Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Energy efficient, microwave-hydro-/solvothermal synthesis of hierarchical flowers and rice-grain like ZnO nanocrystals as photoanodes for high performance dye-sensitized solar cells

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Note: This supplementary information contains supplementary figures S1-S6 and supplementary Table S1to S5.

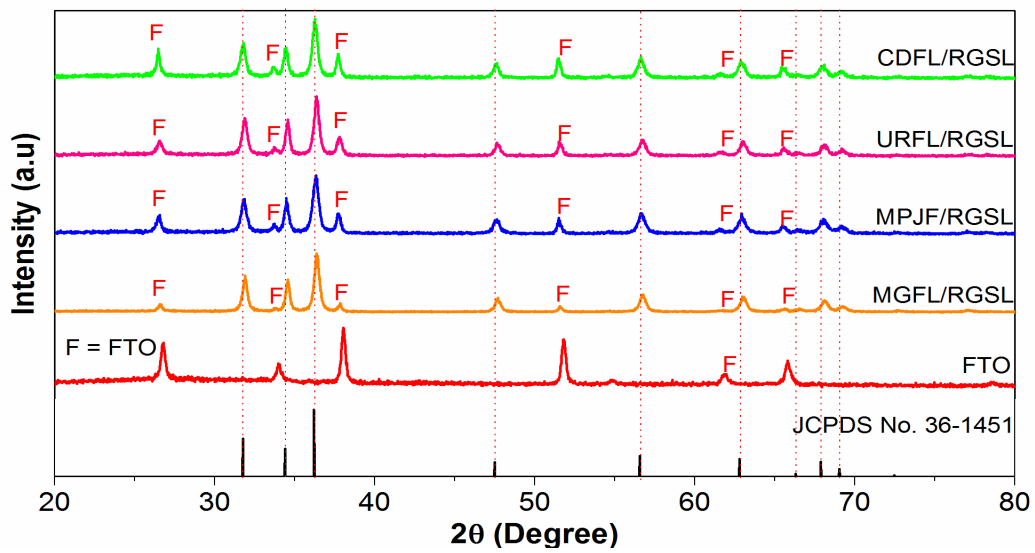


Figure S1 XRD patterns of the different hierarchical integration of CDFL/RGSL, URFL/RGFL, MPJF/RGSL, MGFL/RGSL of ZnO hybrid nanostructured films were coated on fluorine-doped tine oxide (FTO) by doctor blade method and subsequently the coated film substrates were heated in a furnace (400°C for 30 minutes) in air atmosphere. For comparative purpose, FTO and standard JCPDS data of ZnO (Ref . No. 36-1451) are also provided.

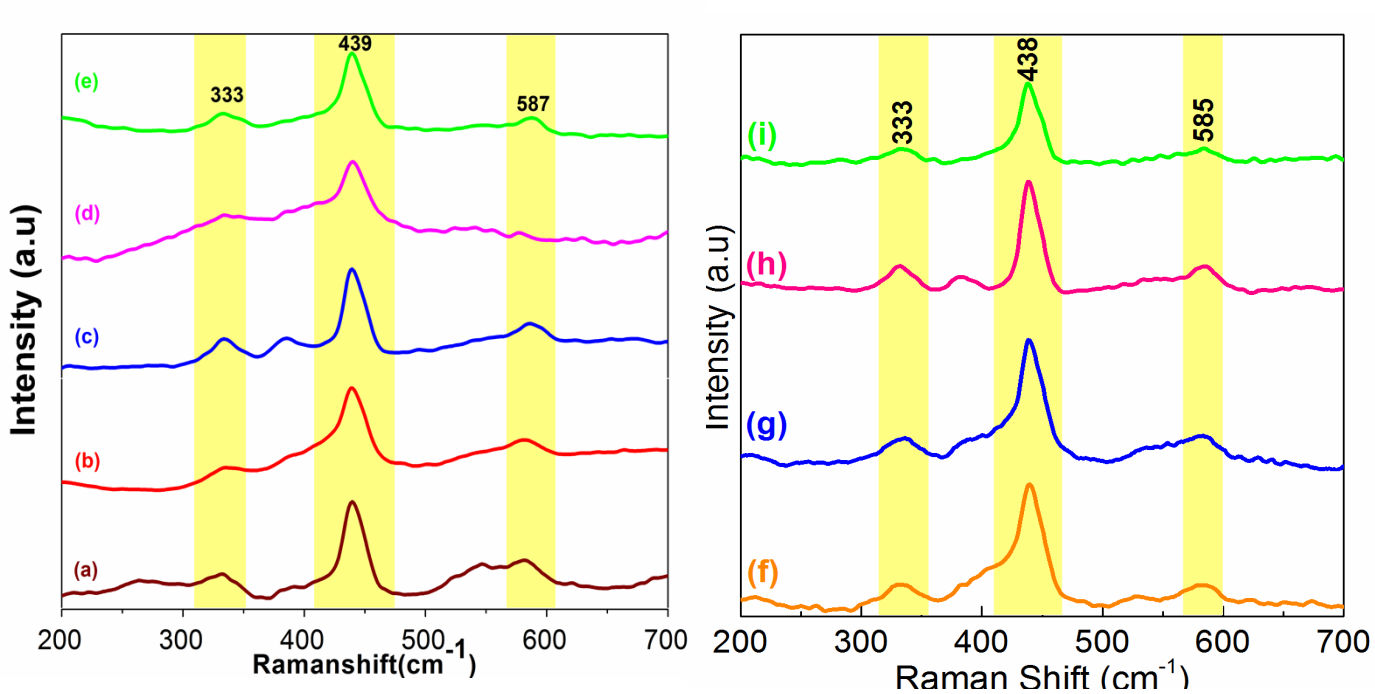
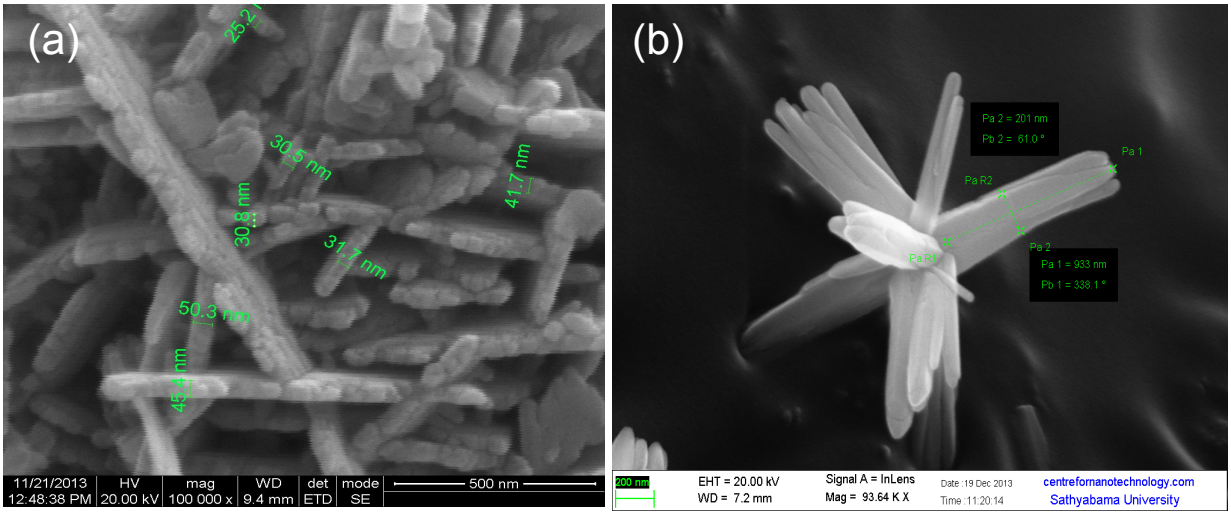


Figure S2 Raman spectra of hierarchical nanoflowers of (a) MGFL and (b) MPJF (c) URFL (d) CDFL and (e) RGSL obtained from MW-ST method and Raman spectrum of integrated ZnO hybrid nanostructures (f) MGFL/RGSL (g) MPJF/RGSL (h) URFL/RGSL (i) CDFL/RDFL. All the samples show the characteristic sharp and dominant peak of wurtzite hexagonal ZnO (E2) at 439 cm^{-1}



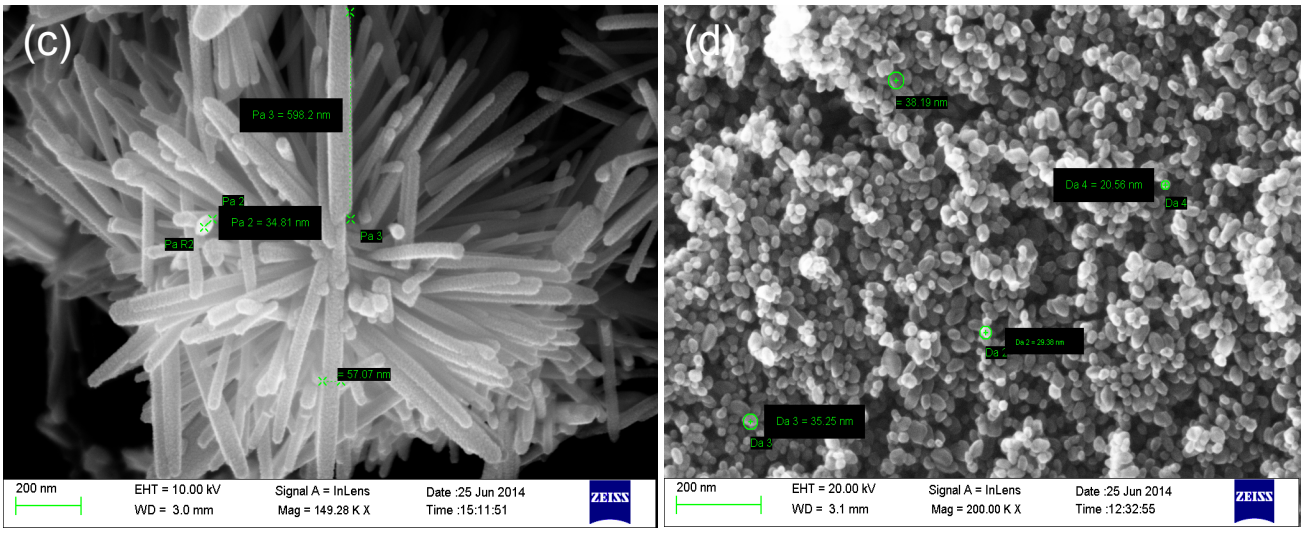


Figure S3, Magnified FESEM images of hierarchical ZnO flowers (a) for MGFL, (b) MPJF, (c) URFL, and (d) RGSL, prepared by MW-HT/ST methods

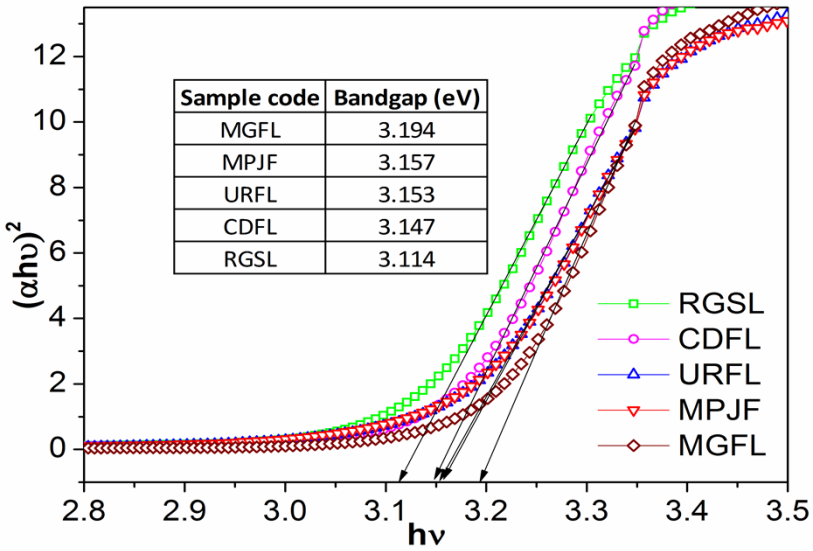


Figure S4 Tauc plot from diffuse reflectance spectra of the different hierarchical nanoflowers such as MGFL, MPJF, URFL, CDFL and RGSL and inset table showing the calculated bandgap for each hierarchical ZnO samples.

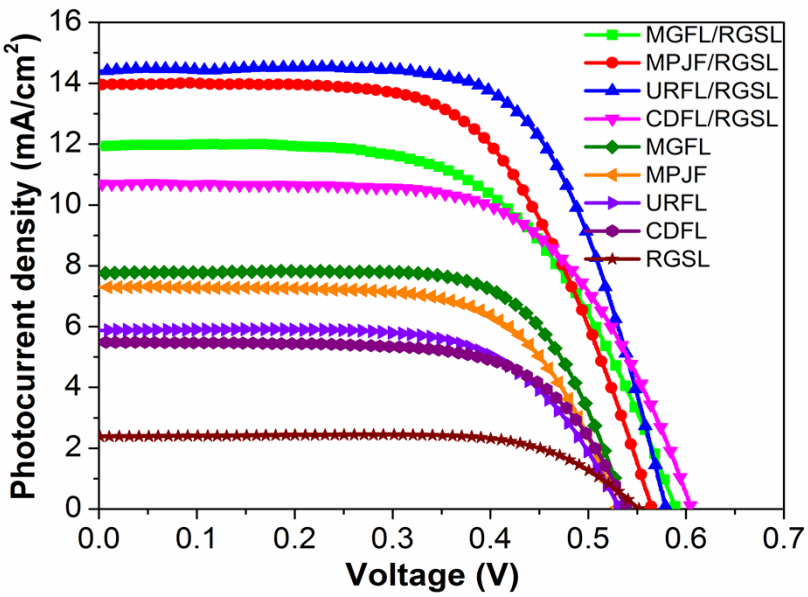


Figure S5 Combined J-V curve of the different hierarchical nanoflowers such as MGFL, MPJF, URFL, CDFL and RGSL and different hierarchical integration of CDFL/RGSL, URFL/RGFL, MPJF/RGSL, MGFL/RGSL of ZnO hybrid nanostructures, showing improved photocurrent density and voltage of hybrid nanostructures compared to individual flower morphological ZnO.

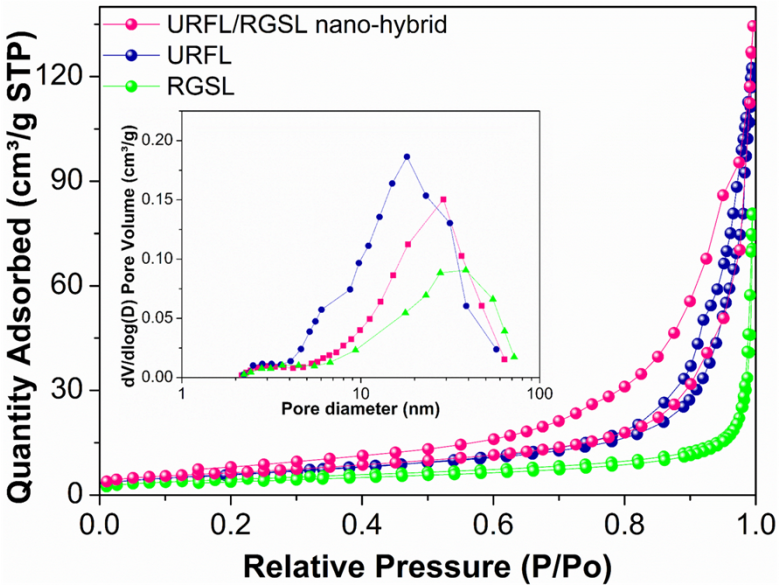


Figure S6 Typical N_2 gas adsorption-desorption isotherm of URFL, RGSL and URFL/RGSL nanohybrid ZnO sample and (inset) corresponding pore size distribution curves.

Table. S1 Different ZnO morphologies and their grain calculated by using Scherrer's equation. FWHM of 002 peak is narrowest for MPJF and URFL sample implies more oriented growth along (001) plane

MGFL sample
Grain size 52.1 nm

	100	002	101	102	110	103
2θ	31.69	34.38	36.21	47.49	56.54	62.805
Intensity	362.09	580.722	1023.8	212.39	337.14	270.88
FWHM	0.2431	**0.2223**	0.2721	0.3241	0.3009	0.3414
d(A°)	2.820	2.6049	2.4791	1.9126	1.62614	1.4780

MPJF sample
Grain size 57.9 nm

	100	002	101	102	110	103
2θ	31.76	34.42	36.26	47.54	56.59	62.84
Intensity	609.16	677.12	1055.01	213.2	341.48	269.46
FWHM	0.285	**0.1825**	0.2719	0.3020	0.2929	0.3442
d(A°)	2.8171	2.6045	2.4736	1.9122	1.6261	1.4784

URFL sample
Grain size 70.5 nm

	100	002	101	102	110	103
2θ	31.79	34.46	36.28	47.57	56.62	62.89
Intensity	585.26	658.8	1013.577	215.30	289.02	303.06
FWHM	0.2802	**0.1879**	0.2775	0.3268	0.3487	0.2885
d(A°)	2.8135	2.6001	2.4744	1.9103	1.6251	1.4778

CDFL prepared sample
Grain size 14.6 nm

	100	002	101	102	110	103
2θ	31.75	34.41	36.24	47.53	56.59	62.84
Intensity	656.2	606.42	1066.19	261.48	364.75	348.82
FWHM	0.5731	**0.4398**	0.5901	0.5534	0.6329	0.5663
d(A°)	2.8171	2.6001	2.4789	1.9089	1.6206	1.4789

RGSL prepared sample
Grain size 18.4 nm

	100	002	101	102	110	103
2θ	31.74	34.41	36.24	47.53	56.58	62.85
Intensity	807.02	738.08	1313	316.52	435.37	418
FWHM	0.4476	**0.3495**	0.4709	0.44	0.5254	0.4730
d(A°)	2.8158	2.6067	2.4776	1.9129	1.6283	1.4797

Table S2. Summarized different morphologies of ZnO prepared by MW-HT/ST methods and their reaction conditions (different precursor concentrations, solvent, temperature, power, and time).

ZnO Sample &code	Precursor and concentration	Solvents	Temperature/Microwave Power	Time (in minutes)	
				Ramp	Hold
Multipod-jasmine-flowerlike **(MPJF)**	$Zn(Ac)_2$ -0.5M NH_4OH- 5M	H_2O	300W	10	10
Marigold-flowerlike **(MGFL)**	$Zn(Ac)_2$ -0.5M NaOH- 5M	H_2O	300W	10	5
Urchin-rod-flowerlike **(URFL)**	$Zn(NO_3)_2$ -0.5M NaOH- 5M Zn powder	H_2O	180°C	10	5
Calendula-flowerlike **(CDFL)**	$Zn(Ac)_2$ -0.5M NaOH- 5M	Ethylene glycol	180°C	10	5
Rice-grain-shapelike **(RGSL)**	$Zn(Ac)_2$ -0.5M NaOH- 5M)	Ethanol	180°C	10	5

Table S3: DSSC photovoltaic performance data determined by photocurrent density-voltage (J-V) characteristics analysis of hierarchical different morphological structure and innovative device architectures of ZnO samples prepared by MW-HT/ST.

Sample code of ZnO	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η (%)	Dye loading (10^{-7} mol cm^{-2})
MGFL	538	7.74	70.2	2.92	6.35
MPJF	530	7.29	66.7	2.58	6.25
URFL	530	5.87	65.8	2.05	6.05
CDFL	539	5.48	67.3	1.99	5.48
RGSL	552	2.41	71.2	0.95	5.25
CDFL/RGSL nanohybrid	604	10.72	63.5	4.11	9.47
MGFL/RGSL nanohybrid	589	11.91	59.4	4.16	11.09
MPJF/RGSL nanohybrid	564	13.96	61.7	4.86	14.67
URFL/RGSL nanohybrid	579	14.33	68.0	5.64	14.91
URFL on top of RGSL bi-layer	493	7.39	62.1	2.26	6.17
RGSL on top of URFL bi-layer	476	5.90	61.9	1.74	5.34

Table S4: Electron dynamic parameters estimated from Nyquist and Bode phase plot of URFL-ZnO, RGSL-ZnO and URFL/RGSL-ZnO photoanode based DSSCs.

Photoanode	$R_s(\Omega)$	R_1 (Ω)	R_2 (Ω)	R_3 (Ω)	τ_e (ms)
URFL	22.1	16.1	77.0	17.9	3.4
RGSL	17.0	10.0	56.0	19.9	5.1
URFL/RGSL nanohybrid	20.4	4.1	29.9	12.1	6.4

Table S5: Variation of surface area, pore volume and pore diameters of different hierarchical ZnO structures such as MGFL, MPJF, URFL, CDFL and RGSL and their respective hybrids obtained from BET surface area analysis.

Sample code	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore size (nm)
MGFL	16.57	0.05	22.01
MPJF	14.74	0.07	19.50
URFL	12.63	0.11	38.71
CDFL	10.65	0.02	11.34
RGSL	14.89	0.16	18.37
MGFL/RGSL	20.18	0.19	34.53
MPJF/RGSL	21.48	0.23	32.48
URFL/RGSL	22.26	0.15	33.69
CDFL/RGSL	19.70	0.09	26.52

References:

1. Maiti, U. N.; Maiti, S.; Chattopadhyay, K. K.; *Cryst Eng Comm* **2012**, *14*, 640-647.
2. Mc Bride, R. A.; Kelly, M. J.; and Mc Cormack, *J. Mater. Chem.,* **2003**, *13*, 1196-1201.