ammonia solution (ammonia/water: 0.5 mL/10 mL). b) The pH level of the ammonia solution. c) The corresponding pH standard color card. d) Dipping the G1 film in the ammonia solution for 3.5 h. e) The ammonia-treated G1 film after being washed and dried at room temperature.



Fig. S7 a-e) SEM images of the G1 film after treated in an alkaline ammonia solution, then washed and dried at room temperature (see procedures in Fig. S6).



Fig. S8 a) Water dispersions of GO, G1 and G2, prepared by sonication treatment and by diluting. b) UV/Vis spectra of the water dispersions of GO, G1 and G2. c) The comparison plot of λ_{max} (the wavelength at the characteristic UV/vis adsorption peak) among GO, G1 and G2.



Fig. S9 Study on the starting water suspension with GO and AA (see experimental) before triggering the reaction to prepare the G1 film, the pH level of the suspension, the resulting G1 film, and the pH level of the G1 water dispersion prepared by sonication treatment of the G1 film in D.I. water. a) A photoimage of the starting mixture of GO, AA, and water (GO concentration: 1.0 mg/mL, GO/AA=1/1). b) The pH test result of the starting aqueous mixture. c) The corresponding pH standard color card. d) Digital images of the resultant G1 film. e) G1 films in D.I. water. f) An aqueous dispersion of G1, prepared by sonication

treatment of the G1 films in D.I. water. g) The pH test result of the G1 aqueous dispersion prepared by sonication treatment of the G1 films in D.I. water.



Fig. S10 Study on the starting water suspension with GO, AA and ammonia (see experimental) before triggering the reaction to prepare the G2 film, the pH level of the starting suspension, the resulting G2 film, and the pH level of the G2 water dispersion prepared by sonication treatment of the G2 film in D.I. water. a) A photoimage of the starting mixture of GO, AA, ammonia and water (GO concentration: 1.0 mg/mL, GO/AA=1/1). b) The pH test result of the starting water suspension. c) The corresponding pH standard color card. d,e) SEM images of the resultant G2 film. f) G2 films in D.I. water. g) A G2 aqueous dispersion prepared by sonication treatment of the G2 films in D.I. water. h) The pH test result of the G2 aqueous dispersion prepared by sonication treatment of the G2 films in D.I. water.



Fig. S11 a) The pH standard color card. b,c) The pH test results of the catalytic solution with the carbocatalyst film G1 (b) and G2 (c).



Fig. S12 a-c) High-resolution XPS C 1s core-level spectra of GO (a), G1 (b) and G2 (c).



Fig. S13 XRD pattern of pristine graphite.



Fig. S14 XRD pattern of GO.



Fig. S15 a) XRD patterns of carbocatalysts G1 and G2. b) Comparison plot of $d_{(001)}$ interlayer spacing values among GO, G1 and G2 sheets, as calculated based on the XRD data and the Bragg's law.



Fig. S16 UV/vis spectra along with the photoimages showing the conversion of 4NP to 4-nitrophenolate ion by addition of NaBH₄.



Fig. S17 a) Digital images showing the results of the catalytic reduction of 4NP over graphene carbocatalysts, as well as the settling separation of the carbocatalyst G2 even without centrifugation and filtration. b) Illustration of the conversion of 4NP to 4AP over the carbocatalyst G2 under a mild reaction conduction (at room temperature without agitation).



Fig. S18 Recyclability test of the carbocatalyst G2 for total 5 runs of catalytic reduction of 4NP.



Fig. S19 a,b) SEM images of the surface of the carbocatalyst G2 film that was reused and recycled from the 5^{th} run.



Fig. S20 Probing the catalytic activity of pure AA. a) UV/vis spectra of the aqueous solution of pure AA and the reaction solution after the catalytic reaction with pure AA as control catalyst for 13 h (the inset shows the molecular structure of AA). b) Photoimages showing the starting reaction solution with 4NP and fresh BH_4^- , pure AA water solution, and the resulting reaction solution after catalytic reaction with pure AA as the catalyst for 13 h.



Fig. S21 Oxidation and hydrolysis of AA. To assist in understanding the limited catalytic activity of AA, the ready structural evolution or degradation of AA under air condition is presented.



Fig. S22 Study on the carbocatalytic reaction over pristine graphite. UV/vis spectra of the reaction solution with pristine graphite as a control catalyst before and after the catalytic reaction. The inset presents the photoimages showing the reaction

solutions containing 4-nitrophenolate and fresh BH_4 - before addition of graphite (left) and after the catalytic reaction with graphite for 1 h (right).



Fig. S23 SEM images of pristine graphite. a) A photoimage of the pristine graphite powder. b, c) SEM images of the pristine graphite under different magnification scales.



Fig. S24 Catalytic activity measurement of GO, together with structure characterization of the GO recycled after the catalytic reaction. a) UV/vis spectra of the starting reaction solution containing 4-nitrophenolate and BH_4 , and the resulting reaction solution after the catalytic reaction with GO for 13 h (inset presents the corresponding photoimages of the reaction solution before and after the catalytic reaction). b) Photoimages showing the aqueous dispersion of the pristine GO and the recycled one. c) Normalized ATR-FTIR spectra of the pristine GO and the recycled one. d) UV/vis spectra for the pristine GO and the recycled one. e) Comparison

histogram of the wavelength at the characteristic UV/vis absorption peak before and after the catalytic reaction with GO. f,g) TGA coupled with DSC curves of the pristine GO (f) and the recycled one (g). h) Comparison plot of the weight loss occurred in the temperature range of 125 to 300 °C between the pristine GO and the recycled one, as calculated from the TGA curves. i) Stacked DSC curves of the pristine GO and the recycled one.

Reference

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