

Supporting Information

Composites of Graphene Quantum Dots and Reduced Graphene Oxide as Catalysts for Nitroarene Reduction

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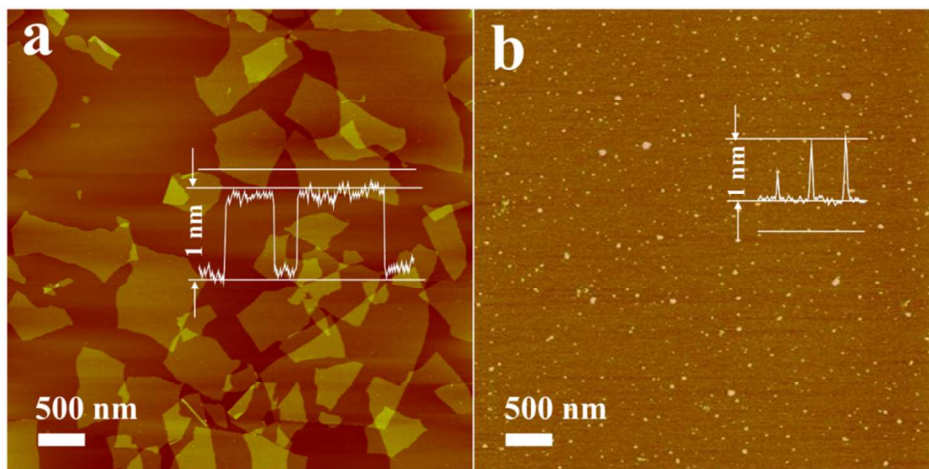


Figure S1. AFM images of GO (a) and GQDs (b) used in the work. Inset in (a) and (b) is the height profile of GO and GQDs, respectively. The heights of GO and GQDs are ~ 1 nm, revealing their single atomic layer motif.¹⁻³

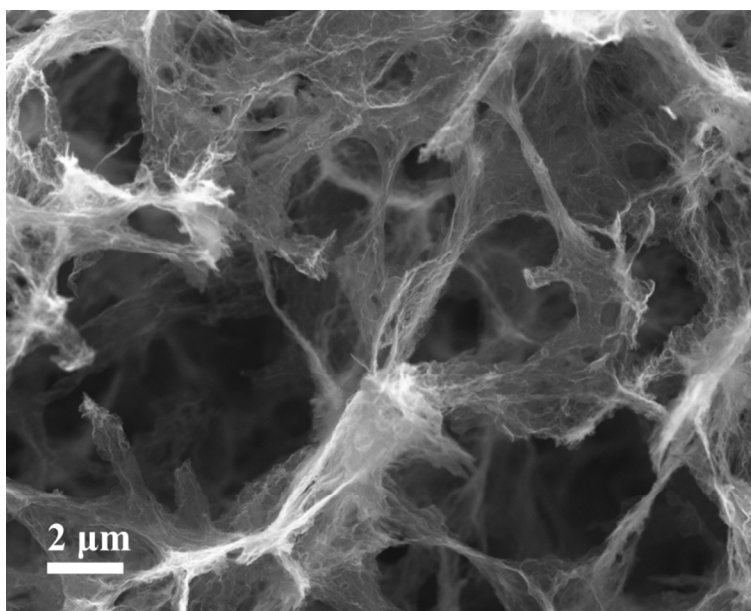


Figure S2. SEM image of the three dimensional rGO.

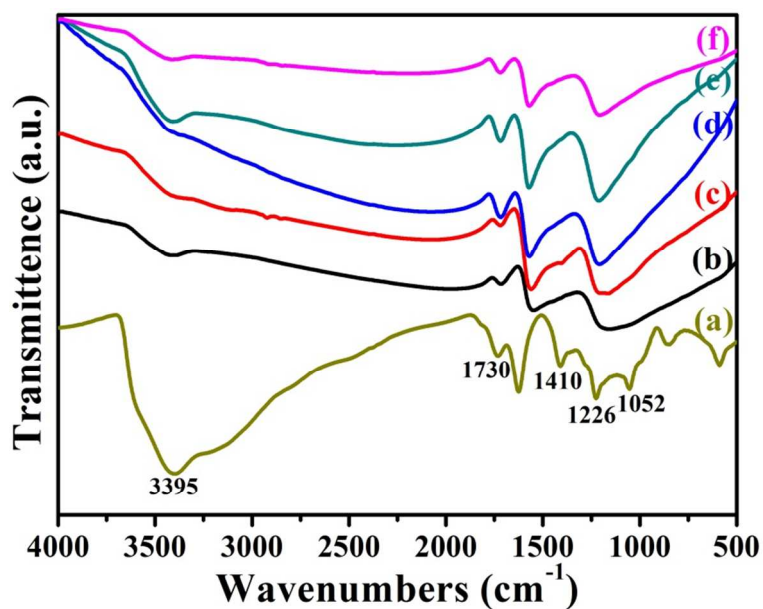


Figure S3. FT-IR spectra of GO (a), rGO (b), GQDs/rGO₁ (c), GQDs/rGO₂ (d), GQDs/rGO₄ (e) and GQDs/rGO₆ (f).

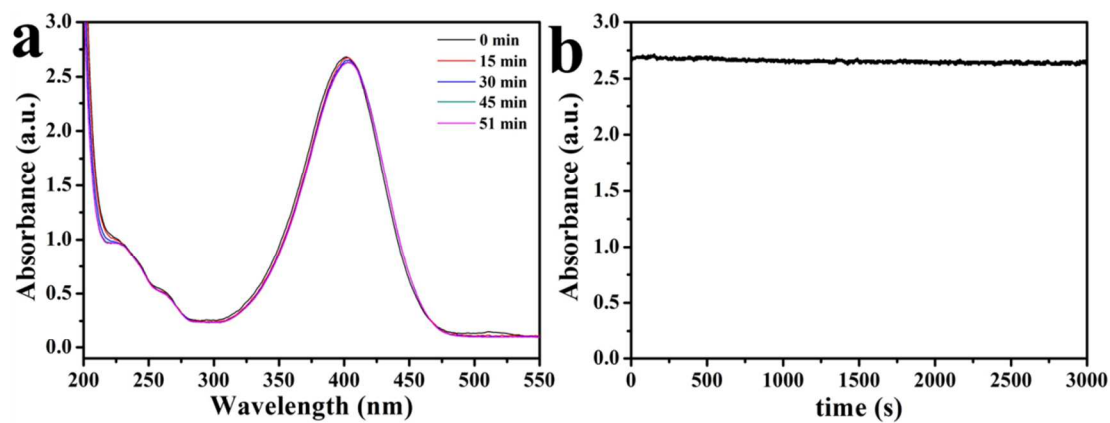


Figure S4. (a) UV-vis spectra of 4-nitrophenol acquired after being reduced without a catalyst for 51 min. (b) Time curves of the absorbance at 400nm measured for the reaction mixture. Reaction condition: 0.5 μmol substrate, molar ratio of 4-nitrophenol and NaBH_4 is 1:53, RT.

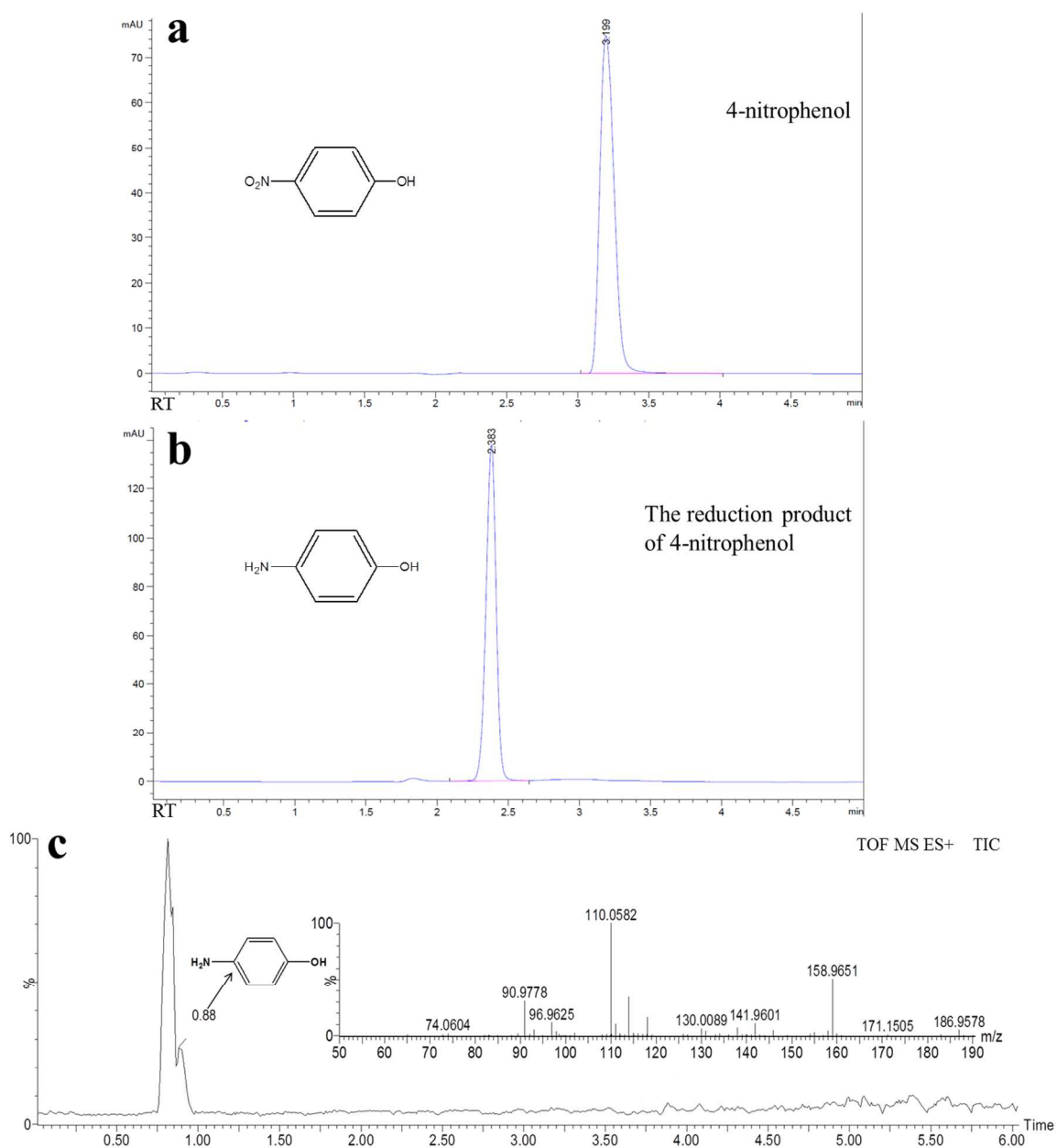


Figure S5. HPCL of 4-nitrophenol (a) and the reduction product of 4-nitrophenol (b), UPLC-Q-TOF-MS total ion chromatogram and mass spectrum of the reduction product of 4-nitrophenol under ESI+ mode (c).

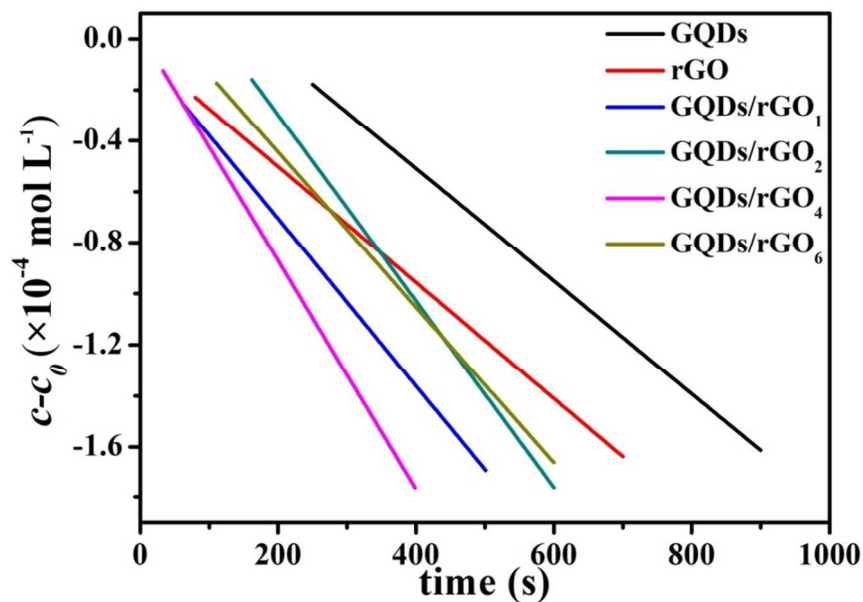


Figure S6. The $c-c_0$ (c and c_0 represent the concentrations of 4-nitrophenol at reaction time of t and 0 , respectively) versus time plots with different three dimensional composites as catalysts. Reaction condition: 0.048 mg catalyst, 0.5 μmol substrate, molar ratio of 4-nitrophenol and NaBH_4 is $1:53$, RT.

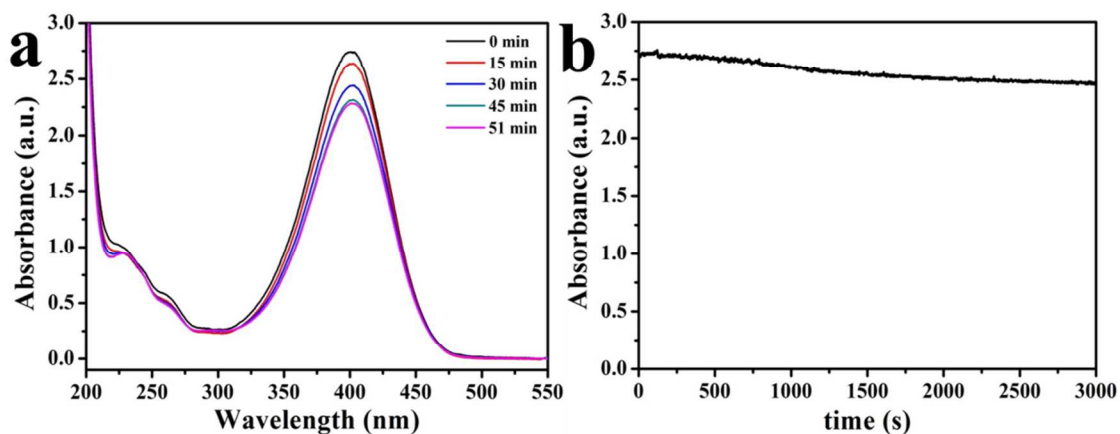


Figure S7. (a) UV-vis spectra of 4-nitrophenol acquired during the reduction with chemically reduced GO as a catalyst for 51 min. (b) Time course of the reaction monitored at 400 nm at RT. Reaction condition: 0.048 mg of catalyst, 0.5 μmol substrate, molar ratio of 4-nitrophenol and NaBH_4 is $1:53$.

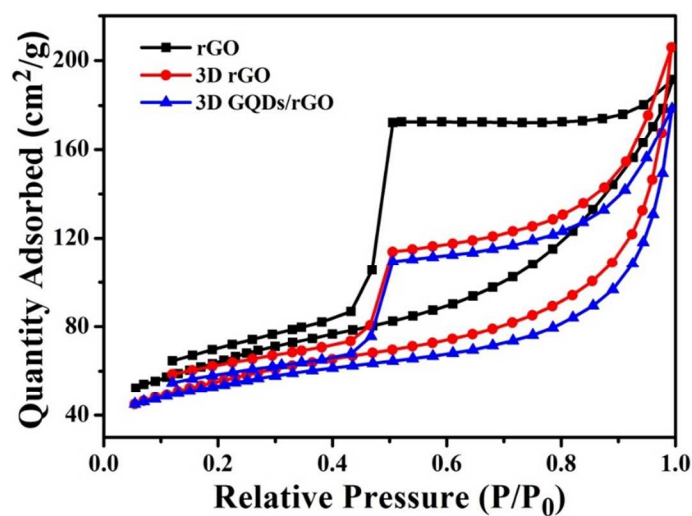


Figure S8. N₂ adsorption/desorption isotherms of rGO, 3D rGO and 3D GQDs/rGO.

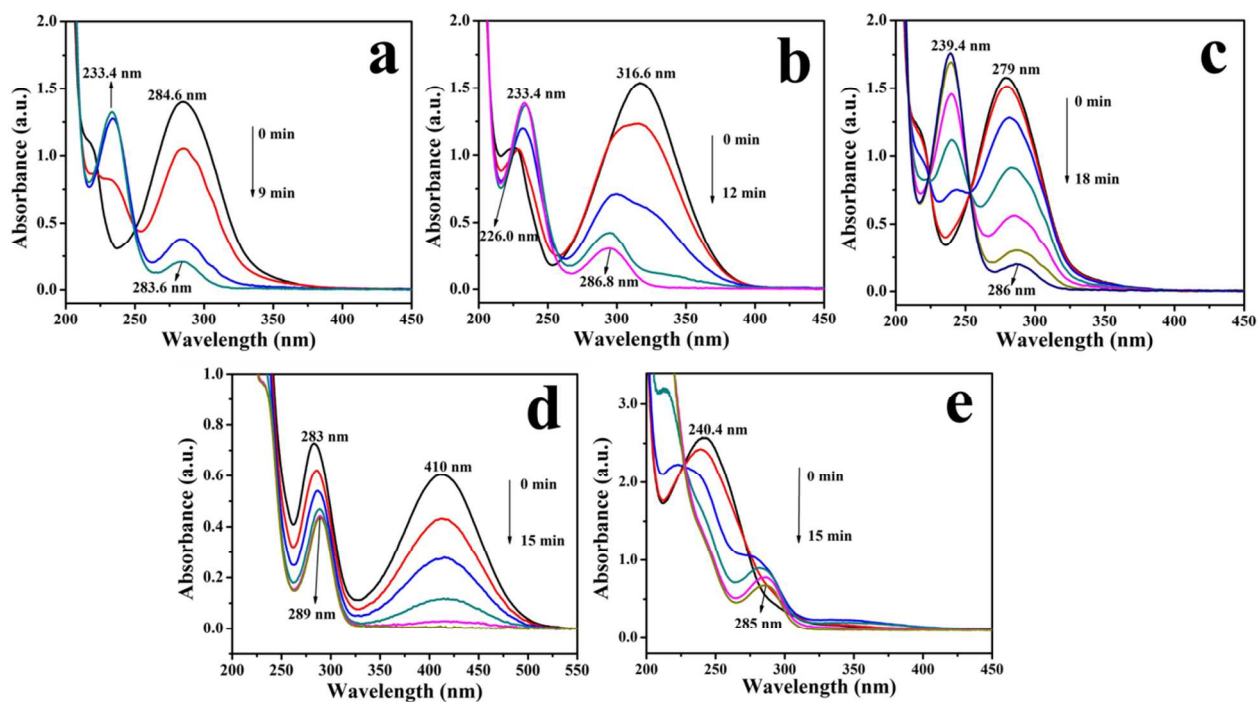


Figure S9. UV-vis spectra for 4-nitrotoluene (a), 4-nitroanisole (b), 4-nitrochlorobenzene (c), 2-nitroaniline (d) and 1,3-dinitrobenzene (e) acquired during the reduction with GQDs/rGO₄ as catalyst. Reaction condition: 0.048 mg catalyst, 0.5 μ mol substrate, molar ratio of 4-nitrophenol and NaBH₄ is 1:53, RT.

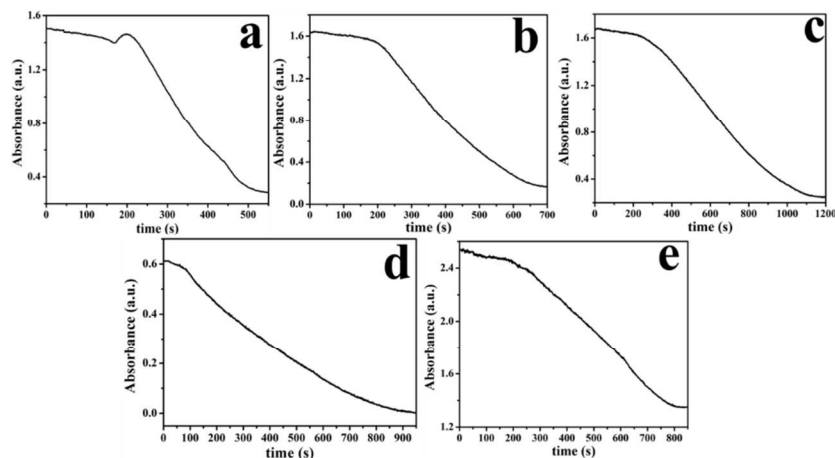


Figure S10. The measured curves of absorbance at λ_{\max} versus time for the catalytic reduction of 4-nitrotoluene (a), 4-nitroanisole (b), 4-nitrochlorobenzene (c), 2-nitroaniline (d) and 1,3-dinitrobenzene (e) with GQDs/rGO₄ as catalyst. Reaction condition: 0.048 mg catalyst, 0.5 μmol substrate, molar ratio of 4-nitrophenol and NaBH₄ is 1:53, RT.

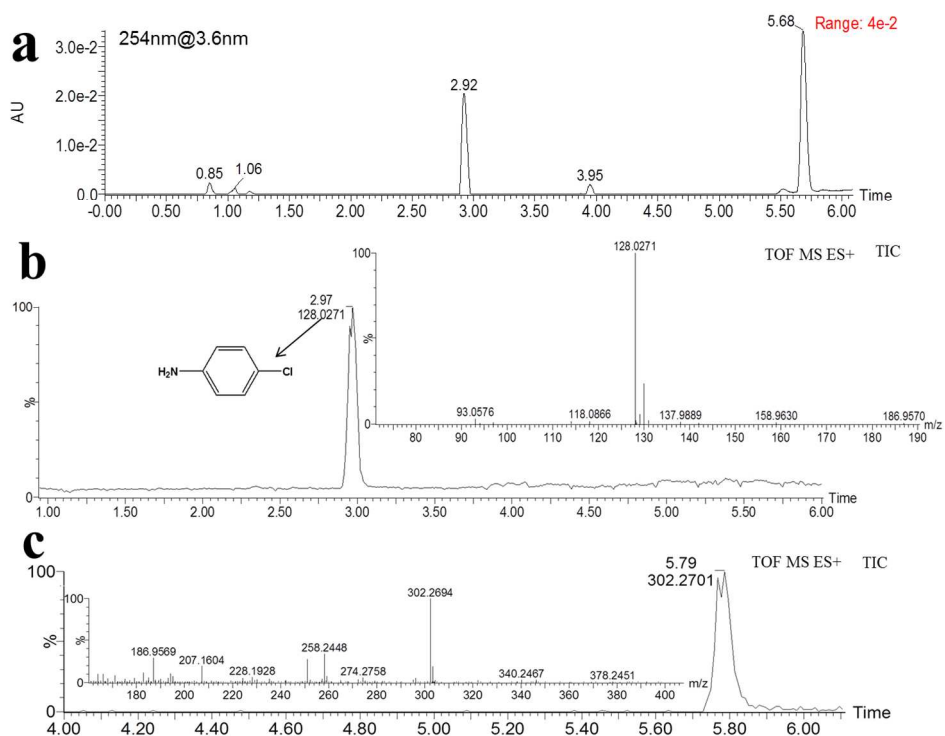
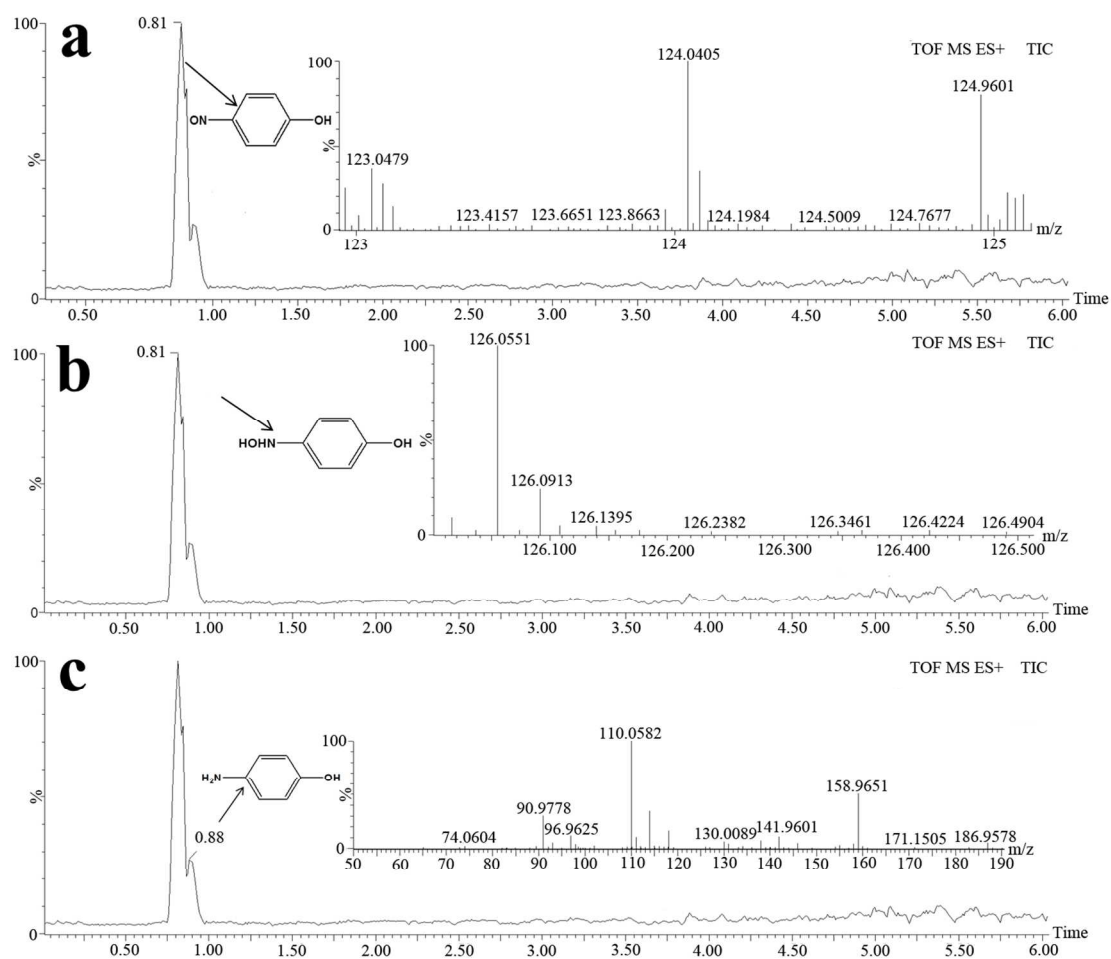


Figure S11. (a) UPLC of the reduction product of 4-chlorobenzene. (b) UPLC-Q-TOF-MS total ion chromatogram and mass spectrum of the reduction product of 4-chlorobenzene under ESI⁺ mode. (c) UPLC-Q-TOF-MS total ion chromatogram and mass spectrum of the reduction by-product under ESI⁺ mode.



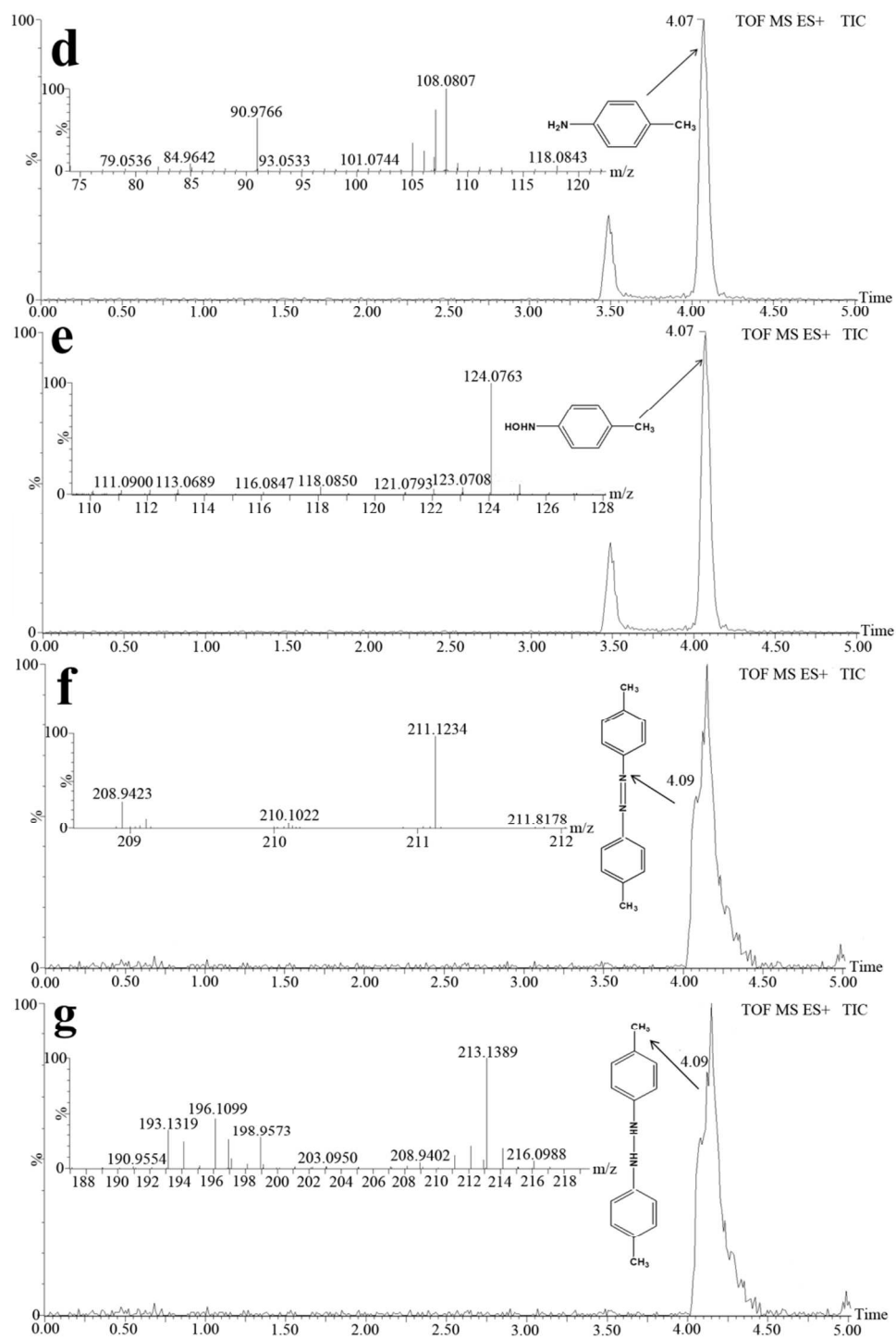


Figure S12. UPLC-Q-TOF-MS total ion chromatogram and mass spectrum of the reaction intermediates of 4-nitrophenol (a-c) and 4-nitrotoluene (d-g) under ESI⁺ mode.

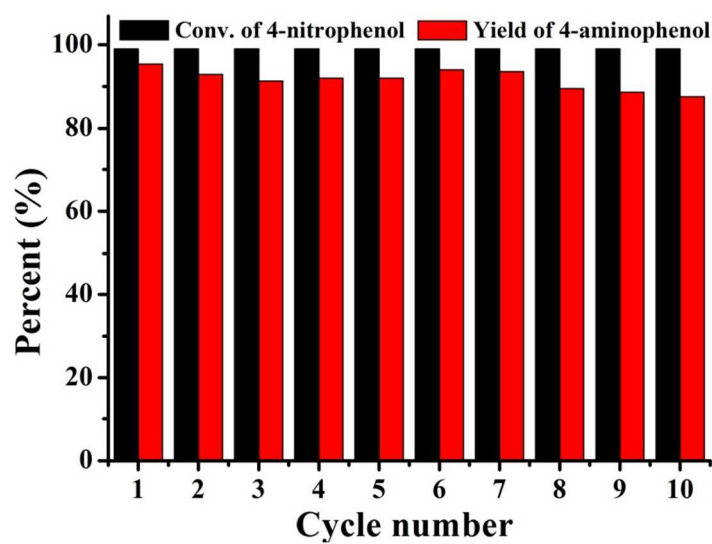


Figure S13. Recycling test of GQDs/rGO₄ as a catalyst in the reduction of 4-nitrophenol.

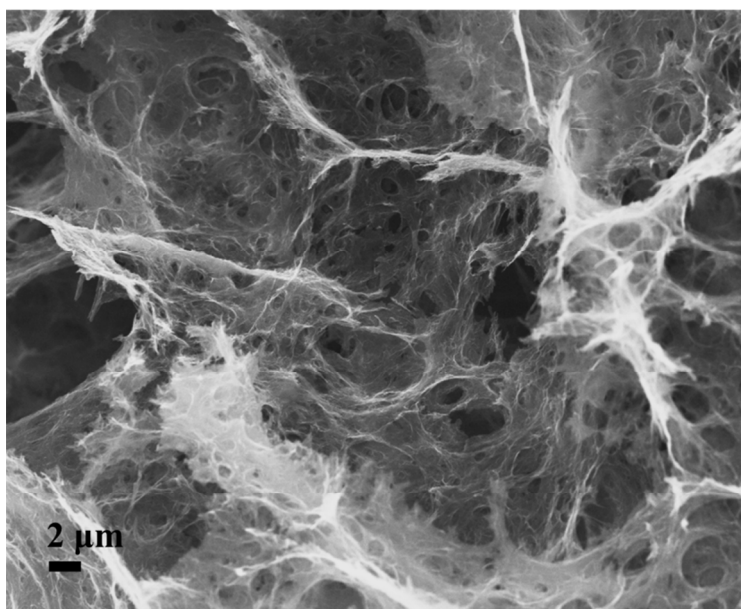


Figure S14. SEM image of the GQDs/rGO₄ after the 10th catalytic cycling run.

References

- (1) Park, S.; Ruoff, R. S., Chemical Methods for the Production of Graphenes. *Nat Nanotechnol* **2009**, *4*, 217-224.
- (2) Zhou, X.; Zhang, Y.; Wang, C.; Wu, X.; Yang, Y.; Zheng, B.; Wu, H.; Guo, S.; Zhang, J., Photo-Fenton Reaction of Graphene Oxide: A New Strategy to Prepare Graphene Quantum Dots for DNA Cleavage. *ACS Nano* **2012**, *6*, 6592-6599.
- (3) Zhang, J.; Yang, H.; Shen, G.; Cheng, P.; Zhang, J.; Guo, S., Reduction of Graphene Oxide Via L-Ascorbic Acid. *Chem. Commun.* **2010**, *46*, 1112-1114.