Electronic Supplementary Information

Green fabrication of 3-dimensional flower-shaped zinc glycerolate and ZnO microstructures for *p*-nitrophenol sensing

Apurba Sinhamahapatra, Dhrubajyoti Bhattacharjya and Jong-Sung Yu.*

Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science & Technology (DGIST), Daegu,

711-873, Republic of Korea

Corresponding Author

Jong-Sung Yu

E-mail: jsyu@dgist.ac.kr

Table S1. Comparison of present and earlier reported methodology of zinc glycerolate prepared with respective synthesis conditions.

No.	Zinc source	Reaction conditions	Morphology	Reference
1.	ZnO nanorod	i) refluxed at 100°C for 4h ii) autoclaved at 150 °C for 24 h	Microstack	1
2.	Zinc acetate	autoclaved at 150 °C for 10 h	hamburger-like	2
3.	Zinc acetate	heated at 160 °C for 1 h	Nanoparticle (~4-6 nm) [a]	3
4.	Zinc acetate	refluxed at 160°C for 1h	platelets	4
5.	Zinc acetate	i) stirred at 80 °C for 15 min ii) microwave treatment for 7 min at 750 W (154 °C)	Microplates	5
6.	[bis(2-hydroxy-1-naphthaldehydato) zinc(II)]	Same as 5	Nanoplates	5
7.	Zinc oxalate	Same as 5	Nanoflowers [a]	5
8.	Zinc ammonium complex	refluxed at 100 °C for 12h	Microflower	Present work[b]

[a] The product is ZnO although it uses glycerol

[b]All the above methods utilized more glycerol than stoichiometric amount. However, only the present methodology recovered and reused the glycerol.

Table S2 General information about synthesis conditions of zinc glycerolate microstructure samples.

Sample name	Zn-source	Reaction conditions	Glycerol : water (V/V)	Temperature (°C and time (h)	Morphology
ZG-1	$Zn(NO_3).6H_2O$	Stirring	1:0.5	25 and 12	Random
ZG-2	$Zn(NO_3).6H_2O$	Reflux	1:0.5	100 and 12	Uniform flower (0.7-0.8 µm) consist of petals
ZG-3	$Zn(NO_3).6H_2O$	Solvothermal	1:0.5	100 and 12	Big flower (~3 µm) consist of rod like structure
ZG-4	$Zn(NO_3).6H_2O$	Reflux	1:5	100 and 12	Star like structure
ZG-5	$Zn(NO_3).6H_2O$	Reflux	1:2	100 and 12	Ununiformed rod assembled flower
ZG-6	$Zn(NO_3).6H_2O$	Reflux	1:1	100 and 12	Flower shape (~2 µm)
ZG-7	$Zn(NO_3).6H_2O$	Reflux	1:0.2	100 and 12	Assembled rod structure
ZG-8	$Zn(NO_3).6H_2O$	Solvothermal	1:5	100 and 12	Random
ZG-9	$Zn(NO_3).6H_2O$	Solvothermal	1:2	100 and 12	Assembled needle shaped big rod structure
ZG-10	$Zn(NO_3).6H_2O$	Solvothermal	1:1	100 and 12	Big flower (~6 µm) consist of rods
ZG-11	$Zn(NO_3).6H_2O$	Solvothermal	1:0.2	100 and 12	Assembled rod structure
ZG-12	$ZnCl_2$	Reflux	1:0.5	100 and 12	Deformed Flower structure (~1 µm)
ZG-13	$Zn(O_2CCH_3)_2(H_2O)_2$	Reflux	1:0.5	100 and 12	Deformed Flower structure (~1 µm)
ZG-14	ZnO	Reflux	1:0.5	100 and 12	Random
ZG-15*	$Zn(NO_3).6H_2O$	Reflux	1:0.5	100 and 12	Flower structure same as ZG-2

* In this case, the glycerol used for the sample ZG-2 was recovered and reused

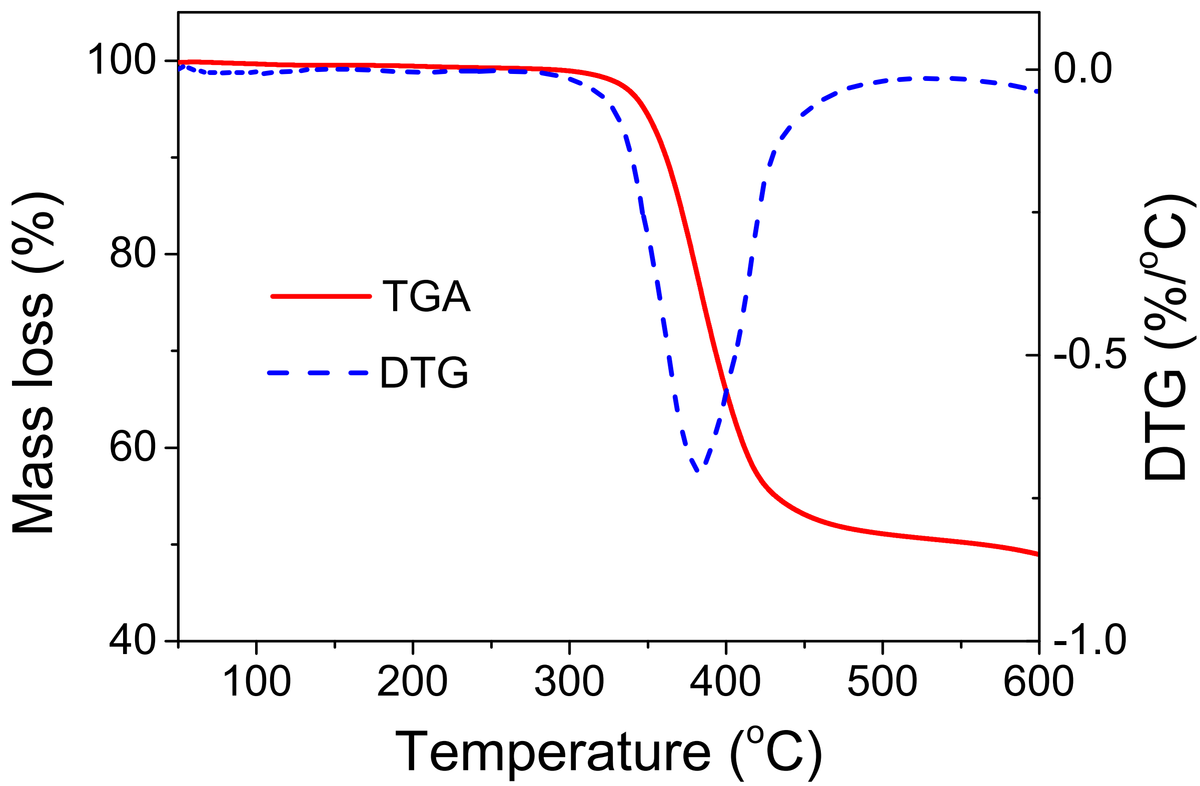


Fig. S1 TGA and DTG curves for Zn glycerolate.

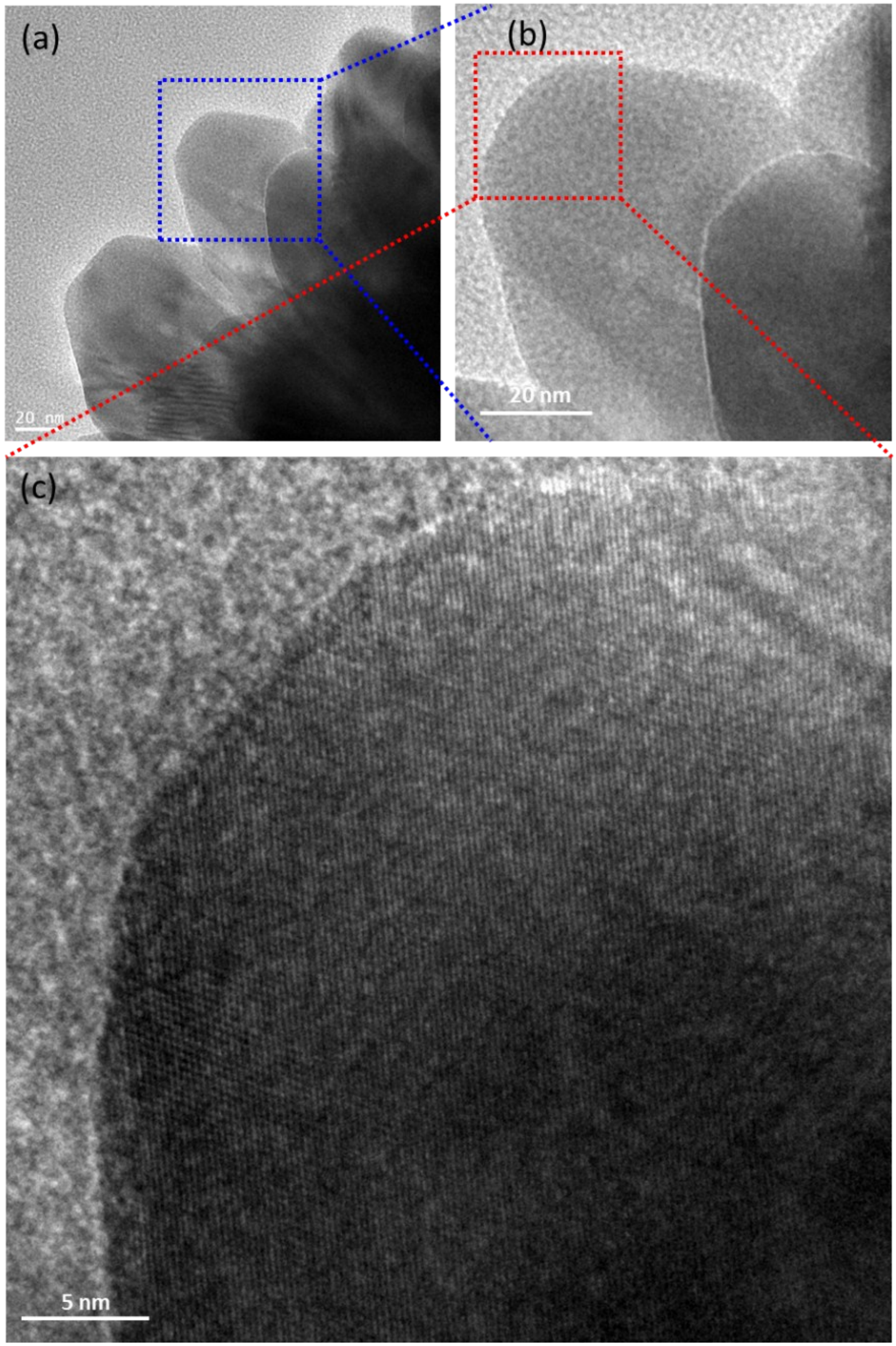
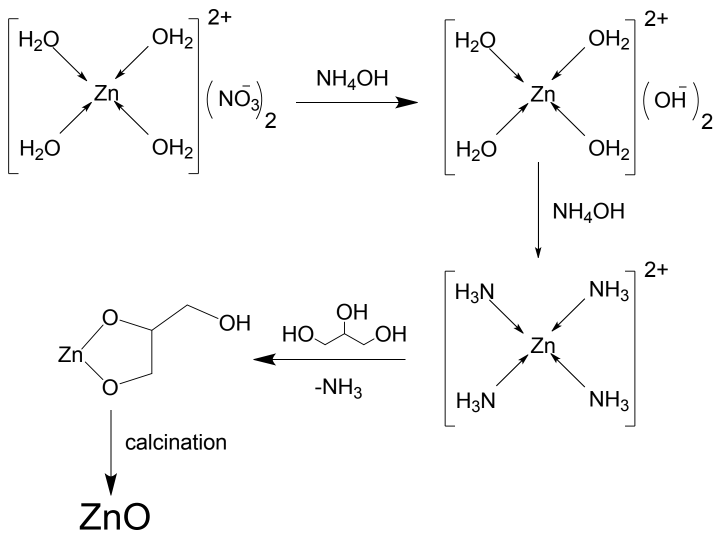


Fig. S2 HRTEM images (a and b) and lattice fringe pattern (c) of calcined ZG-2



Scheme S1 Probable chemical reactions involved during formation of zinc glycerolate and ZnO.

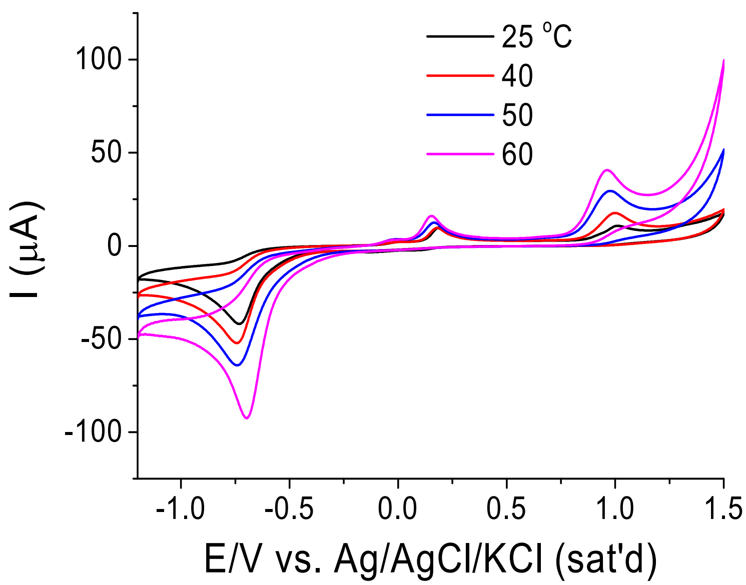


Fig. S3 CVs at different temperature in presence of 0.5 mM PNP at 50 mVs^{-1} scan rate over ZnO/GCE electrode.

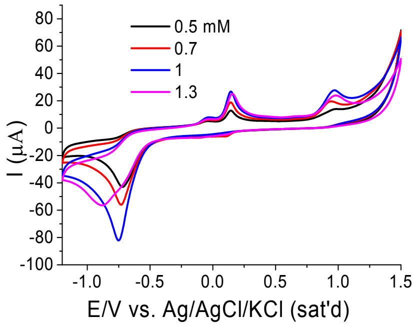


Fig. S4 CVs for different concentration of PNP at 50 mVs^{-1} scan rate over ZnO/GCE electrode

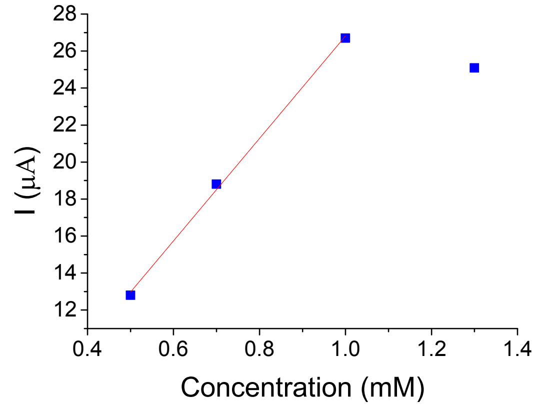


Fig. S5 Linear correlation between current response and concentration

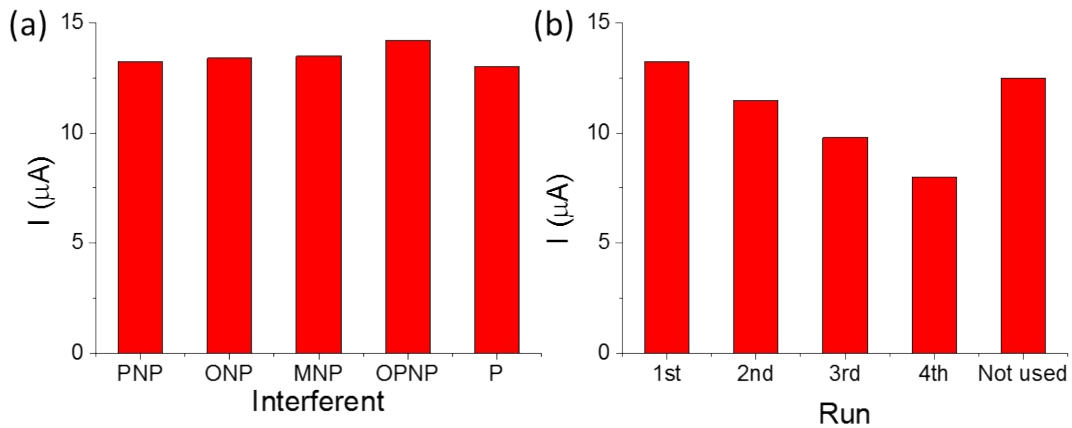


Fig. S6 Peak currents of O_1 peak (a) of ZnO/GCE in the presence of different interferents (ONP: *o*-nitro phenol, MNP: *m*-nitro phenol, OPNP: *o*-*p*- di nitro phenol and P: phenol) and (b) of the same ZnO/GCE electrode used during each 7 days for one month period and the electrode stored without use. CVs are recorded at 50 mVs^{-1} scan rate in the presence of 0.5 mM PNP using currently-developed ZnO/GCE.

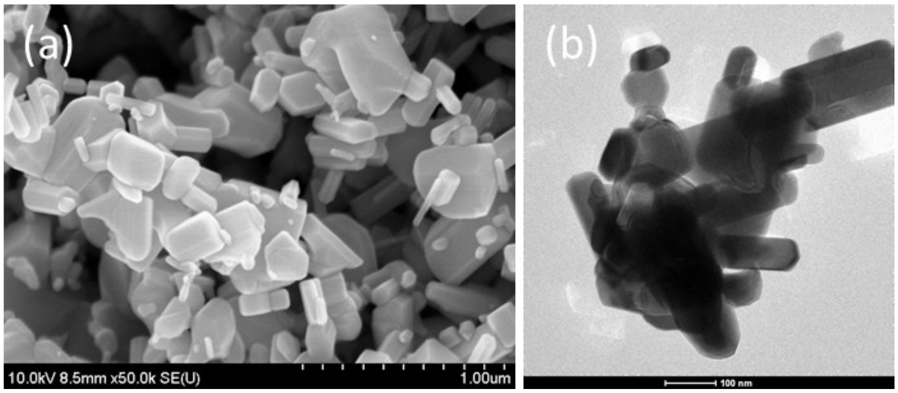


Fig. S7 SEM (a) and TEM (b) image of commercial nanocrystaline ZnO used to modify the GCE electrode for comparison study.

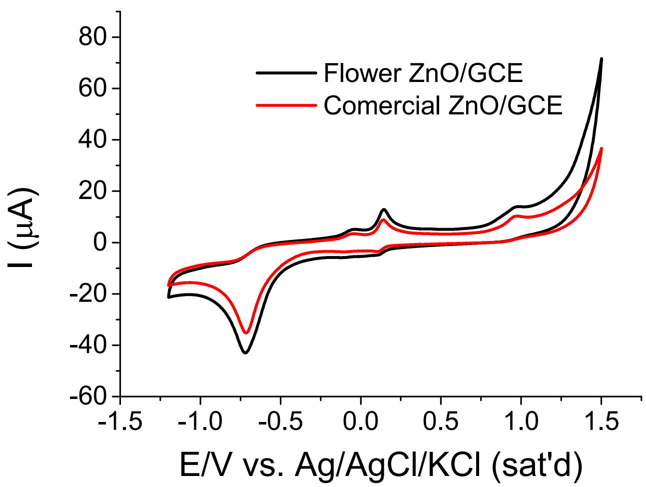


Fig. S8 CVs for different ZnO modified GCE electrode for 0.5 mM concentration of PNP at 50 mVs^{-1} scan rate

References

1. R. Rémiás, Á. Kukovecz, M. Darányi, G. Kozma, S. Varga, Z. Kónya, and I. Kiricsi, *Eur. J. Inorg. Chem.* 2009, 3622–3627

2. S. Zhang, P. Yang, A. Zhang, R. Shi and Y. Zhu, *CrystEngComm*, 2013, **15**, 9090–9096

3. A. Mezni, F. Kouki, S. Romdhane, B. Warot-Fonrose, S. Joulié, A. Mlayah, and L. S. Smiri, *Mater. Lett.,* 2012, **86**, 153–156

4. H. Dong, and C. Feldmann, *J. Alloy. Compd.,* 2012, **513** 125-129

5. N. Mira, M. S. Niasaria, and F. Davarc, *Chem. Eng. J.,* 2012, **181-182**, 779-789