Supporting Information for

MnO_2/Graphene Oxide: a Highly Active Catalyst for Amides Synthesis from Alcohols and Ammonia in Aqueous Media

Renfeng Nie, [a] Juanjuan Shi, [a] Shuixin Xia, [a] Lian Shen, [b] Ping Chen, [a] Zhaoyin Hou*[a] and Feng-Shou Xiao [a]

[a] *Institute of Catalysis, Department of Chemistry, Zhejiang University, 310028 Hangzhou, P.R. China. Fax: +86 571 88273283; Tel: +86 571 88273283; E-mail: zyhou@zju.edu.cn*

[b] *College of Chemical Engineering and Materials Science, Zhejiang University of Technology, 310014 Hangzhou, P.R. China.*

1 Experimental section

1.1 GO synthesis

GO was prepared by oxidation of graphite according to the Hummers and Offemann's method [**1**]. Graphite powder (10.0 g) and sodium nitrate (5.0 g) were first mixed and stirred in concentrated sulfuric acid (230 mL) at 0 °C for 1 h. Potassium permanganate (30.0 g) was added gradually to above solution with vigorous stirring. The ice-bath was then removed and the temperature of above suspension was brought to 35 °C, where it was maintained for 30 min. Then distilled water (460 mL) was added slowly into the paste and the temperature was raised to 98 °C. One hour later, the suspension was further diluted to 1.4 L with warm water and treated with 3 % hydrogen peroxide aqueous solution. Finally, the resulting suspension was filtered and washed with 5 % HCl aqueous solution.

1.2 Synthesis of MnO_2/GO

The typical route of MnO_2/GO synthesis, for example, when the feeding ratio of MnO_2/GO is 3:1, is as follows [**2**]: GO (0.5 g) and $MnCl_2\cdot 4H_2O$ (2.05 g) were dispersed in isopropyl alcohol (378 mL), with ultrasonication for 2 h. Subsequently, the slurry was heated to approximately 75 °C with vigorous stirring, and $KMnO_4$ (1.14 g) dissolved in (37.8 mL) of deionized (DI) water was added rapidly into the above solution. After refluxing for 15 to 120 min, the mixture was cooled to room temperature. The nanocomposite, labeled as MnO_2/GO was then **filtered, washed, and finally dried** overnight. For comparison, nano-MnO_2 was synthesized chemically in the absence of GO via a similar procedure.

1.3 Characterization

X-ray diffraction (XRD) spectra of the catalysts were carried out on a **RIGAKU D/MAX 2550/PC** diffractometer at 40 kV and 100 mA with Cu Kα radiation (k = 1.5406 Å) in the range from 5 to 80^o. N_2 adsorption was carried out at -196 ^{o}C using an auto-adsorption analyzer (Micromeritics, TriStarII). Raman spectra were collected from 200 to 2000 cm^{-1} on a Renishaw 2000 Confocal Raman Microprobe (Rhenishaw Instruments, England) using a 514.5-nm argon ion laser. Scanning electron microscopy (SEM) images were obtained on a HITACHI (S-4700) scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using an accelerating voltage of 200 kV (TEM, JEOL-135 2010F).

1.4 Synthesis of amides

A typical procedure for the reaction was as follows: benzyl alcohol (0.5 mmol), MnO_2/GO (0.13 g), water (4 mL), an aqueous solution of ammonia (28 wt%, 0.1 mL, ca. 2.6 equiv with respect to benzyl alcohol), were placed in a custom designed stainless autoclave with a Teflon inner layer and a magnetic stirrer. The Teflon vessel was attached inside an autoclave and the reaction was carried out at 150 ^{o}C in O_2 (3 Mpa). The reactants were analyzed by GC (HP 5890, USA) with a 30 m capillary column (HP-5) using a flame ionization detector. And all products were confirmed by GC–MS (Agilent 6890) and quantified via external calibration method. After the reaction was completed, the spent MnO_2/GO catalyst was retrieved by filtration, washed with acetone, and then dried in vacuum prior to being recycled.

2.1 XRD

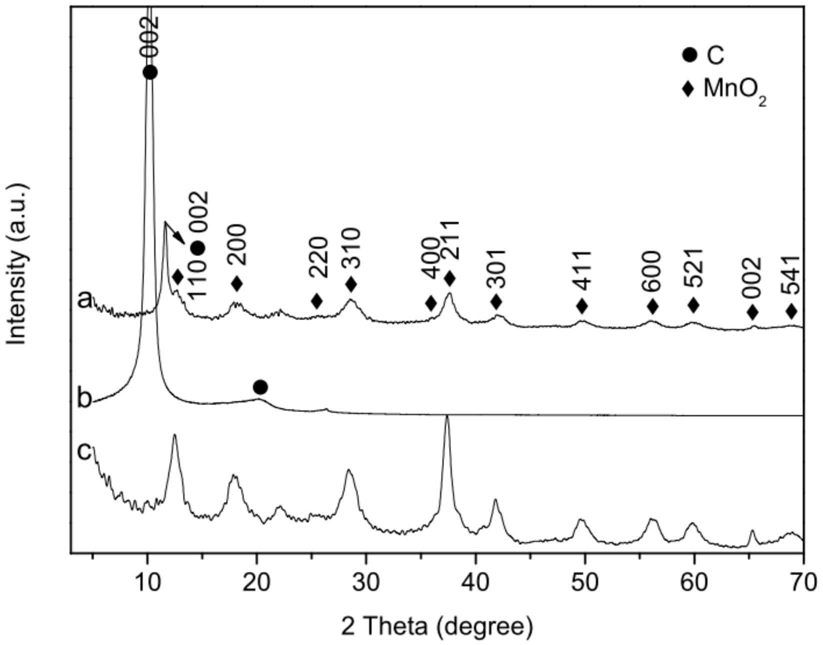


Figure S1 XRD patterns of (a) MnO_2/GO, (b) GO, and (c) MnO_2.

2.2 SEM and TEM images

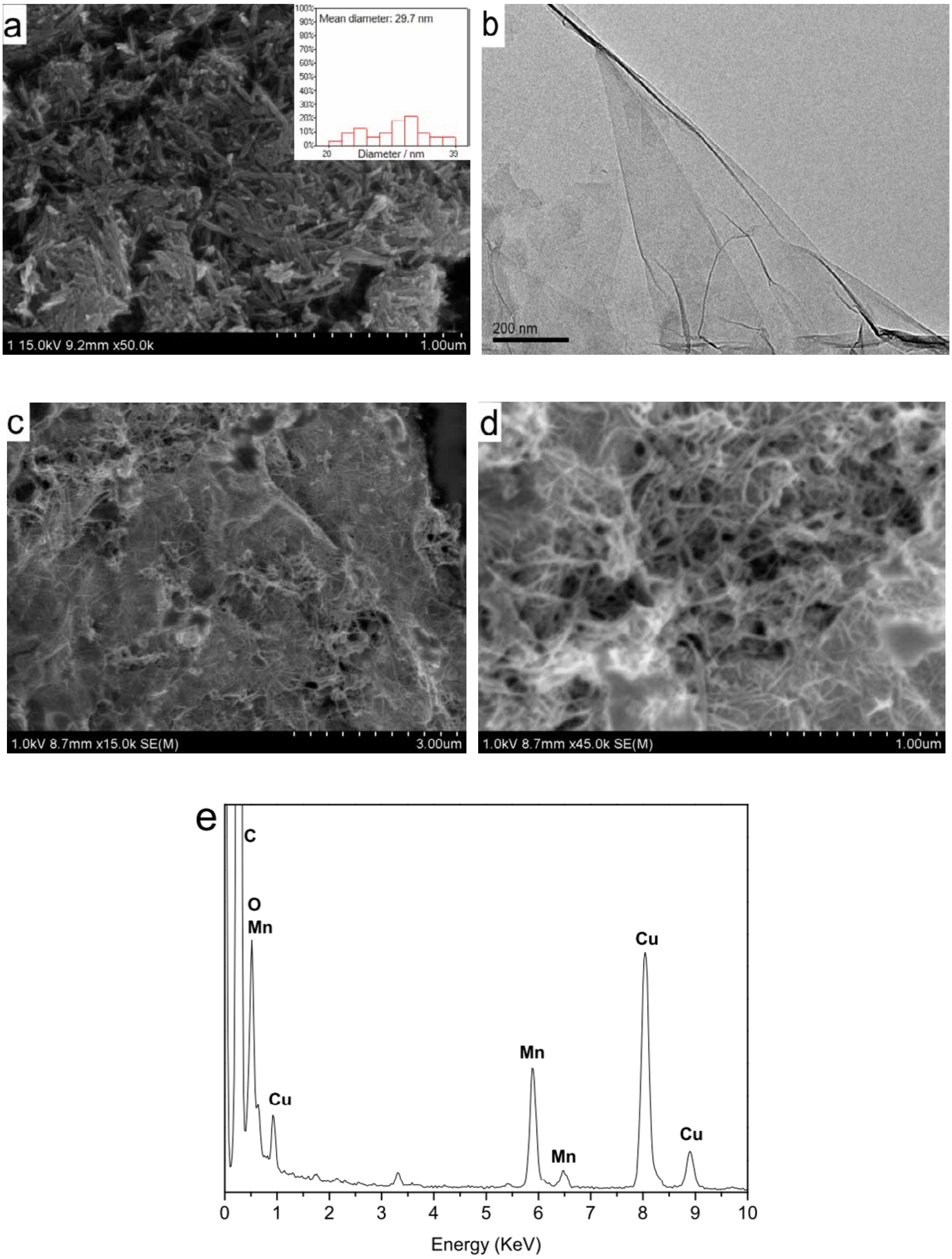


Figure S2. (a) SEM image of bare α-MnO_2 (inset: particle size distribution); (b) TEM image of pure GO; (c, d) SEM image of MnO_2/GO nanocomposites obtained at 2 h, and (e) its EDX analysis.

2.3 Nitrogen adsorption

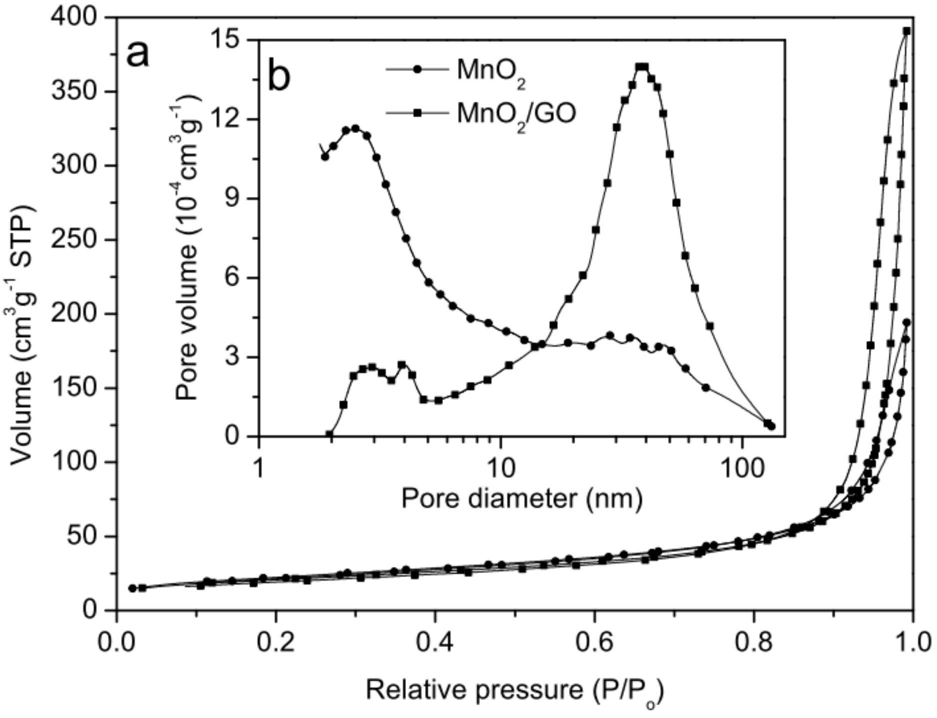


Figure S3. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of MnO_2 particles and MnO_2/GO nanocomposites.

2.4 Raman spectroscopy

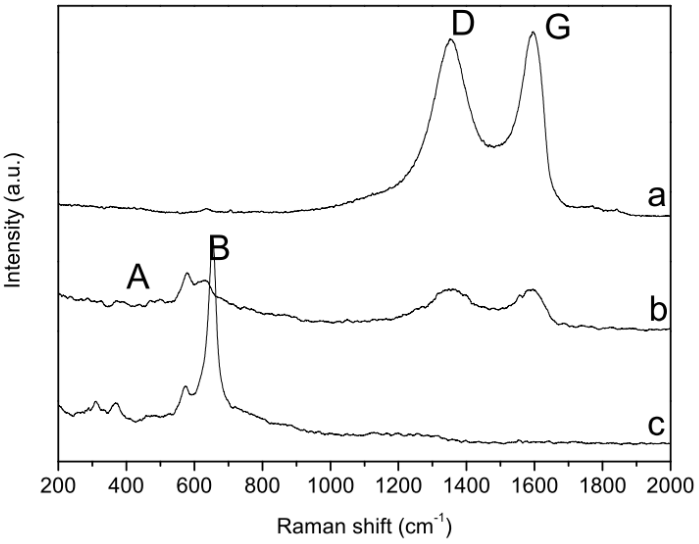


Figure S4 Raman spectra of (a) GO, (b) MnO_2/GO and (c) MnO_2.

2.5 XPS

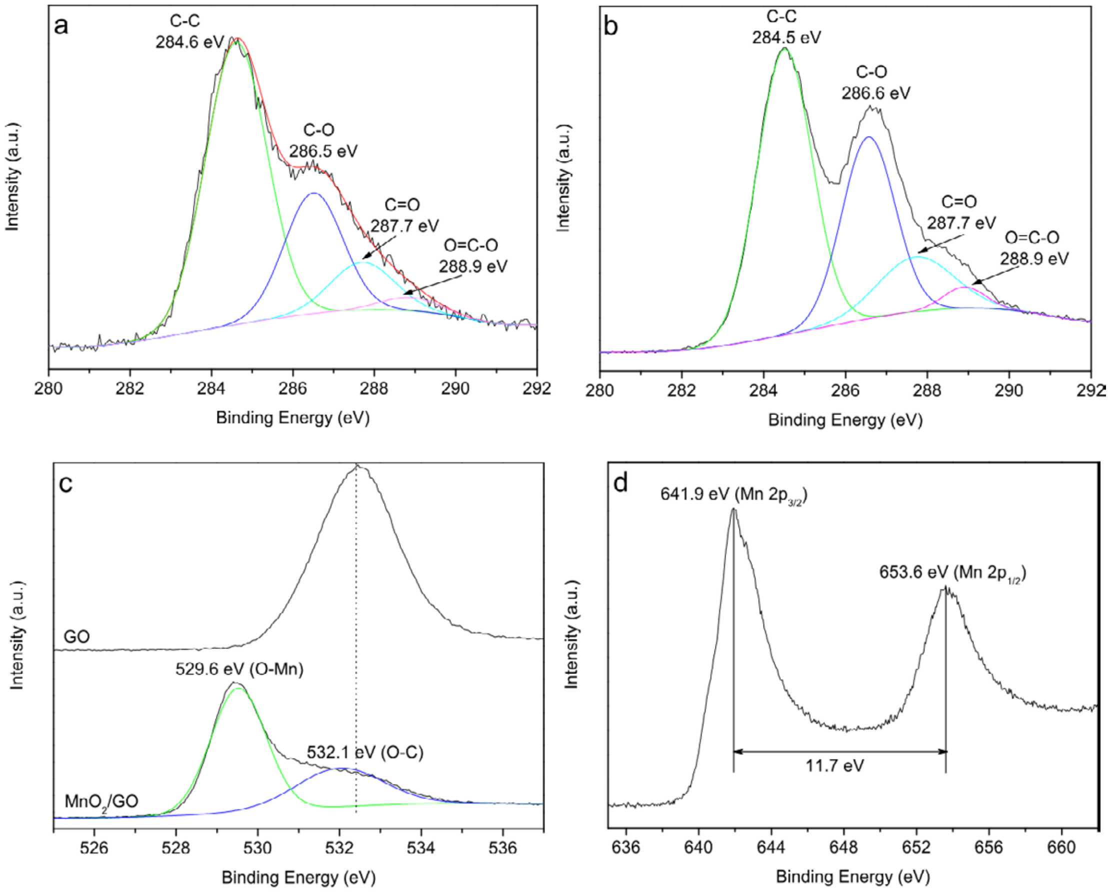


Figure S5. **XPS** spectra of the C1s region of (a) MnO_2/GO, (b) GO, (c) O1s region, and (d) Mn2p region of the MnO_2/GO composite.

Table S1. XPS data of distribution of functional groups.

Sample name	Relative atomic percentage (%)				Heterocarbon component (%)
	C=C	C-O	C=O	O-C=O	
GO	51.8	32.0	13.2	3.0	48.2
MnO_2/GO	61.4	25.0	10.7	2.8	38.6

Figure S6. Digital photos of MnO_2/GO (left) and bare MnO_2 (right) into water (0.1g/mL). MnO_2/GO was well dispersed in water, this can be attributed to a large amount of oxygen-containing groups existed on GO sheets. In contrast, bare MnO_2 nanocrystals have not good dispersion in water.

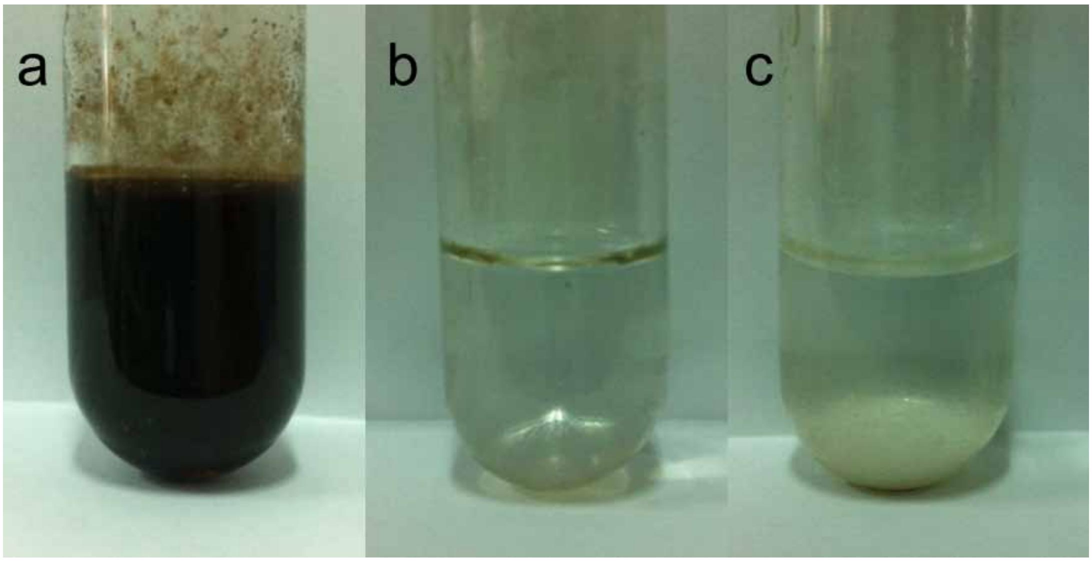
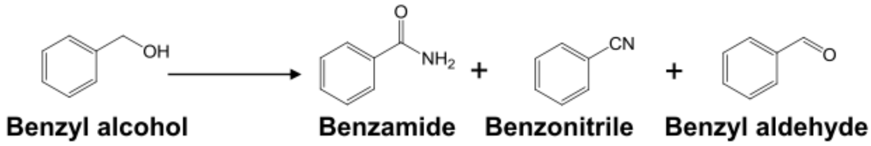


Figure S7. Digital photos of catalyst and product separation. (a) Reaction mixture, (b) Catalyst separation by hot filtration, (c) Pure white crystals of benzamide appeared when the filtrate was cooled in ice.

Table S2. Synthesis of benzamide from benzyl alcohol and ammonia.[a]



Entry	Catalyst	Solvent	Time (h)	Conv. (%)	Yield (%)		
					Benzamide	Benzonitrile	Benzyl aldehyde
1	MnO_2/GO	H_2O	1	94.6	58.5	36.0	0.1
2	MnO_2/GO	1,4-Dioxane	1	98.4	20.0	78.1	0.2
3	MnO_2/GO	DMF	1	88.2	8.5	79.1	0.6
4	MnO_2/GO	DMSO	1	99.6	23.0	76.5	0.1
5	MnO_2/GO	Toluene	1	40.9	0.4	31.2	9.3
6	MnO_2/GO	THF	1	20.8	0.4	11.7	8.7
7[b]	MnO_2	H_2O	1	57.0	5.0	49.1	2.9
8[c]	$MnCl_2\cdot 4H_2O$	H_2O	1	74.2	9.0	6.5	37.5
9[d]	GO	H_2O	1	10.8	0.0	3.0	7.8
10	no catalyst	H_2O	1	7.0	0.0	1.5	5.4
11	MnO_2/GO	H_2O	3	100	97.0	3.0	0
12[e]	MnO_2/GO	H_2O	3	100	96.9	3.1	0

[a] Reaction conditions: benzyl alcohol (0.5 mmol), catalyst (0.13 g), 28 % aq. ammonia (0.1 mL), solvent (4 mL), O_2 (3 Mpa), 423 K. The conversion and selectivity were determined by GC with an internal standard, carbon balance for each reaction was greater than 95 %. [b] MnO_2 (0.1 g). [c] $MnCl_2\cdot 4H_2O$ (1 equiv.). [d] GO (0.03 g). [e] Fifth reuse.

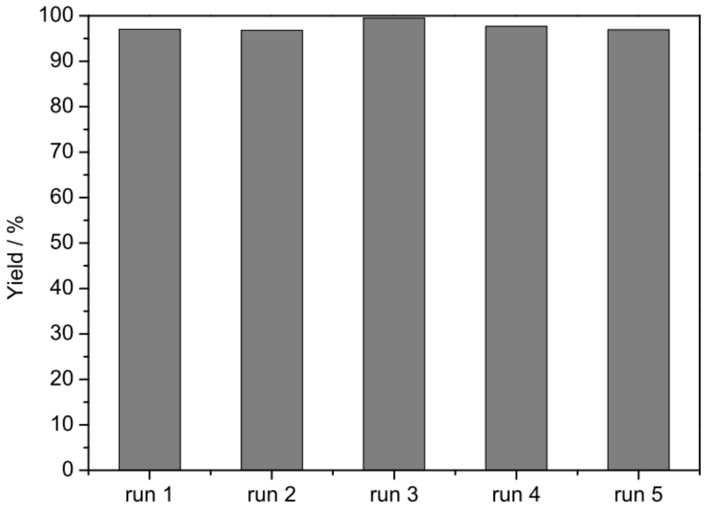


Figure S8. Recycles of MnO_2/GO catalyst for benzamide formation.

Reaction conditions: benzyl alcohol (0.5 mmol), catalyst (0.13 g), 28 % aq. ammonia (0.1 mL), solvent (4 mL), O_2 (3 Mpa), 423 K, 3h.

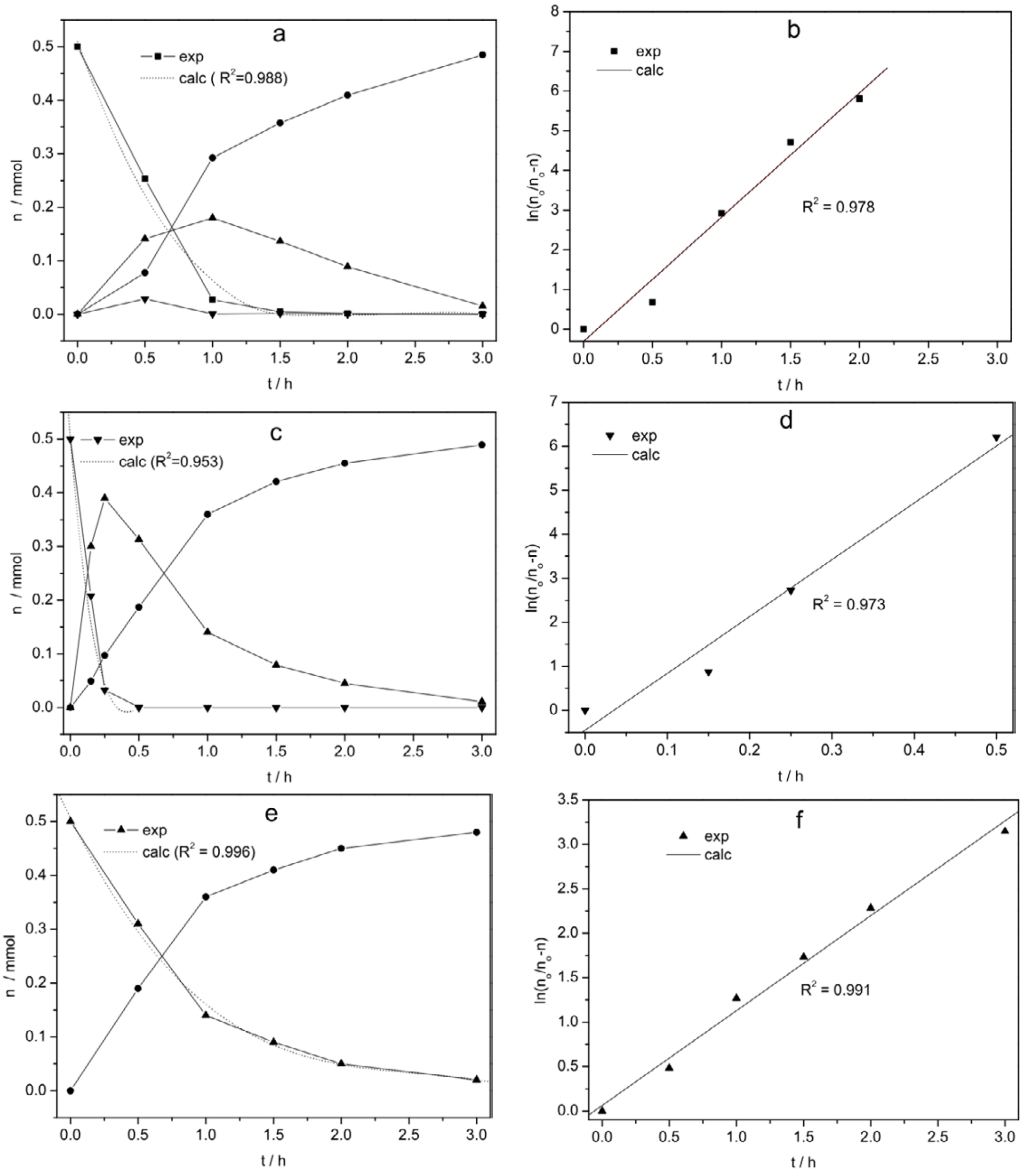


Figure S9. Catalytic kinetics for the transformation and their nonlinear regression analyses of (a,b) benzyl alcohol (■), (c,d) benzyl aldehyde (▼) and (e,f) benzonitrile (▲) to benzamide (●) over MnO_2/GO catalyst. Reaction conditions: substrate (0.5 mmol), catalyst (0.13 g), 28 % aq. ammonia (0.1 mL), solvent (4 mL), O_2 (3 Mpa), 423 K.

References

[1] W. S. Hummers, R. E. Offemann, *J. Am. Chem. Soc.* **1958**, *80*, 1339-1339.
[2] S. Chen, J. W. Zhu, X. D. Wu, Q. F. Han, X. Wang, *ACS Nano* **2010**, *4*, 2822–2830. 2010.
[3] J. Su, M. H. Cao, L. Ren, C. W. Hu, *J. Phys. Chem. C* **2011**, *115*, 14469–14477.