

## Supplementary Information for

# 0D-2D heterostructures as nanocatalysts for self-oscillating reactions: An investigation into chemical kinetics

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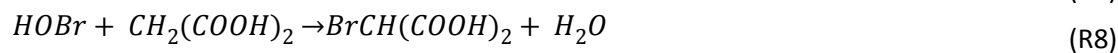
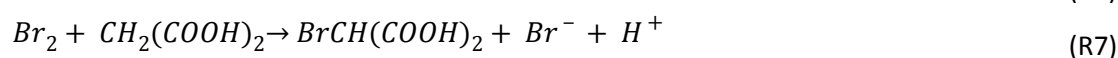
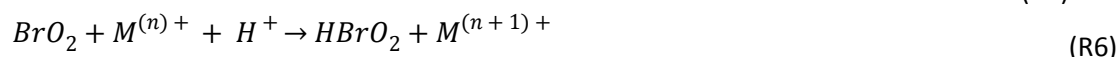
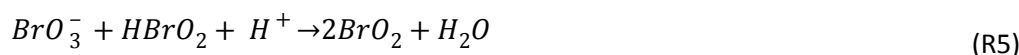
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## S1. Nanocatalyzed BZ Reaction

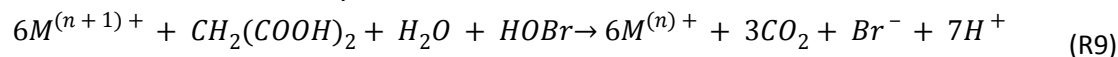
Process A: Three step reduction of bromate to bromine by bromide ion



Process B: Reduction of bromate to bromous acid, oxidation of metal ion



Process C: Reduction of catalyst and formation of bromide ion



In a typical BZ reaction with solution-based cerium catalyst the catalyst switches between oxidation (R6) in process B and reduction in process C (R9 and R10).<sup>1</sup> The catalyst cycles through oxidised and reduced states in the chemical milieu of the BZ reaction until all the organic acid present in the system exhausts.<sup>2,3</sup> The reactions R9 and R10 show that catalyst being used in the reactions of the organic substrates malonic acid (MA) and bromo malonic acid (BrMA). These reactions produce bromide ion ( $Br^-$ ) and reduced catalyst ( $M^{(n)+}$ ) there by paving the way for the process A and B. Likewise, in the case of our nanocatalyst, i.e., the ceria nanoparticle decorated graphene, the catalyst is in the form of Ce (III) as revealed by XPS measurements. Ceria nanoparticle decorated graphene, therefore, participates in the aforementioned reactions as the solution-based cerium catalyst on the similar grounds via the formation of a chelate between the organic substrate and the catalyst. Contrary to the solution-based catalysts, however, our catalyst has an added advantage that the highly

conductive electron rich graphene substrate provides rapid shuttling of electrons to the active catalyst site and nanocatalyst readily reduces by the reactions R9 and R10. This reaction also produces ( $Br^-$ ) and reduced catalyst ( $M^{(n)+}$ ) using MA and BrMA with a faster reaction rate thereby speeding up the other processes A and B, in turn increasing the overall kinetics of the BZ reaction.

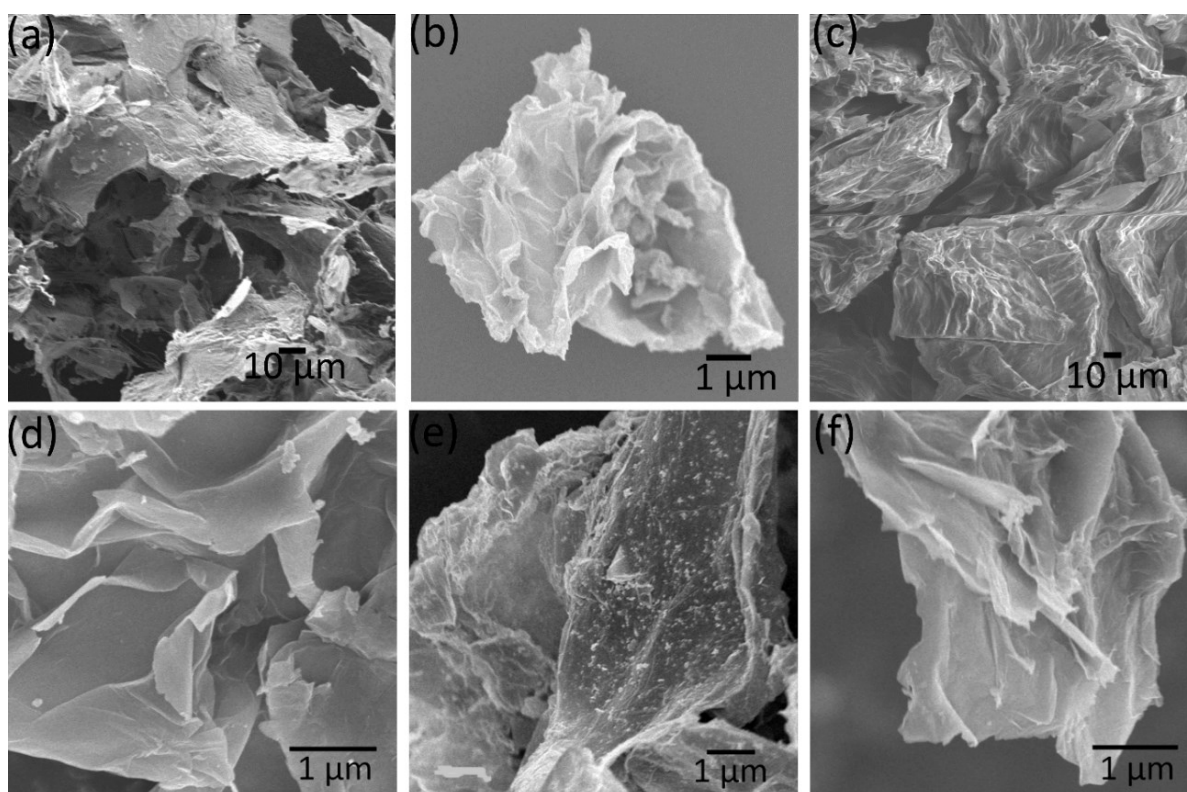


Figure-S1. (a)-(c) depicts FESEM images of GO, rGO, and graphene, (d)- (f) corresponds to Ce-GO, Ce-rGO, and Ce-graphene. Images show wrinkled sheet-like structures with lateral dimensions approximately 1-10 μm with Ceria nanoparticles attached on to the surface.

## S2. FE-SEM of Bare and Ce Decorated Nanosheets

Figure S1(a)-(c) depicts the FESEM images of GO, rGO, and graphene demonstrating wrinkled sheet like structures with lateral dimensions upto few micrometers. Likewise, Fig. S1(d)-(f) revealed wrinkled sheet-like structures with ceria nanoparticles attached over the surface. The samples for FESEM were prepared by dropcasting 0.1 mg/mL of dispersions on silica wafer and the sample dried in a desiccator

Catalyst	C (Atomic %)	O (Atomic %)	Ce (Atomic %)
Ce-GO	49.12	47.68	3.20
Ce-rGO	57.69	39.28	3.03
Ce-graphene	59.39	39.45	1.17

for 24 hours. The EDS analysis of the sample is given below:

### S3. UV and FTIR spectra of Ce Decorated Nanosheets

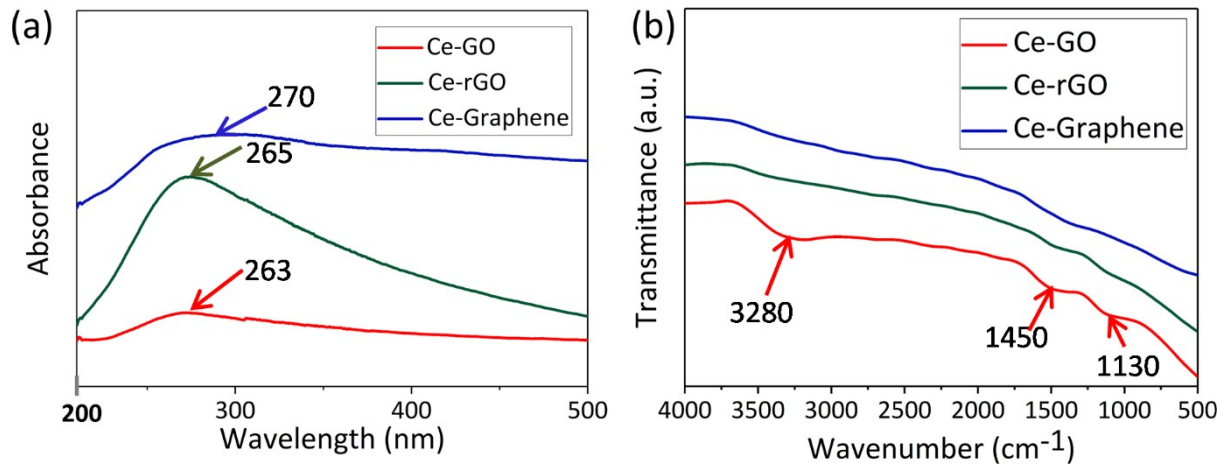


Figure-S2. (a) UV-Vis spectra of Ce-GO, Ce-rGO, and Ce-Graphene, shows a peak around 260-270 nm indicating GO, and rGO have reduced completely. (b) FTIR spectra confirms the removal of oxygen functional groups for Ce-GO, Ce-rGO, and Ce-Graphene suggesting highly conductive graphene has formed during the process of reduction with ascorbic acid.

The UV-Visible absorption spectra synthesized Ce-GO, Ce-rGO and Ce-graphene nanocomposites are shown in Fig. S2(a). All the composites have shown absorption peak around 260-270 nm indicating GO and rGO are reduced completely by ascorbic acid and  $\pi$  conjugation network restored.<sup>4</sup> Fig. S2(b) shows the IR spectra of synthesized Nano composite, here, the Ce-GO shown negligible peaks of C-O (epoxy) stretching vibration peak at 1130 cm<sup>-1</sup>, C-OH stretching peak 1140 cm<sup>-1</sup>, O-H vibration and deformation peaks at 3280 cm<sup>-1</sup>; and this peak almost disappeared for rGO during in situ reductions of ceric nitrate hexahydrate on rGO with ascorbic acid.<sup>5</sup> Thus FTIR spectra provided an evidence that all the oxygen functionalities removed significantly from GO and rGO.

### S4. Survey scans for the Ce-GO, Ce-rGO, and Ce-graphene nanocomposite

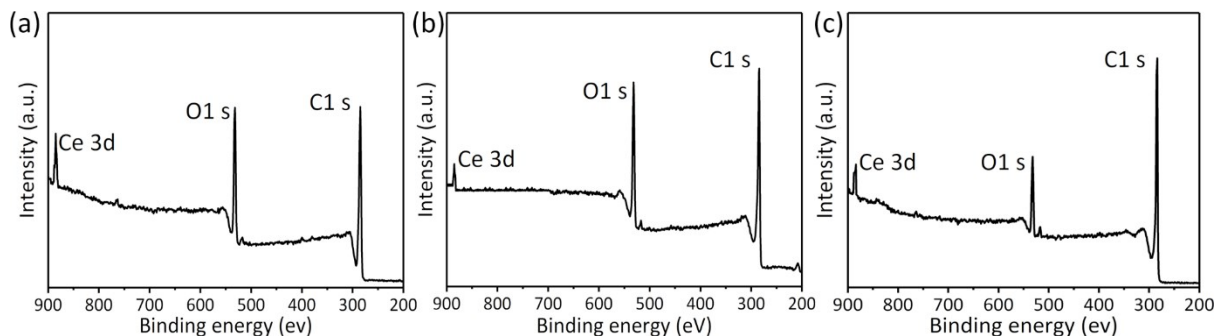


Figure-S3. (a)-(c) Exhibits the survey scan for Ce-Go, Ce-rGO, and Ce-graphene with three peaks around 284.0 eV, 530.0 eV, and 884.0 eV correspond to the C 1s, O 1s, and Ce 3d spectra respectively.

## S5. Sample calculation for determination of reaction rate parameters

The equation of regression lines obtained from Figs. 6a & 6b are given below:

Catalyst	Fig. 6a		Fig. 6b	
	Equation	$R^2$	Equation	$R^2$
Ce-GO	$y = (5540.60)x + 18.97$	0.9994	$y = (0.27)x + 2.77$	0.9759
Ce-rGO	$y = (5625.00)x + 18.25$	0.9996	$y = (0.34)x + 3.39$	0.9763
Ce-graphene	$y = (4536.60)x + 16.40$	0.9985	$y = (0.67)x + 6.55$	0.9634

For Ce-GO, the values of  $E_a/R$  and  $\alpha$  are directly determined from the slopes (of Fig. 6a & 6b) as 5540.60 and 0.27, respectively. From the above data, the intercept for  $T = 30^\circ\text{C}$  for the curve in

Fig. 6b is  $I_b = 2.77$  and therefore, from Eq. 4,  $k_{50} = \text{Exp}\left[I_b + \frac{E_a}{RT}\right]$ . Plugging the values of  $E_a/R$ ,  $I_b$  and  $T$  in the above equation, we get  $k_{50} = 1.39 \times 10^9$ . The value of  $k_{50}$  can also be calculated using the data from Fig. 6a above. In this case, the intercept  $I_a = 18.97$  and  $k_{50} = \text{Exp}[I_a + \alpha \ln [C]]$  from Eq. 4. Using the value of  $\alpha = 0.27$  and  $[C] = 6 \times 10^{-4}$  along with the value of  $I_a$  we calculate,  $k_{50} = 1.34 \times 10^9$ .

### References:

- 1 R. M. Noyes, R. Field and E. Koros, *J. Am. Chem. Soc.*, 1972, **94**, 1394–1395.
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- 3 S. A. Levin, M. Feldman, J. B. Keller, M. Kimura, R. May, A. S. Perelson and L. A. Segel, *Frontiers in mathematical biology*, Springer-verlag, Berlin, Heidelberg, 1994, 1996, vol. 44.
- 4 J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang and S. Guo, *Chem. Commun.*, 2010, **46**, 1112–1114.
- 5 J. Zhao, W. Hu, H. Li, M. Ji and C. Zhao, *RSC Adv.*, 2014, **5**, 7679–7686.