Electronic Supplementary Information

Rapid and green synthetic approach for hierarchically assembled porous ZnO nanoflakes with enhanced catalytic activity

Apurba Sinhamahapatra, Arnab Kanti Giri, Provas Pal, Sandip Kumar Pahari, Hari C. Bajaj, Asit Baran Panda *

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSIR), G.B. Marg, Bhavnagar-364002, Gujarat, India. Fax: +91-2782567562; Tel: +91-2782567760 Ext. 704;

E-mail: abpanda@csmcri.org.

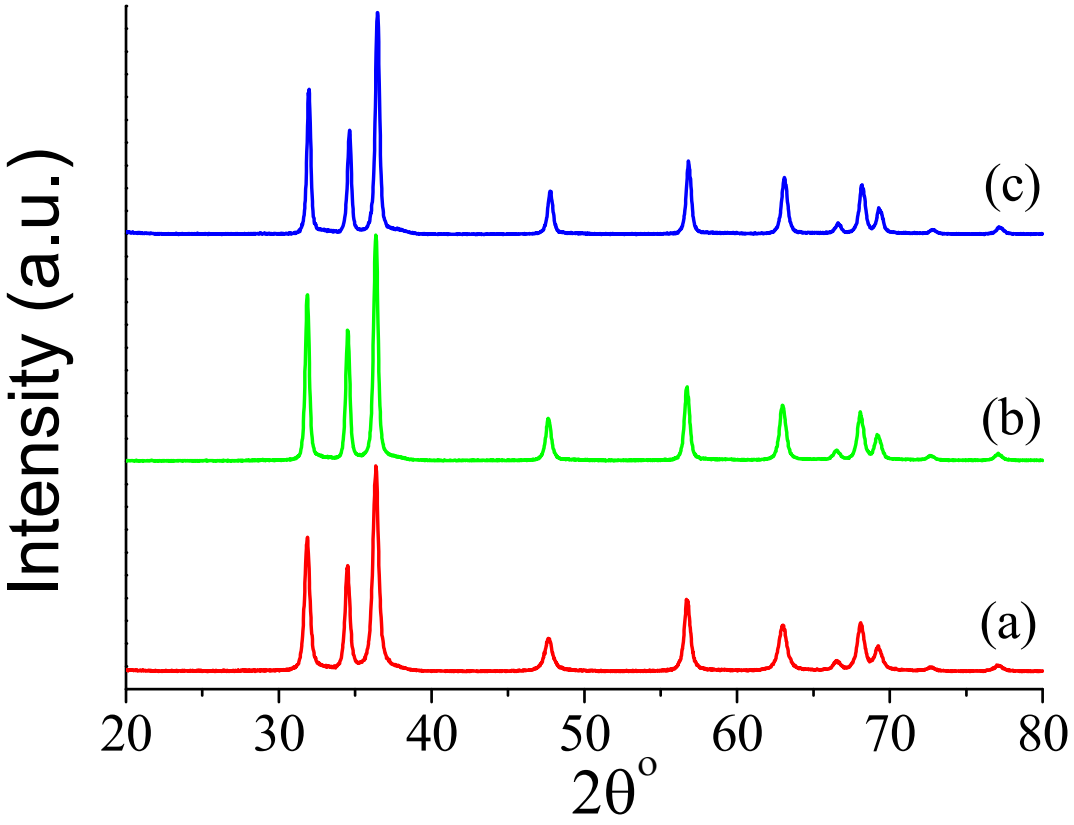

Fig. S1. X-ray diffraction pattern of the hierarchically assembled porous ZnO nanoflakes after calcination at 450 °C (a), 500 °C (b) and 600 °C (c).

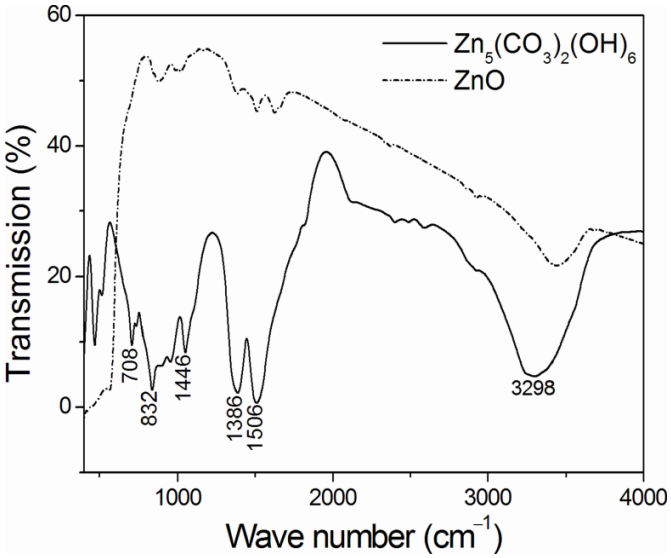

Fig. S2. FT-IR spectra of (a) hydrozincite intermediate and (b) the corresponding porous ZnO obtained after calcination at 500°C for 5 h.

To confirm the formation of intermediate hydrozincite and the corresponding calcined product ZnO, the FT-IR experiment was performed in the detection range of 400-4000 cm^{-1}. The FTIR spectrum of the synthesized hydrozincite intermediate and product ZnO (Fig. S2) is very similar to that of the reported results.[1-2] The characteristic sharp bands of hydrozincite at 708, 832, 1386, 1506 cm^{-1} can be attributed to the C-O bending vibration of CO_3^{2-}. The broad band at 3298 cm^{-1} is due to the hydroxyl group of hydrozincite and adsorbed water molecule. On calcination, the bands correspond to C-O bending vibration of CO_3^{2-} and hydroxyl or water molecules substantially weakened and confirm the decomposition of hydrozincite precursor to ZnO. However, the existence of the respective bands C-O vibration and water molecule with low intensity in the calcined ZnO can be attributed to the surface adsorbed CO_2 and water. In the previous reports the similar observation was reported [2] except the report of Wang *et al.*[1], where they have not identified any band for corresponding adsorbed water molecule.

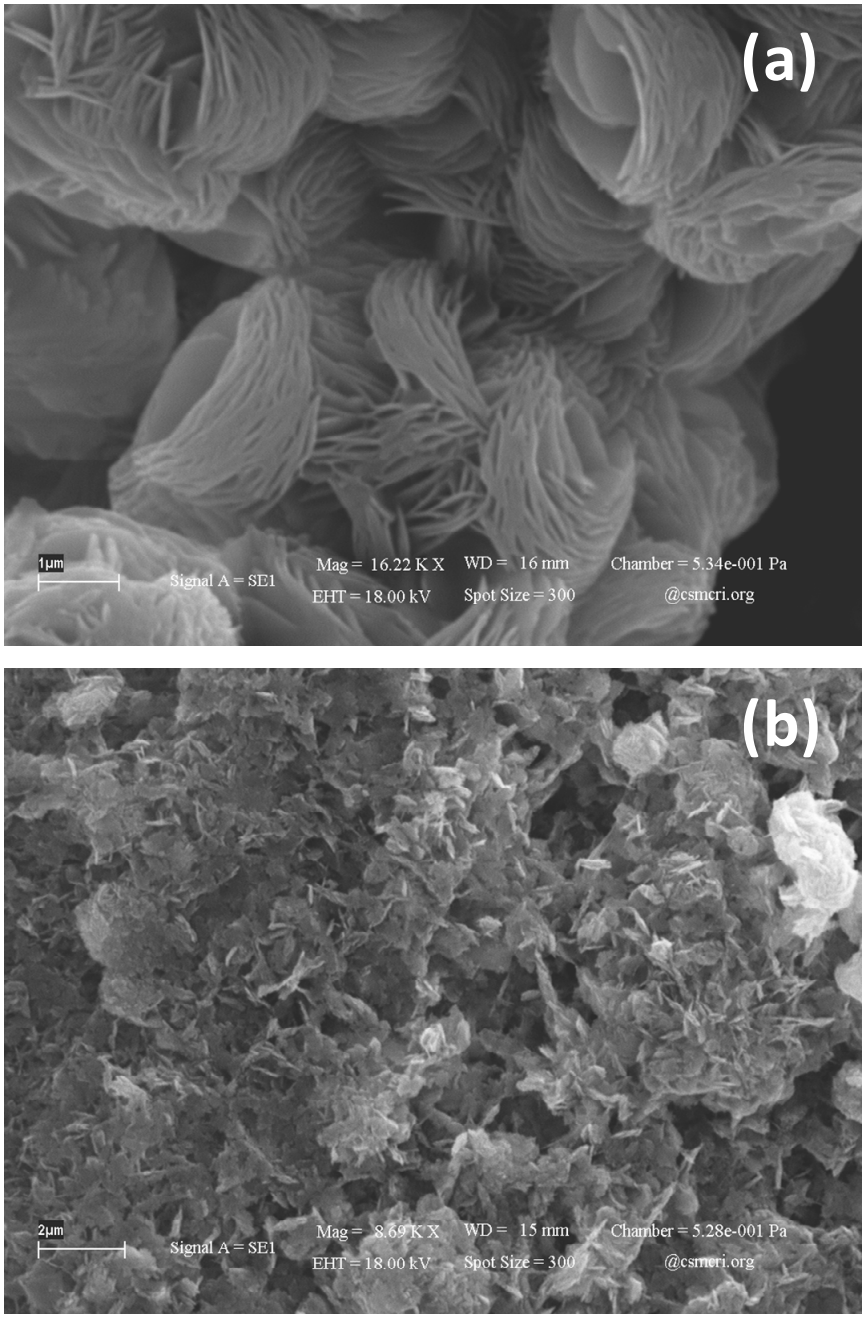

Fig. S3. SEM image of the hydrozincite after 8 h (a) and 20 h (b) of stirring at room temperature using 10 g ammonium carbonate for 4 g bulk ZnO.

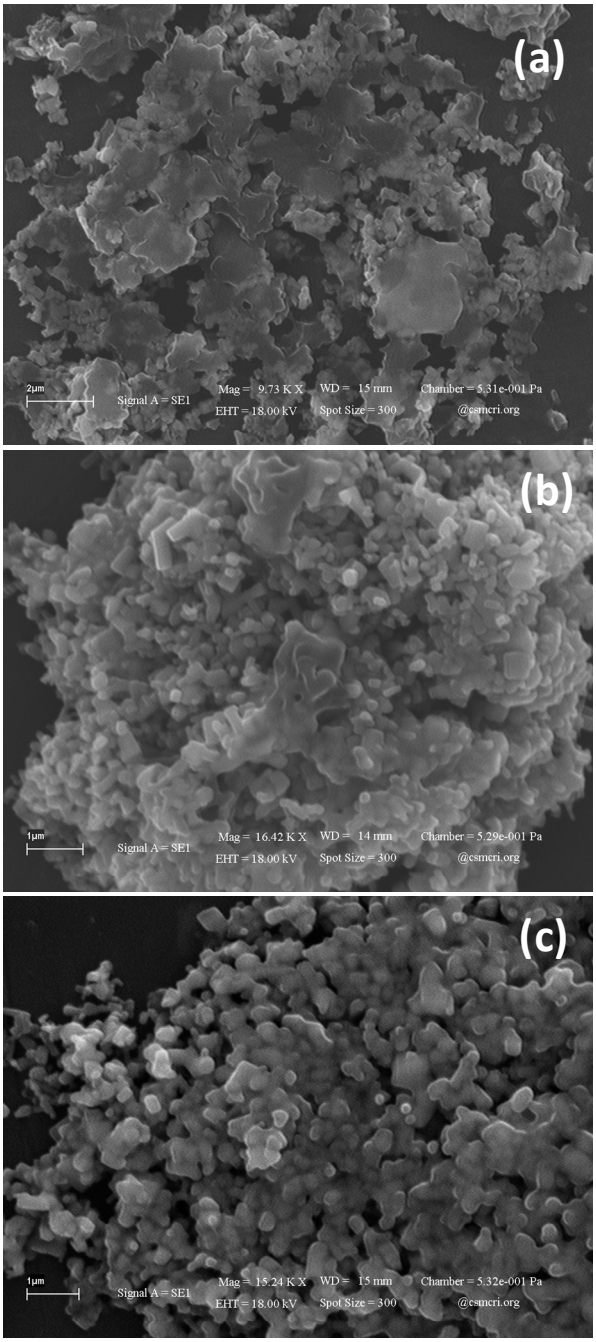

Fig. S4. SEM image of the hydrozincite after 30 min in the control reactions using (a) sodium carbonate, (b) sodium hydroxide and (c) ammonium hydroxide instead of ammonium carbonate.

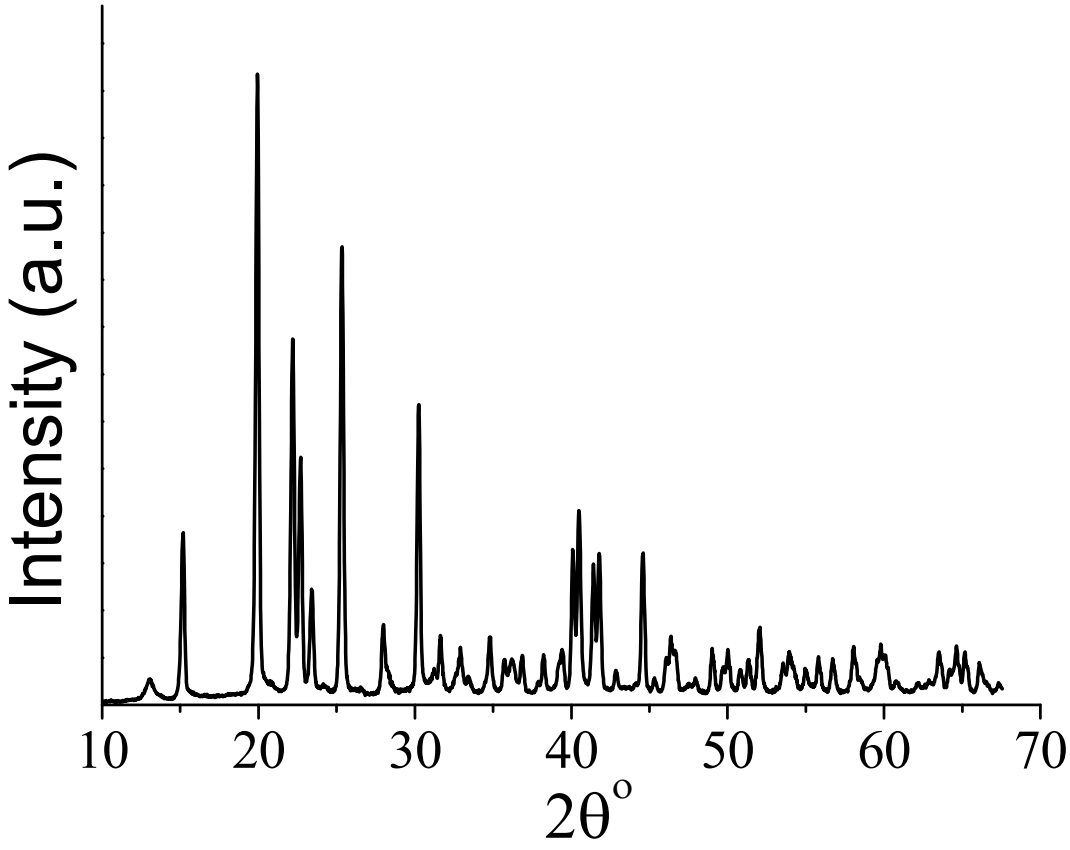

Fig. S5. X-ray diffraction pattern of intermediate obtained after 5 min for the of reaction at room temperature using 10 g ammonium carbonate for 4 g bulk ZnO.

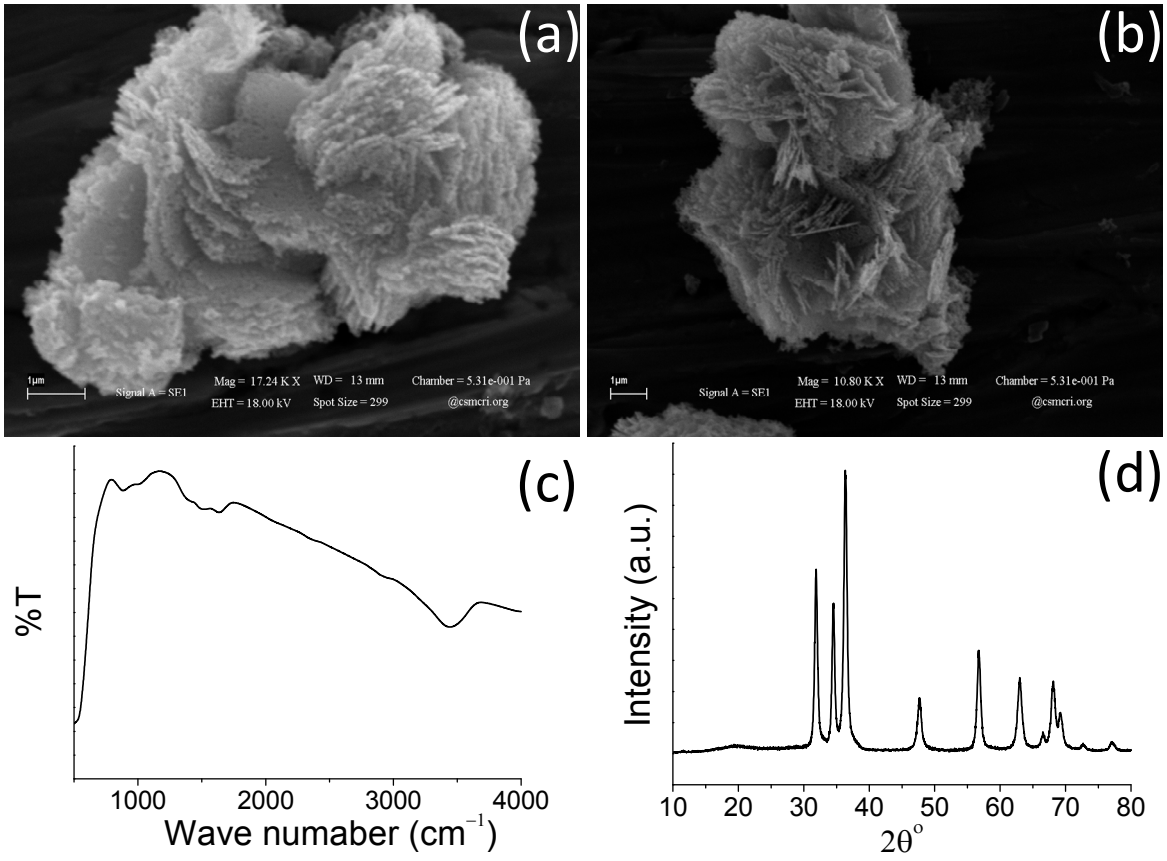

Fig. S5. Re-generated hierarchically assembled porous ZnO nanoflakes after 4th cycle (a & b) SEM image (c) FT-IR spectrum, and (d) X-ray diffraction pattern and.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Table S1. Details of the experimental for different hydrozincite synthesized.

Entry	Synthetic conditions					Shape
	Bulk ZnO (g)	Ammonium carbonate (g)	Water (mL)	Temperature (°C)	Time (h)	
1.	4	2	160	30	0.5	Random
2.	4	4	160	30	0.5	Small flowers
3.	4	8	160	30	0.5	Assembly of small flowers
4.	4	10	160	30	0.5	3D assembled flakes
5.	4	11	160	30	0.5	3D assembled flakes
6.	4	12	160	30	0.5	3D assembled flakes
7.	4	11	160	30	0.084	Melted morphology
8.	4	11	160	30	0.167	Sludge like morphology
9.	4	11	160	30	0.25	Sludge wavy morphology
10.	4	11	160	30	0.3	3D assembled flakes
11.	4	11	160	30	8	3D assembled flakes
12.	4	11	160	30	20	Small flakes
13.	4	11	160	45	0.3	3D assembled flakes
14.	4	11	160	60	0.3	3D assembled flakes with small length
15.	4	11	160	90	0.3	3D assembled small flakes
16.	4	NH_3OH	160	30	0.3	Sludge like morphology
17.	4	NaOH	160	30	0.3	Sludge like morphology
18.	4	Na_2CO_3	160	30	0.3	Sludge like morphology

For entry 16-18 160 ml of aqueous solution was used maintain the pH of the solution as entry 5

Table S2. The catalytic activity of all the synthesized ZnO shapes synthesized varying reaction conditions.

Entry	Catalyst	Yield (%)[a]	TON[b]	TOF (h^{-1})[c]
1.	3D porous ZnO (10)[d] (400)[e]	87	1.77	0.1266
2.	3D porous ZnO (10)[d] (450)[e]	88	1.79	0.1280
3.	3D porous ZnO (10)[d] (500)[e]	87	1.77	0.1266
4.	3D porous ZnO (10)[d] (600)[e]	71	1.44	0.1033
5.	3D porous ZnO (11)[d] (500)[e]	86	1.75	0.1251
6.	3D porous ZnO (12)[d] (500)[e]	87	1.77	0.1266
7.	3D porous ZnO (8)[d] (500)[e]	68	1.38	0.0989
8.	3D porous ZnO (4)[d] (500)[e]	72	1.46	0.1047
9.	[f]3D porous ZnO (10)[d] (500)[e]	84	1.71	0.1222
10.	[g]3D porous ZnO (10)[d] (500)[e]	81	1.65	0.1178
11.	[h]3D porous ZnO (10)[d] (500)[e]	76	1.54	0.1106
12.	bulk ZnO (commercial)	51 (56[i])	1.12	0.0800

Reaction condition: Benzonitrile, 2.5 mmol; sodium azide, 2.75 mmol; DMF, 5 ml; reaction temperature, 125°C; reaction time, 14 h; catalyst amount, 0.1g.

[a]isolated yield

[b]moles of product form per mole of catalyst

[c]TON/reaction time (h)

[d]amount of ammonium carbonate in gram used per 4 g of bulk ZnO for the synthesis of 3D porous ZnO

[e]calcination temperature (°C)

[f]3D porous ZnO was synthesized at 45 °C

[g f]3D porous ZnO was synthesized at 60 °C

[h f]3D porous ZnO was synthesized at 90 °C

[i]reaction time was 24 h

References

1. X. Wang, W. Liu, J. Liu, F. Wang, J. Kong, S. qiu, C. He, L. Luan, *ACS Appl. Mater. Interf.*, 2012, **4**, 817.
2. Z. Xing, B. Geng, X. Li, H. Jiang, C. Feng, T. Ge, *CrystEngComm.*, 2011, **13**, 2137.