Electronic Supplementary Material (ESI) for CrystEngComm

Evolution of space-efficient and facet-specific ZnO 3-D nanostructures and their application in photocatalysis

Seewon Kim,[a] Minsik Kim,[a] Taekhoon Kim,[a] Hionsuck Baik[b] and Kwangyeol Lee*[,a]

[a] *Department of Chemistry, Korea University, Seoul, Korea 136-701. Fax: +82-2927-3121; Tel: +82-23290-3139; E-mail: kylee1@korea.ac.kr*

[b] *Korea Basic Science Institute (KBSI), Seoul, Korea 136-701.*

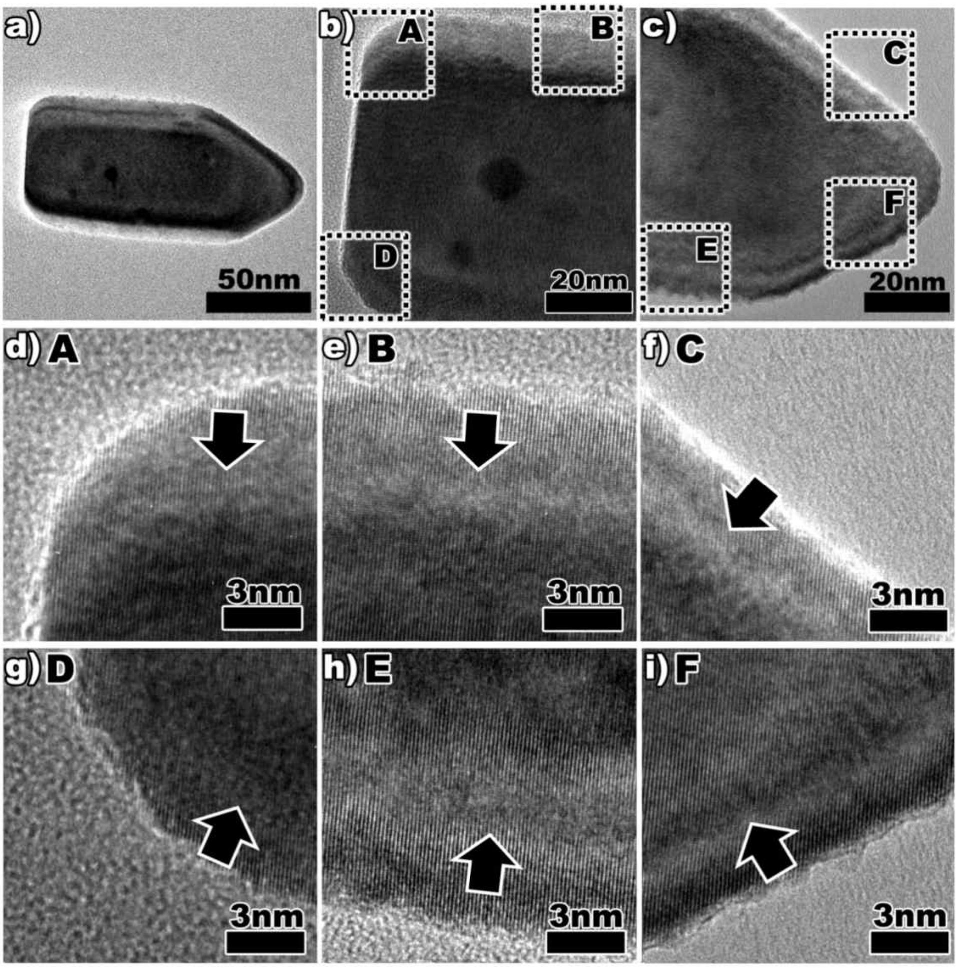


Fig. S1 TEM images of a) bullet-shaped multiwalled ZnO nanotube, b) its open-end and c) its closed tip part. d-i) HRTEM images of selected area in (b) and (c). Arrows in (d-i) indicate the lattice mismatch between grains.

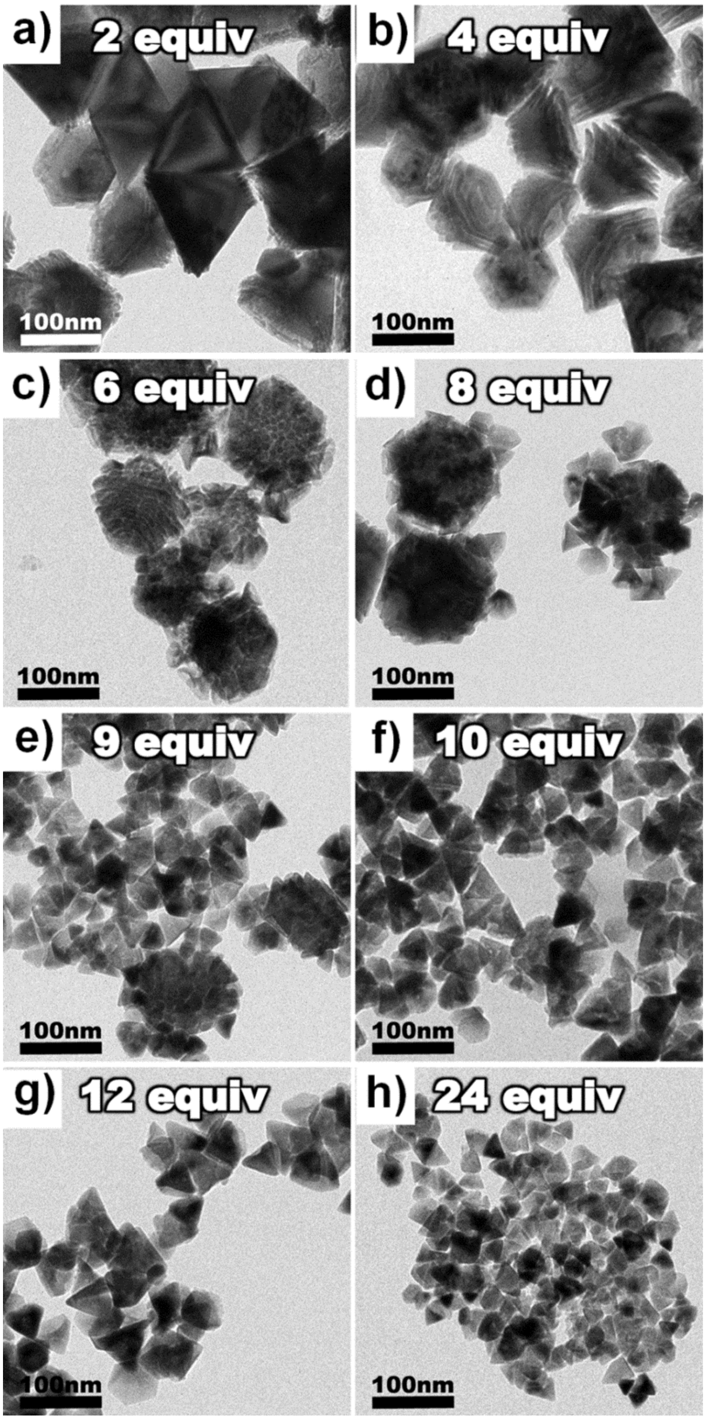


Fig. S2 TEM images of the products after etching process, showing the effect of the concentration of oleic acid as etchant. The amount of oleic acid used a) 1 mmol (2 equiv) b) 2 mmol (4 equiv) c) 3 mmol (6 equiv) d) 4 mmol (8 equiv) e) 4.5 mmol (9 equiv) f) 5 mmol (10 equiv) g) 6 mmol (12 equiv) h) 12 mmol (24 equiv). The proportion of the etchant (oleic acid) is the crucial factor to control the etching degree of ZnO hexagonal cones.

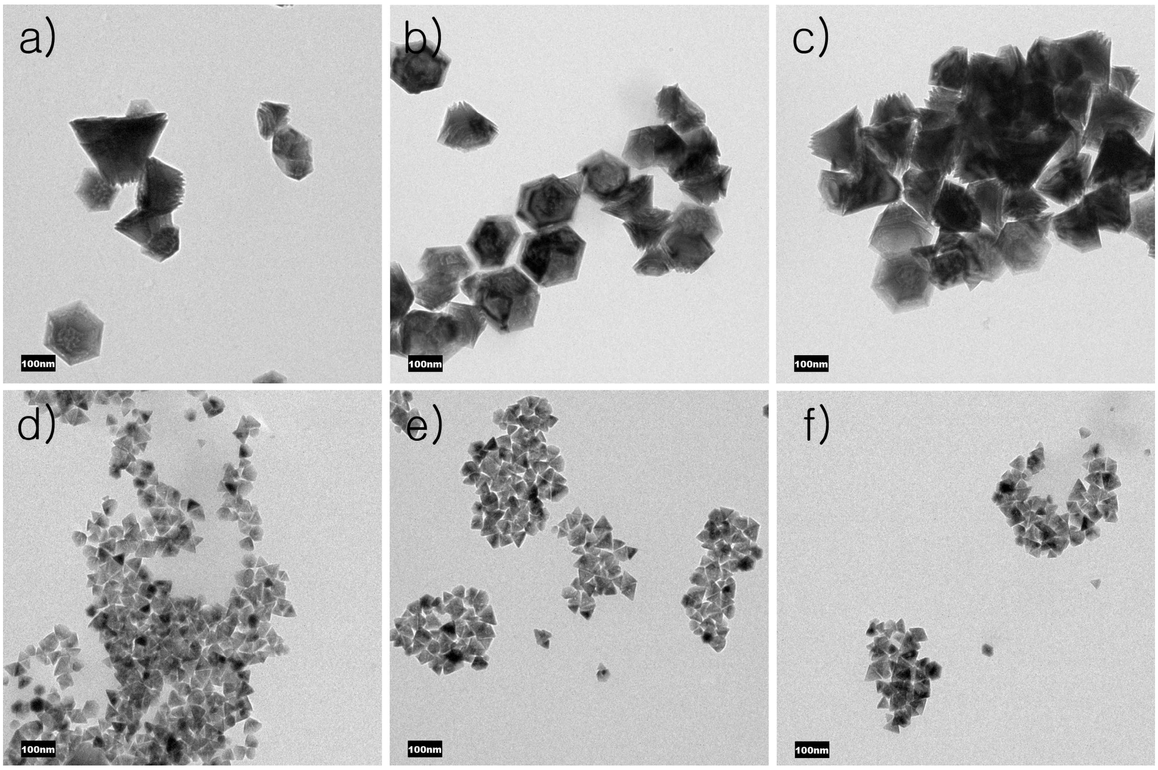


Fig. S3. Temporal TEM images for OA-dependent and etching time-insensitive etching behavior of ZnO nanocone. 4 equiv OA (Top): (a) 10 min, (b) 20 min, (c) 30 min under refluxing TOA and 12 equiv OA (Bottom): (d) 10 min, (e) 20 min, (f) 30 min under refluxing TOA.

Table S1 BET data of zinc oxide samples

Sample	**Specific surface area [m^2 g^{-1}]**
ZnO hexagonal nanocones	11.79
ZnOnanoforest	22.27
ZnO stacked nanocones	47.27

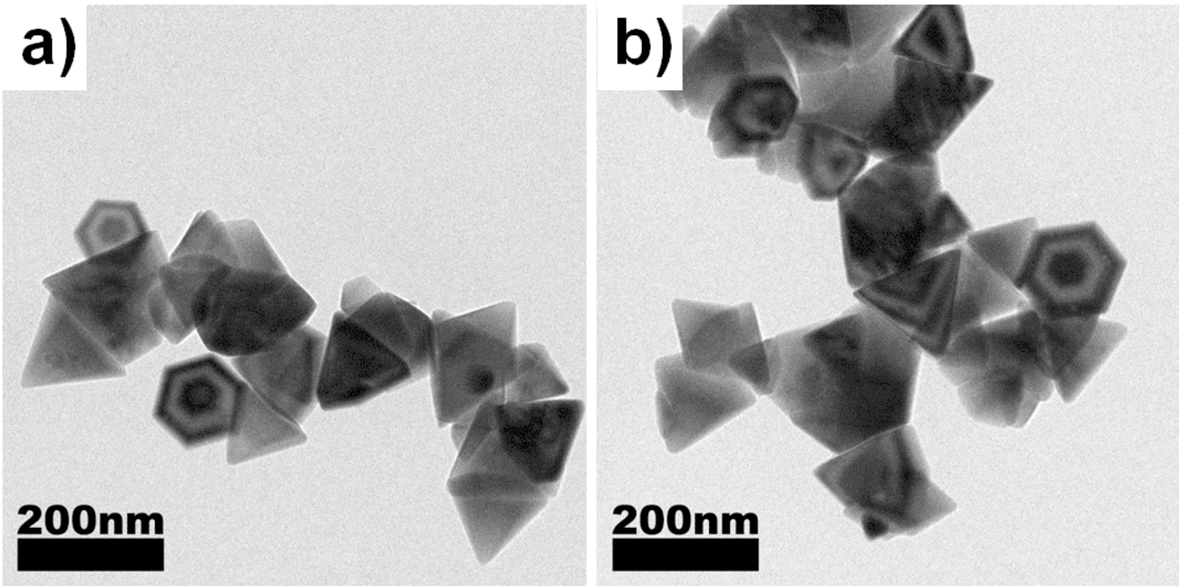


Fig. S4 TEM images of the ZnO nanostructures after heating with a) 4 equiv of oleylamine in TOA or b) 2g of TOA at 450 ^{o}C.Oleylamine and TOA showed no distinct effect on the shape of the hexagonal cones.

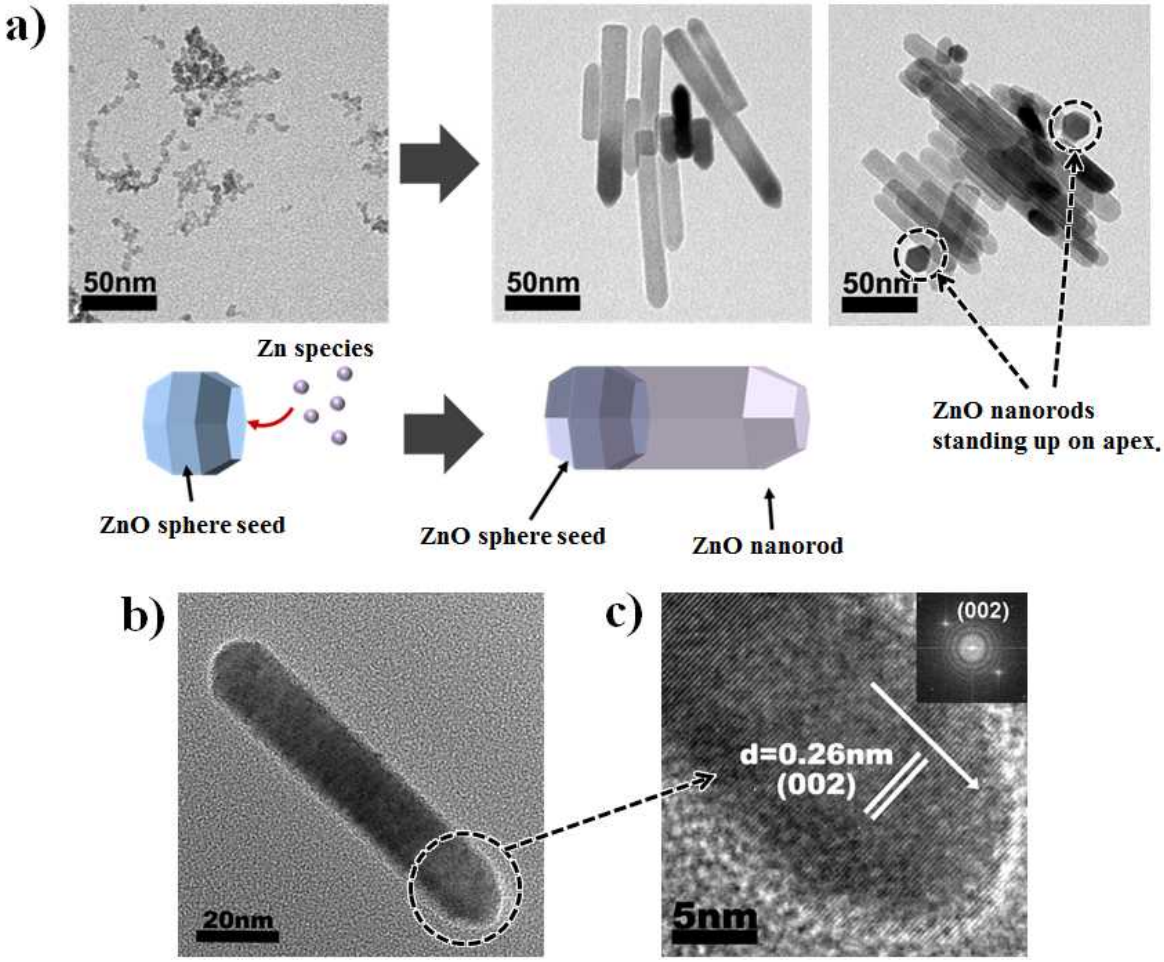


Fig.S5 a) Schematic illustration and the corresponding TEM images of ZnO nanorod grown from ZnO seeds. b) TEM image of ZnO nanorod and c) HRTEM image of the selected area in (b).

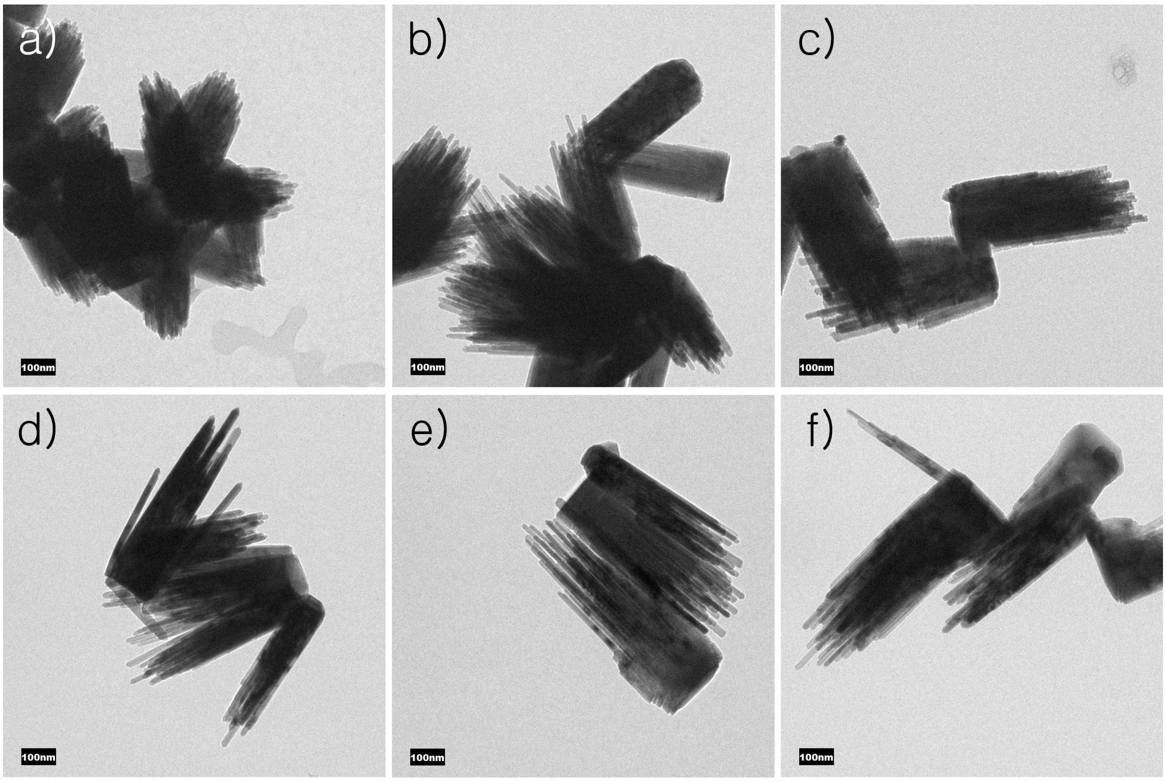


Fig. S6 TEM images of reaction products after reaction time of (a) 3 min , (b) 5 min, (c) 7 min, (d)10 min, (e) 30 min, and (f) 60 min, demonstrating extremely fast ZnO nanoforrest growth.

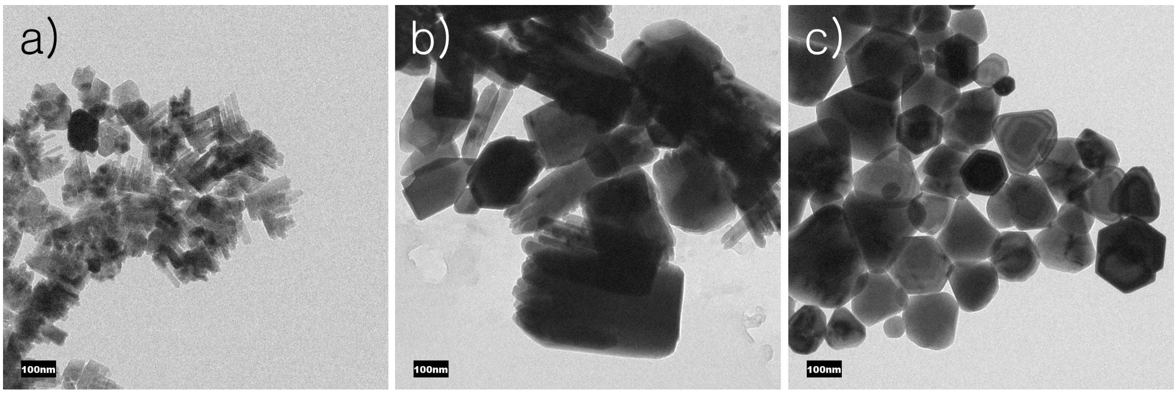


Fig. S7. OAm effect on the ZnO nanoforrest structure: (a) 1 equiv, (b) 8 equiv, (c)16 equiv of OAm. Higher OAm content leads to growth of fewer thicker nanorods on the ZnO nanocone surface. In the case of (c), the nanocone surface is very strongly protected by the OAm and therefore no growth of nanorods is observed.

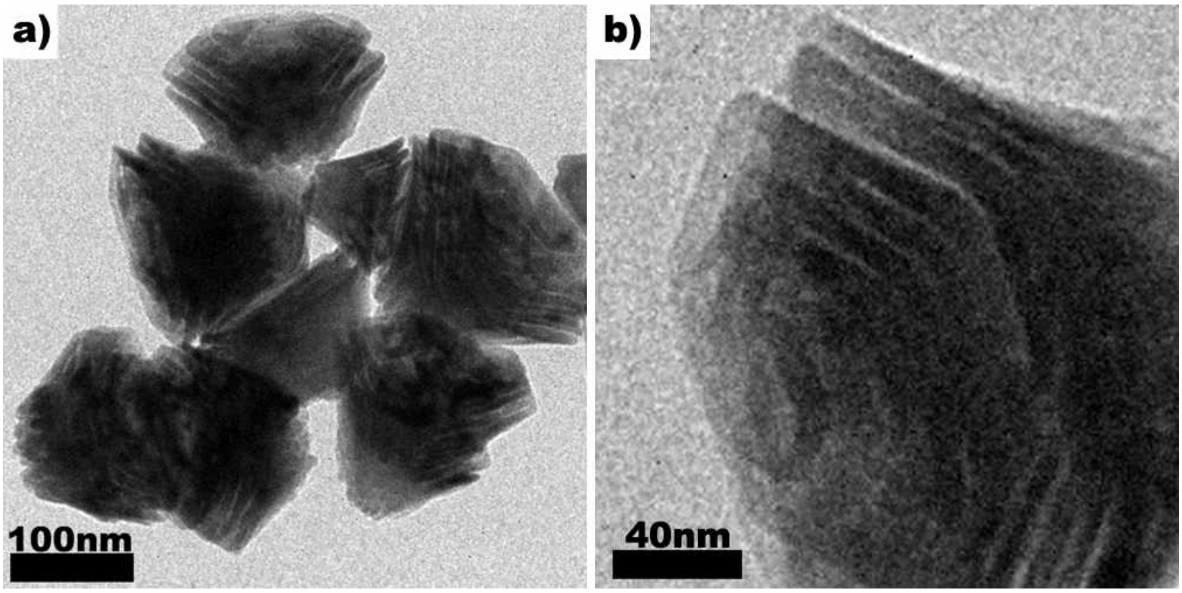


Fig. S8 a) Low and b) high magnification TEM images of ZnO stacked hollow nanocones.

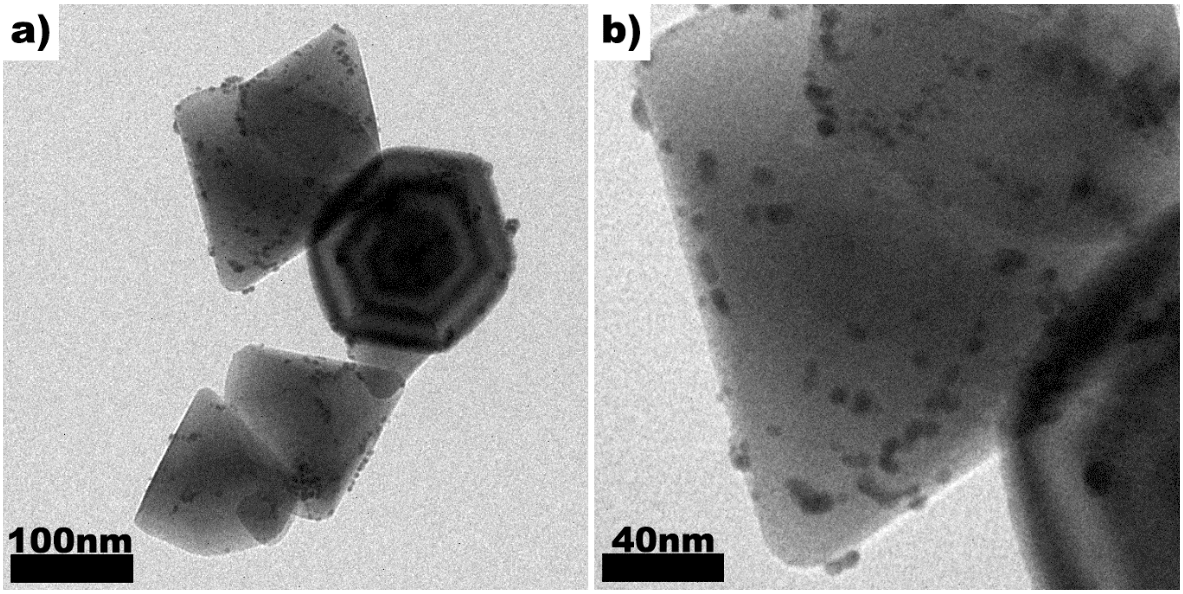
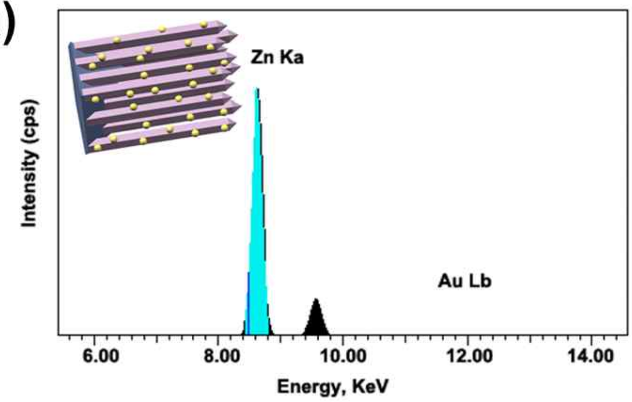


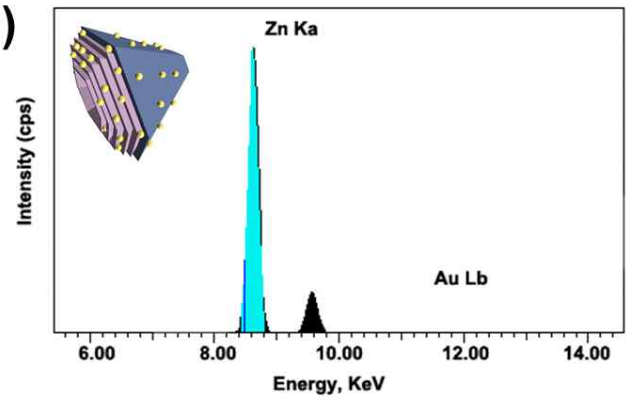
Fig. S9 a) Low and b) high magnification TEM images of Au/ZnO hexagonal nanocones.

a)



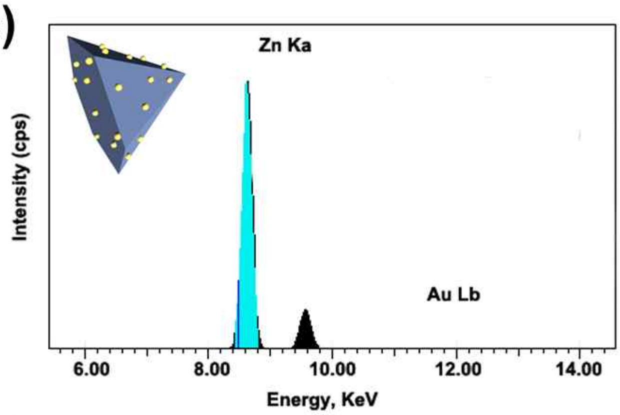
Zn	98.656(± 0.208)(wt%)	33512.906(± 72.122)(cps)
Au	1.344(± 0.049)(wt%)	95.826(± 3.842)(cps)

b)



Zn	98.852(± 0.164)(wt%)	59038.237(± 100.092)(cps)
Au	1.148(± 0.036)(wt%)	143.396(± 4.923)(cps)

c)



Zn	99.013(± 0.166)(wt%)	57680.144(± 98.944)(cps)
Au	0.987(± 0.034)(wt%)	119.919(± 4.517)(cps)

Fig. S10ED-XRF (Energy-dispersive X-ray fluorescence) data of a) Au/ZnO stacked hollow nanocones and b) Au/ZnO nanoforest c) Au/ZnO hexagonal nanocones.

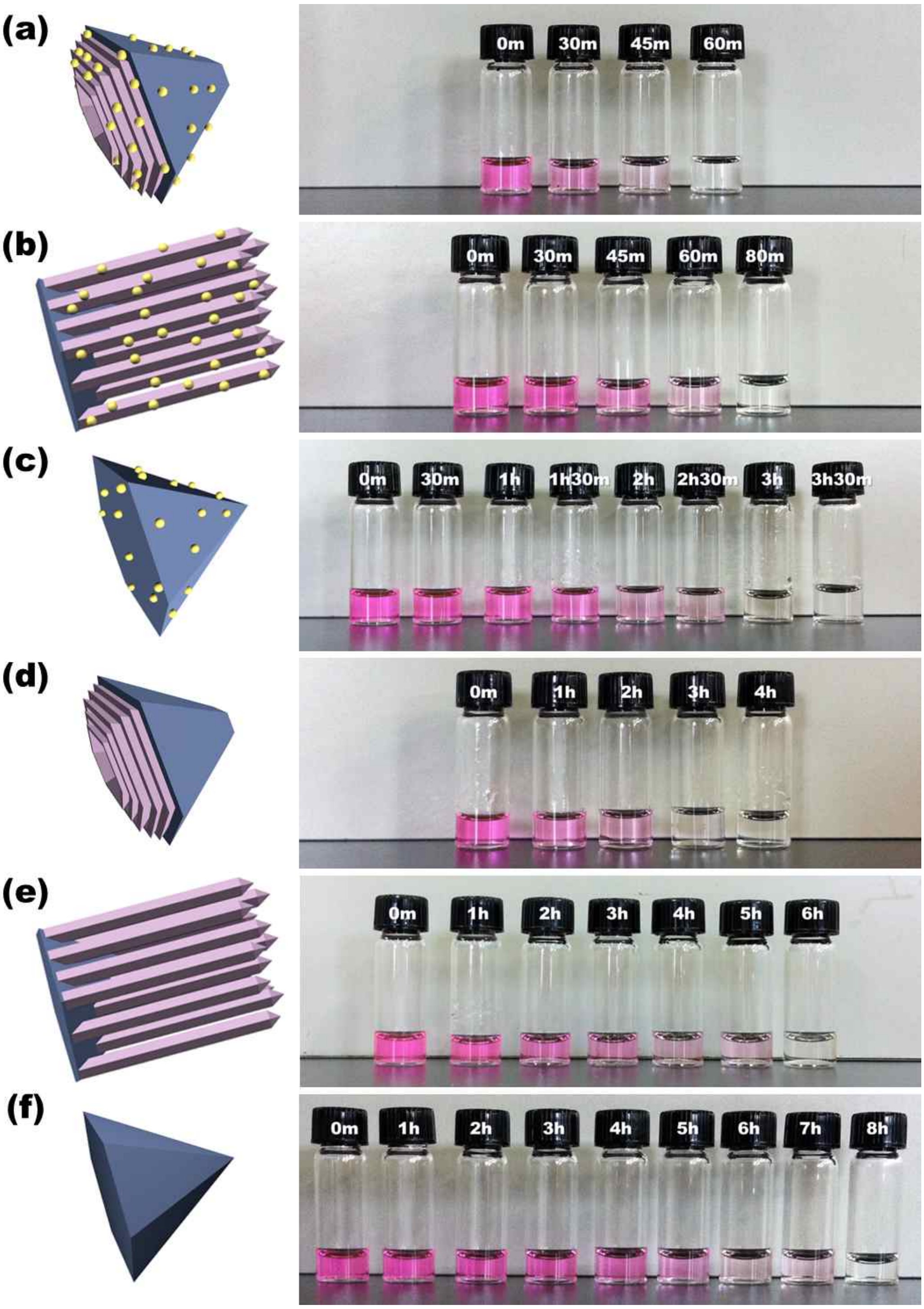


Fig. S11 Photodegradation of the RhB under irradiation in the presence of a) Au/ZnO stacked nanocones b) Au/ZnO nanoforest c) Au/ZnO hexagonal nanocones d) ZnO stacked nanocones e) ZnO nanoforest f) ZnO hexagonal nanocones.

Electronic Supplementary Material (ESI) for CrystEngComm
This journal is © The Royal Society of Chemistry 2012

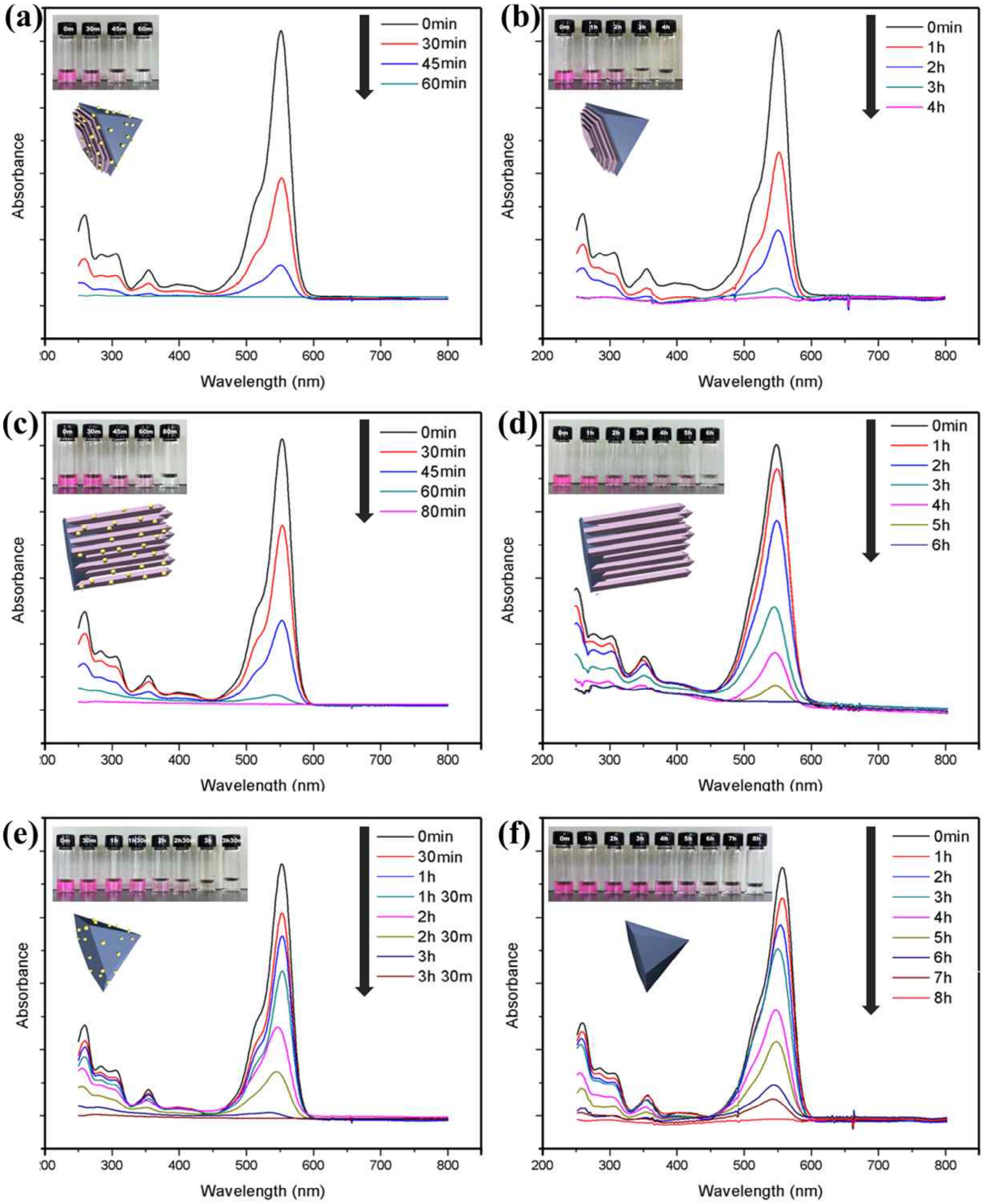


Fig. S12 Time-dependent UV-vis absorption spectra of RhB aqueous solution after different irradiation times with different samples of a) Au/ZnO stacked nanocones b) ZnO stacked nanocones c) Au/ZnOnanoforest d) ZnOnanoforest e) Au/ZnO hexagonal nanocones f) ZnO hexagonal nanocones.

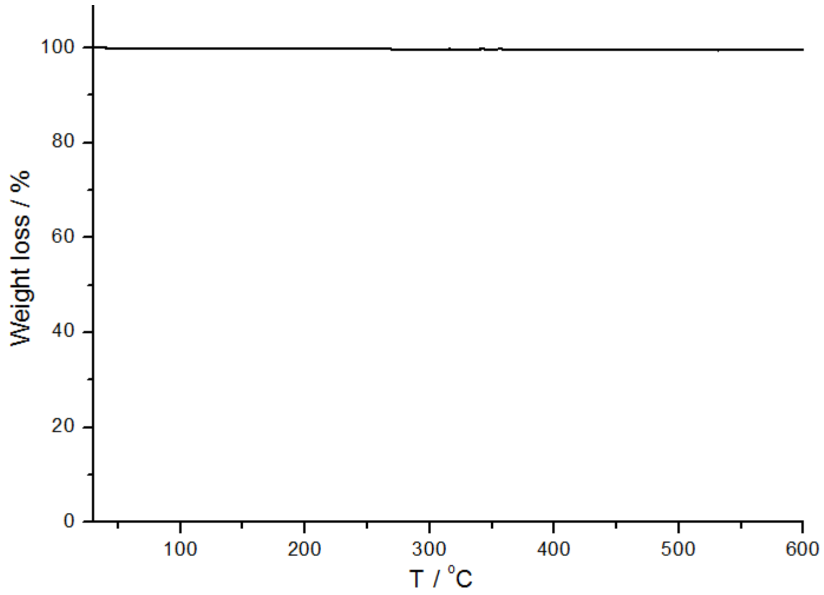


Fig S13. TGA data for ZnO nanocone (after being treated by 4 h UV irradiation) demonstrating the absence of coordinated surfactants on ZnO surface