Electronic Supplementary Information

Biogenic gold nanoparticles-reduced graphene oxide nanohybrid: synthesis, characterization and application in chemical and biological reduction of nitroaromatics

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Electronic supplementary information consists of "Experimental", 14 figures and 1 table, 19 pages in total.

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Experimental

Preparation of GO

GO was prepared from graphite powder by modified Hummers' method. In brief, 1.0 g of graphite powder was mixed with 10 mL of HNO_3 and 46 mL of H_2SO_4 in an ice bath under stirring for 30 min. Then, 6.0 g of $KMnO_4$ was slowly added to the mixture with stirring for 20 min and kept in an ice bath for at least 120 min. This solution was then heated at 35°C overnight, and subsequently diluted with 46 mL of ultrapure water (the temperature went up to about 98°C) and kept for 120 min. After that, the solution was further diluted by the addition of 200 mL ultrapure water, followed by adding 20 mL H_2O_2 dropwise. The obtained bright yellow solution was centrifuged at 5000 rpm for 30 min to isolate graphite oxide precipitate, which was washed with 10% HCl for three times and ultrapure water for several times till the supernatant became neutral, and finally re-suspended in ultrapure water. The aqueous graphite oxide solution was then sonicated for 3 h to facilitate the exfoliation of stacked graphite oxide sheets into mono- or few-layered GO sheets.

Characterization methods

The UV-vis spectra of GO and bio-AuNPs/rGO were obtained with JASCO V-560 spectrophotometer. Tansmission electron microscopy (TEM) images of bio-AuNPs/rGO were obtained with Tecnai G2 spirit TEM operating at 120 kV and a NOVA nanosem 450 high resolution transmission electron microscopy (HRTEM) operating at 300 kV. Energy dispersive X-ray (EDX) analysis was performed using EDX analyzer fitted with the TEM. X-ray diffraction (XRD) studies were performed with a Rigaku D/max 2400 X-ray diffractometer (Cu Kα radiation, λ= 0.1541 nm). Fourier Transformation Infrared

spectroscopy (FTIR) was recorded by a Bruker Equinox 55 FTIR spectrometer over the wavenumber range of 4000-400 cm^{-1}. The X-ray photoelectron spectroscopy (XPS) analyses of GO and bio-AuNPs/rGO were conducted with Thermo Scientific K-Alpha X-ray photoelectron spectrometer. XPS peaks were deconvoluted by using Gaussian components after a Tougaard background subtraction. The concentrations of bio-AuNPs/rGO, bio-AuNPs, and bio-rGO suspensions were determined through the dry weight method. The samples were re-dissolved in aqua regia for the measurement of Au concentration with a Perkin-Elmer 200-DV inductively coupled plasma optical emission spectrometer.

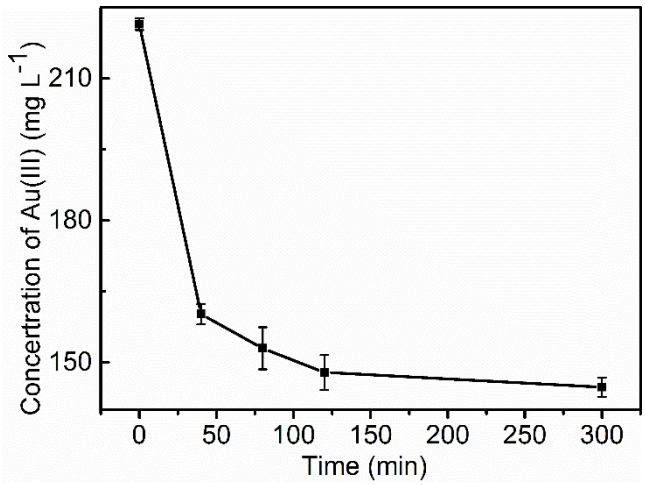

Fig. S1. Adsorption of Au(III) ions on GO. The change of Au(III) concentration in a separated adsorption experiment of $HAuCl_4$ by GO (the initial concentrations of GO and Au(III) were 950 mg/L and 221 mg/L, respectively, 30°C, 150 rpm).

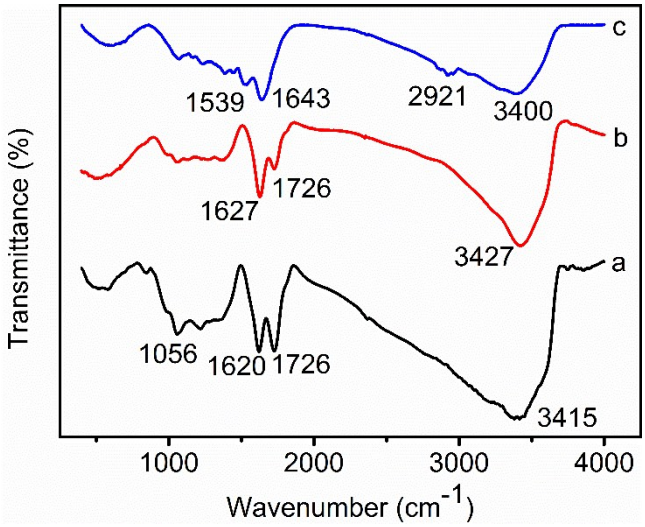

Fig. S2. FTIR spectra of (a) GO, (b) GO and $HAuCl_4$ mixture, and (c) bio-AuNPs/rGO.

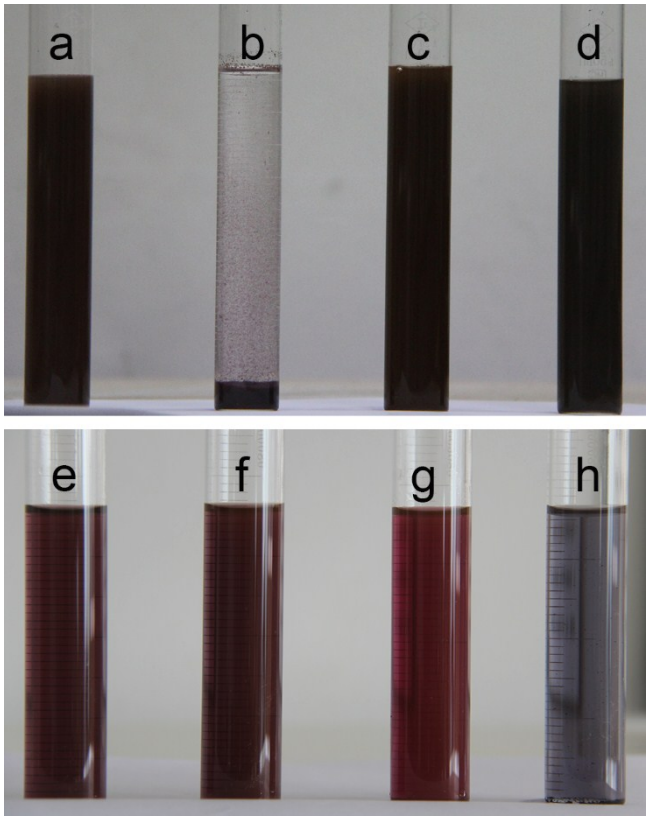

Fig. S3. Digital pictures of reduction products obtained under different conditions before (upper line) and after (lower line) alkaline washing. (a, e) GO and $HAuCl_4$ were added together into MR-1 culture in LB medium, (b, f) MR-1 suspension in pure water, (c, g) spent LB medium without cell and (d, h) fresh LB medium without inoculation to test the involvement of different components in formation of bio-AuNPs/rGO.

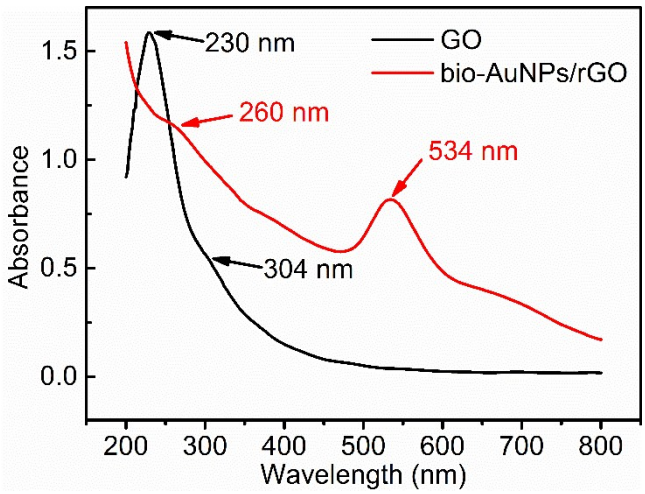

Fig. S4. UV-vis absorption spectra of GO and bio-AuNPs/rGO.

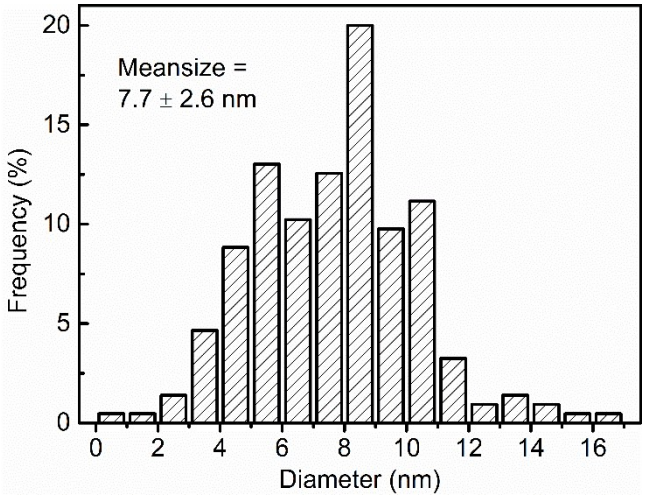

Fig. S5. Histogram of the AuNPs size distribution analysis of the bio-AuNPs/rGO nanocomposite from TEM images.

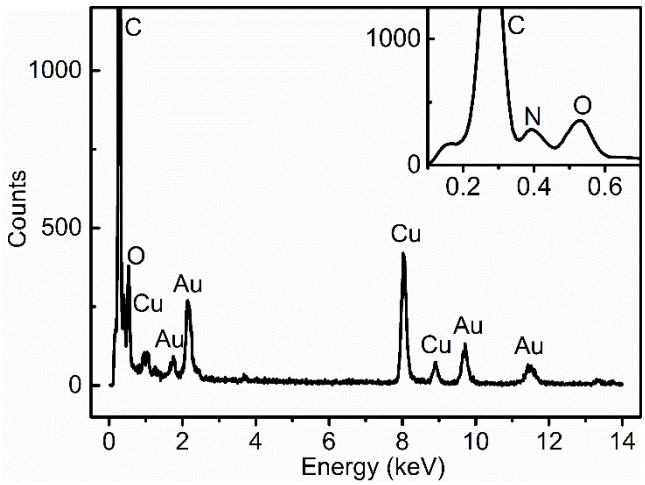

Fig. S6. EDX analysis of bio-AuNPs/rGO. The inset is the detailed view of the energy range from 0.1 to 0.7 keV.

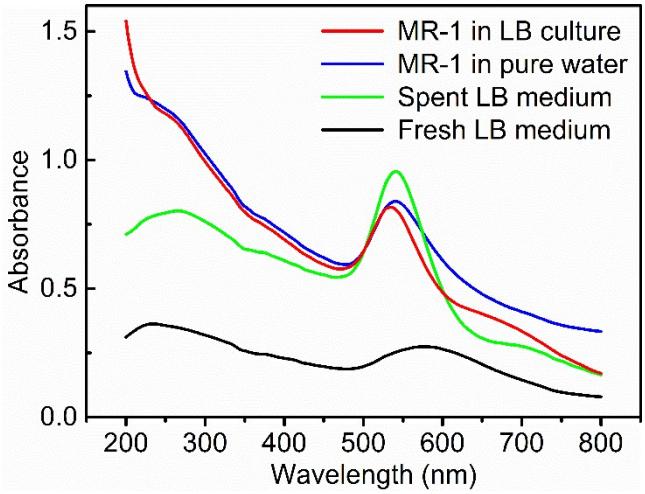

Fig. S7. UV-vis absorption spectra of reduction products synthesized under different conditions (MR-1 in LB culture, MR-1 in pure water, spent LB medium without cell and fresh LB medium without inoculation).

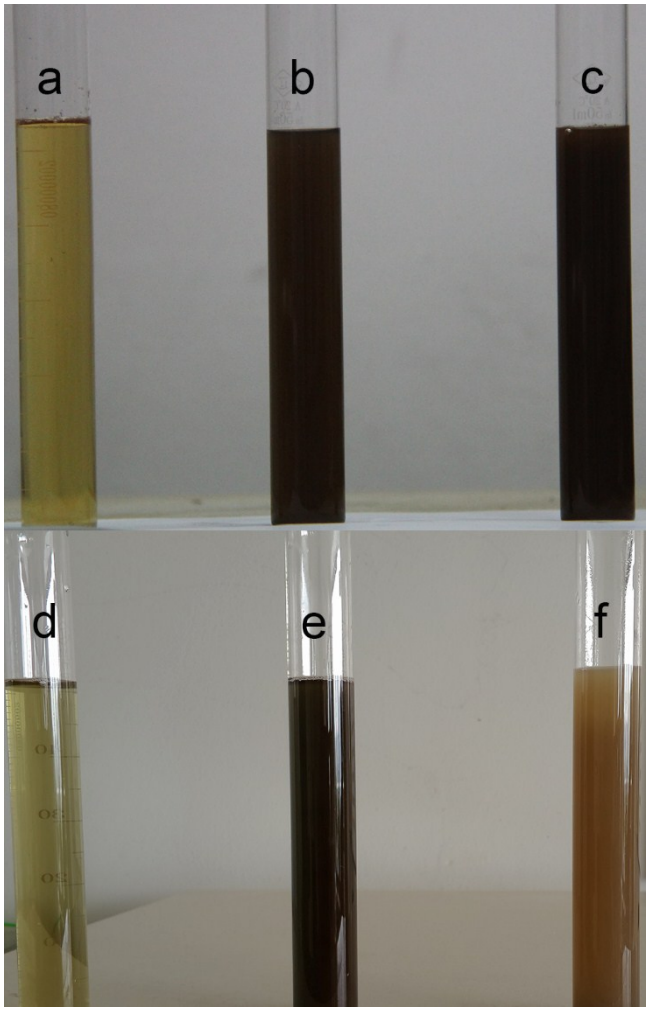

Fig. S8. Digital pictures of spent LB medium without cell (upper line) and fresh LB medium without inoculation (lower line) after incubating with (a, d) $HAuCl_4$, (b, e) $HAuCl_4$ and GO mixture, and (c, f) GO for 48 h.

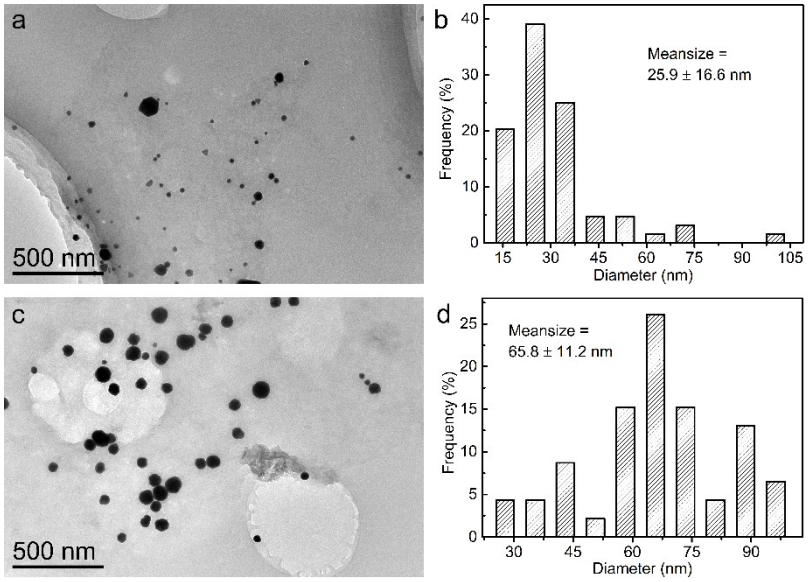

Fig. S9. TEM images and corresponding AuNPs size distribution analysis of AuNPs/rGO nanocomposites prepared by MR-1 suspension in (a, b) pure water and (c, d) spent LB medium.

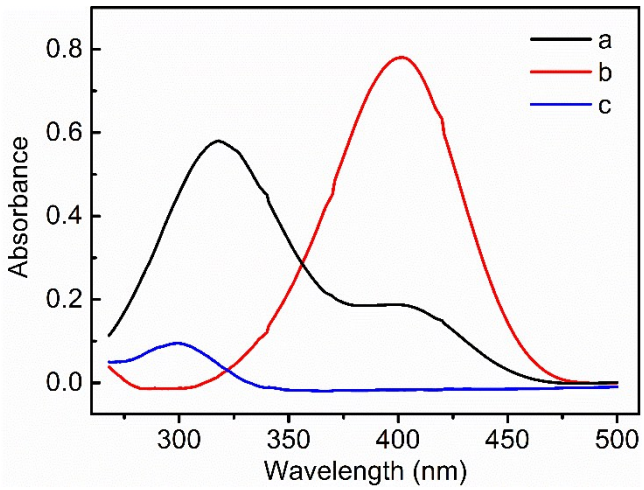

Fig. S10. UV-vis spectra of (a) the 4-NP solution, the aqueous mixture of 4-NP and $NaBH_4$ (b) before and (c) after reduction.

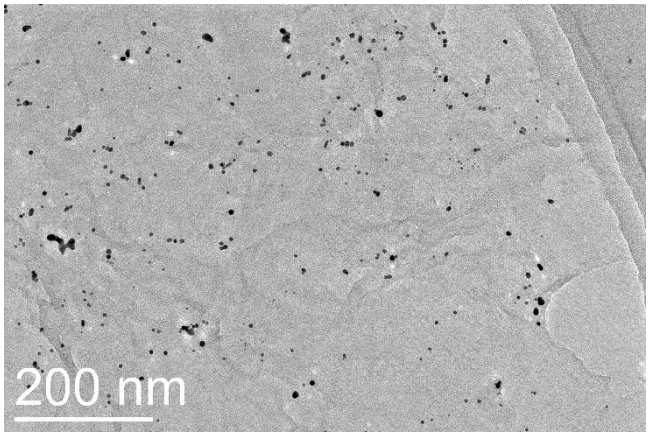

Fig. S11. TEM image of bio-AuNPs/rGO after catalyzing ten rounds of chemical reduction of 4-NP.

Table S1. Nitrobenzene bioreduction by *Shewanella* species in different studies.

Initial nitrobenzene concentration (mg/L)	Reduction time (h)	Species	Biomass amount (mg (dry weight)/mL)	Nanomaterials	NB reduction rate (mg (NB) mg^{-1} (cell dry weight) h^{-1})	Refs
220	48	*Shewanella oneidensis* MR-1	0.049		0.0452	this study
				bio-AuNPs/rGO	0.0678	
				bio-AuNPs	0.0466	
				bio-rGO	0.0540	
				bio-AuNPs + bio-rGO	0.0514	
				chem-AuNPs/rGO	0.0462	
18	24	*Shewanella putrefaciens* CN32	0.028		0.0268	ref. 1
185	24	*Shewanella oneidensis* MR-1	0.140		0.0551	ref. 2
200	24	*Shewanella* sp. XB	0.200		0.0417	ref. 3
100	174	*Shewanella oneidensis* MR-1	0.014,	CNT	0.0392	ref. 4

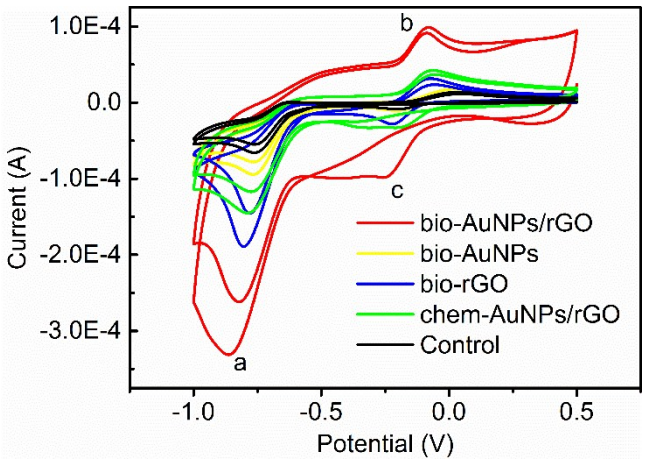

Fig. S12. Effects of different nanomaterials on electrochemical reduction of nitrobenzene. Cyclic voltammograms for polished glass carbon electrode and different nanomaterials modified electrodes in M-R2A medium containing nitrobenzene (200 mg/L) at a scan rate of 100 mV/s.

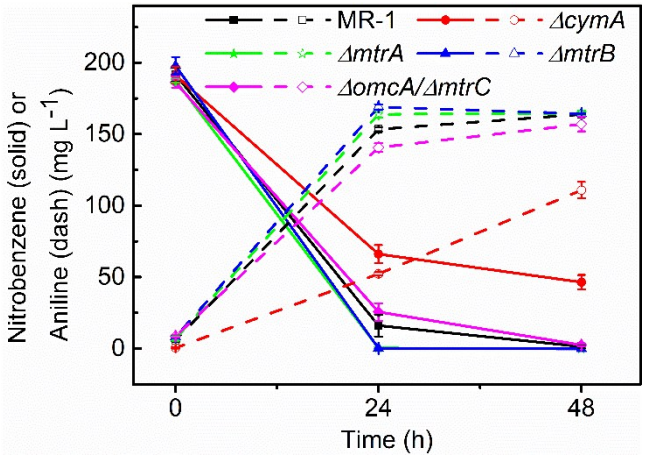

Fig. S13. The changes of nitrobenzene (solid) and aniline (dash) concentrations during nitrobenzene bioreduction by *S. oneidensis* MR-1 wild-type and mutant strains at cell concentration of 6×10^8 cells/mL.

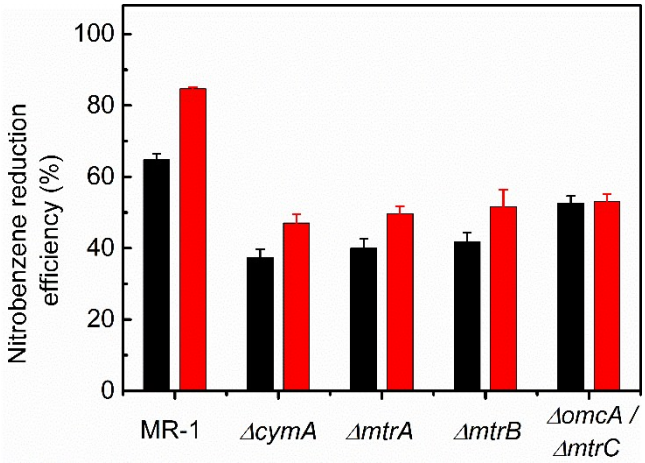

Fig. S14. Nitrobenzene reduction efficiency in 120 h by *S. oneidensis* MR-1 wild-type and mutant strains in the absence (black) or presence (red) of bio-AuNPs/rGO.

References

1. F. Luan, W. D. Burgos, L. Xie and Q. Zhou, *Environ. Sci. Technol.*, 2009, **44**, 184-190.
2. P. Cai, X. Xiao, Y. He, W. Li, L. Yu, M. H.W. Lam and H. Yu, *Biochem. Eng. J.*, 2012, **68**, 227-230.
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