Electronic Supplementary Information (ESI)

In_{1-x}Ga_xN Quantum dots Integrated with ZnO: A Rationally Designed Solar

harvesting material

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Supporting Information 1 (ESI-1):

Mechanism of Material Formation: During the combustion of the homogenous reactant mixture at 500 $^{\circ}$ C, plenty of in-situ ammonia is produced due to urea decomposition. Under this condition, nascent Zn_xO_y (x > y) clusters grow with ample oxygen vacancies due to high temperature. In-situ generated ammonia interacts with growing Zn_xO_y clusters and thereby nitrogen incorporation was facilitated at the expense of oxygen vacancies. Discussion on the mechanistic aspects of nitrogen incorporation metal oxo clusters has been established.^{27,29-30} On account of high negative enthalpy of forming metal nitride bonds in ammonia environment, available In and Ga atoms in vapour-phase status form nitride species. Self assembly behavior of In-Ga-N is noted recently. This possibly induces QD formation. The present preparation conditions provide suitable platform to combine three operations namely, nitrogen incorporation in growing Zn_xO_y clusters, metal nitride formation and self assembly of formed nitride species. As the InGaN species possess wurtzite structure and similar to ZnO, stablization of InGaN in ZnO becomes feasible. Formation of Zn-N through nitrogen incorporation plays a main role in integrating InGaN in ZnO as single phase material. For the first time, the design in making use of three effects combinedly is succesfully attempted.

InGaN@ZnO material compositions, especially with In (or Ga) content higher than 8 % (12 %), shows the impurity phases, such as In_2O_3 and Ga_2O_3 . This is due to crossing the combined solubility limit. The small peak identified with * symbol refers to the major peak of In_2O_3 impure phase. Majority (\geq 90%) of In+Ga still forms the InGaN, as denoted by the peak shift.



Figure ESI-1: XRD for the compositions containing In_2O_3 as impurity phase, indicated by star symbol. Higher magnification (x10) pattern is given to show the impurity phase in red color. Diffraction pattern of ZnO is also given for comparison.

Supporting Information 2 (ESI-2): HRTEM IMAGES



(b)







(g)

Figure ESI-2: HRTEM images of (a) I3G2, (b) I5G5, (c and d) I5G8. High resolution lattice planes can be easily distinguished. (e-g) TEM images to show the distribution of different size of InGaN particles (given in rounded rectangles) in InGaN@ZnO; HRTEM confirmation was carried out and necessary to confirm from the lattice d-spacing values. It is to also be noted that all the black contrast was not InGaN and few overlayers of ZnO alone gives such black contrast.

Supporting Information 3 (ESI-3):



Figure ESI-3: SIMS fragment mapping of I2G2 showing images for the fragments labeled respectively below each image. Similar trend as that of I5G5 (given in the main manuscript) is observed.

Supporting Information 4 (ESI-4):



Figure ESI-4: UV-Visible spectra recorded for ZnO, I5G8 material, spent I5G8 extracted out from reaction after continuous irradiation of 48 hours, calcined I5G8 at 500 °C and at 800 °C.

Effect of calcination on optical absorption property has been analyzed. Fresh I5G8 was calcined in air at 500 $^{\circ}$ C for 48 h and the calcined sample was analyzed by UV-Visible and the results are displayed above. The absorption of calcined material at 500 $^{\circ}$ C, indicated in green line, shows that >90 % absorption that of fresh material is retained. Though nitrides are prone to oxidation and volatilization, stability of InGaN in this case is dramatic due to the integration with ZnO lattice. As the preparation condition was maintained at 500 $^{\circ}$ C, the stability of the material up to that temperature is easily attained. When the calcination temperature rises to 800 $^{\circ}$ C for 3 hours, the material loses its reddish yellow colour and becomes pale yellow colour. Visible light absorption, after calcination at 800 $^{\circ}$ C, reduces dramatically and the absorption edge is blue shifted to 400 nm. This result illustrates material stability at least up to 500 $^{\circ}$ C. In the perspective of enhanced visible light absorption, this result strongly supports the sole responsibility of embedded InGaN QDs for bringing visible light absorption. Owing to withstanding thermal stability, high photostability, InGaN QDs integrated with ZnO as single photocatalyst system can be suitable for sustainable solar photocatalysis.

Supporting Information-5 (ESI-5): TG/DTA analysis of InGaN@ZnO:



Figure ESI-5. TG/DTA analysis for the sample I5G5 is carried out in air atmosphere.

The experiment has been carried out with the sample denoted as I5G5 for analysing thermal stability of nitride component over oxidation. When the temperature increases there is steady weight loss due to the removal of adsorbed moisture and atmospheric gases. When the temperature reaches 700 °C there is gain in weight indicative of In, Ga nitrides oxidation. Therefore, the nitride component remains stable and intact within structure up to 700 °C. This result is in concordance with the calcination study (**ESI-4**).

Supporting Information 6 (ESI-6):



Figure ESI-6: Room temperature Photoluminescence Spectra of InGaN@ZnO of different compositions indicated with respective codes. Excitation wavelength employed was 550 nm. An emission feature is observed between 735 and 775 nm with low intensity. Above emission is attributed to the emission of InGaN QDs.

Supporting Information 7 (ESI-7):

Table ESI-7: ICP analysis carried out to measure the extent of photocorrosion through Zn^{2+} estimation for the materials irradiated with 400 W UV light for 48 hours. ZnO* was irradiated for 6 hours is given for comparison purpose.

Material Code	Zn ²⁺ Estimated by ICP, after UV irradiation
	(in ppm)
I3G5	1.77
I2G5	1.96
I5G5	1.39
I5G8	1.31
ZnO*	186

There is no trace of In³⁺ and Ga³⁺ in the analyzed fraction.

The photostability of the material was experimentally verified by continuous UV irradiation studies carried out using 400 watts mercury vapour lamp for 48 hours. The materials are suspended in methanol aqueous mixture and irradiated under UV for 48 hours. Then solution was filtered and subjected to ICP analysis for detecting Zn ion concentration that leached out from the material due to photocorrosion. Even after 48 h irradiation, InGaN@ZnO shows less than 2 ppm; whereas ZnO shows 186 ppm in just 6 h. Similar low Zn-leaching was observed with other compositions of InGaN@ZnO also. The suppression of Zn ion concentration is up to 4 orders of magnitude ensuring the high photostability of InGaN@ZnO. This is mainly attributed to the suppression of oxygen vacancies as well as the nitride introduction in the form of QDs.

Supporting Information 8: (ESI-8):



Figure ESI-8: (a) UV-Visible spectra, and (b) IR spectra of the 2-butanol reactant and reactant mixture after 3 hours of irradiation. The dotted line indicates characteristic absorption peak or carbonyl stretching for 2-butanone confirming the formation of product. (c) Recyclability analysis carried out for visible light induced dehydrogenation of 2-butanol in 6 cycles with I5G8. Each cycle time is 3 hours of irradiation. The mol conversion % of 2-butanol into 2-butanone in each cycle is plotted.