Electronic Supporting Information (ESI)

Synthesis of Z-scheme 0D-3D Heterojunction Bi-functional Photocatalyst with ZnInCuS Alloyed QDs Supported BiOI MF for H_2O_2 Production and N_2 Fixation

Deeptimayee Prusty, Sriram Mansingh and K.M. Parida*

Centre for Nanoscience and Nanotechnology, Siksha 'O' Anusandhan (Deemed to be University), Bhubaneswar-751030, Odisha (India)

*Corresponding author

E-mail: paridakulamani@yahoo.com &

kulamaniparida@soa.ac.in

Experimental section

Chemicals Requirement

Copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99%), Potassium iodide (KI, >99.5%), Thioglycolic acid (TGA, 79%), sodium hydroxide (NaOH, 97%), $Zn(OAc)_2.2H_2O$ (>99%), Ethylene glycol (EG, >99%), TA (Terepthalic Acid), NBT (nitro blue tetrazolium chloride), Nafion, EDTA, H_2O_2 Methanol, Na_2SO_4, Thiourea were purchased from Merck and Indium chloride ($InCl_3$, 98%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 58%), Ammonium molybdate, DMSO from Himedia Pvt. Ltd. All reagents in the experiment areanalytical grade and used without further purification.

Synthesis of BiOI Micro-flower (BOI MF):

BOI MFs were developed *via.* simple hydrolysis strategy in the presence of EG (as a structure directing reagent) at ordinary temperature. For this reason, 10.0 mL EG along with 0.0028 mol of $Bi(NO_3)_3 \cdot 5H_2O$ were mixed drop-wise into aqueous KI solution (10.0 mL) with 5 h of continuous stirring. A brick-red color appeared which was subsequently filtered and washed with ethanol water solution. Then the filtrate was dried at 60°C for 8 h to acquire BOI MFs.[1]

Synthesis of Zn-Cu-In-S Quantum dot (ZCIS QD):

The ZCIS quaternary alloyed QDs were fabricated in a one pot reflux approach. In the executed experiment, 2.0, 0.5, 20.0 mmol of $InCl_3 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, and TGA respectively, were diluted in requisite amount of de-ionized (DI) water in a two-necked flask. The pH of the above solution was accustomed to 10.5 by adding 1M NaOH solution. Aqueous solution of 1.3 mmol of $Na_2S \cdot 9H_2O$, as a sulfur source was introduced into the round-bottom-flask, and the entire solution was refluxed for 4 h at 100°C. Then, a solution of 2.0 mmol $Zn(OAc)_2.2H_2O$, 3.0 mmol TGA, and 2.0 mmol thiourea were inserted into the flask, and subjected to reflux at the same

temperature for an hour to obtain ZCIS colloidal solution. Then the entire solution was treated with ethanol for precipitation, and dehydrated at room temperature under vacuum to get ZCIS alloyed QDs.[2]

Characterization

Structural and morphological analysis of synthesized samples was characterized by X-Ray Diffraction technique (XRD), High-Resolution-Transmission-Electron-Microscopy (HRTEM), Field Emission Scanning Electron Microscopy (FESEM), X-ray photoelectron-spectroscopy (XPS), and Raman analysis. The crystallinity and phase purity of the catalysts were examined by using Powder-XRD in a RigakuUltima-IV diffractometer (40 KV/40 mA), outfitted with a radiation of Kα Cu (λ = 1.54 Å), and at 2θ= 10-60^{o}. XPS analysis was performed with a spectrometer (VG MicrotechMultilab ESCA 3000) by using a Kα Mg X-ray source to evaluate the surface elemental states, and chemical compositions of the materials. C 1s (binding energy= 284.8 eV) is considered as a reference for the calibration of spectrum. The morphological characterization of the synthesized materials was evaluated by FESEM tool (FEI Quanta 400FEG-SEM). Additionally, the particle size and core structure of the materials were estimated by JEOL-2100 HRTEM analyzer (200 kV). Raman spectrometer is used to know oxygen vacancy and composite formation of the materials and here a laser of 332 nm RENISHAW via Raman spectrometer was used for the analysis. To estimate the optical properties of the prepared samples, Photoluminescence (PL) and UV- VIS diffuse-reflectance-spectroscopy (UV-Vis DRS) were used. The absorbance spectra were obtained by JASCO-V-750 UV-Visible spectrophotometer (λ = 200-800 nm, $BaSO_4$ as reference) to elucidate the absorbance and bandgap energy of the materials. The excitation and PL emission spectra were evaluated with the help of JASCO-FP-8300 spectrometer, using Xenon lamp as excitation source. The

electrochemical characteristics were performed by using multichannel Iviumpotentiostat analyzer in a three electrode system, where Ag/AgCl used as reference, Pt as counter, and the synthesized sample as working electrode. Here, 0.1M Na_2SO_4 (pH = 6.8) solution acted as electrolyte for the electrochemical analysis. 300W Xe-lamp was used as light radiance by using 400 nm cut-off filter.

Photocatalytic H_2O_2 Evolution:

The oxygen reduction to H_2O_2 was carried out following our previous reported paper.[2] The H_2O_2 evolution capacity of prepared quantum dots was tested in the photoreactor (Fig.S3) having a 250 W Hg light source (cut-filter > 420nm) and refrigerated water circulation to control the reaction temperature. In the preformed reduction reaction, 10 mg of QD sample was added to 10 vol% 20 mL of deionised water/alcohol mixed solution and dispersed for 15 min by ultrasonication. The above catalyst mixed suspension was then saturated with oxygen gas (99% purity) for 1 h under dark with stirring to achieve both O_2 saturation and adsorption-desorption equilibrium. Afterwards, the above suspension was agitated with the Hg lamp for 2 h. Then the light treated solution was centrifuged followed by filtration to separate the catalyst from the solution, similar type of reduction procedure was also adopted for all the samples. Further, the concentration of H_2O_2 in catalyst free solution (filtrate) was then determined using iodine-colorimetric method at 350 nm by our JASCO-750 spectrophotometer. Additionally, blank experiment was also carried out in the absence of photocatalyst and light to justify that the performed H_2O_2 production is through photocatalysis pathway using supplied O_2 and light.

Photocatalytic NH_3 Evolution:

The photocatalytic reduction of N_2 to NH_3 was also experimented with the best catalyst (ZCIS-BOI(1:1)) using the same quartz reactor as mentioned above under similar experimental

condition only change in place of O_2 gas, N_2 gas was purged to form N_2 saturated mixed solution. Priors to photocatalytic reduction reaction, the above suspension, i.e., catalyst mixed N_2 saturated solution was stirred in dark for 30 min to attained adsorption-desorption equilibrium. At last, the concentration of NH_3 generated by the reduction of supplied N_2 was determined spectrometrically by indophenol method using UV−vis spectrometer following our previous paper.[3] Blank experiments were also carried out in the absence of a catalyst(light presence) and light(catalyst absence) to full proof that the N_2 reduction reaction (NRR) proceeds via. photocatalysis route using the supplied N_2 and light source.

Fabrication of working electrodes:

The electrodes were made by drop casting method taking 0.25 mg of the prepared catalysts. At first the photocatalysts were dispersed in 0.4 ml ethanol along with 20µL nafion solution. Then the ensuing suspensions were sonicated for 10 minutes to get homogeneous mixture. Further, the solutions were drop-casted on surface of the conducting sides of 1 cm^2 area of FTO (Fluorine-Doped-Tin-Oxide). The photocatalysts loaded FTO were then dehydrated by keeping in a vacuum-oven overnight at ordinary temperature for electrochemical study.

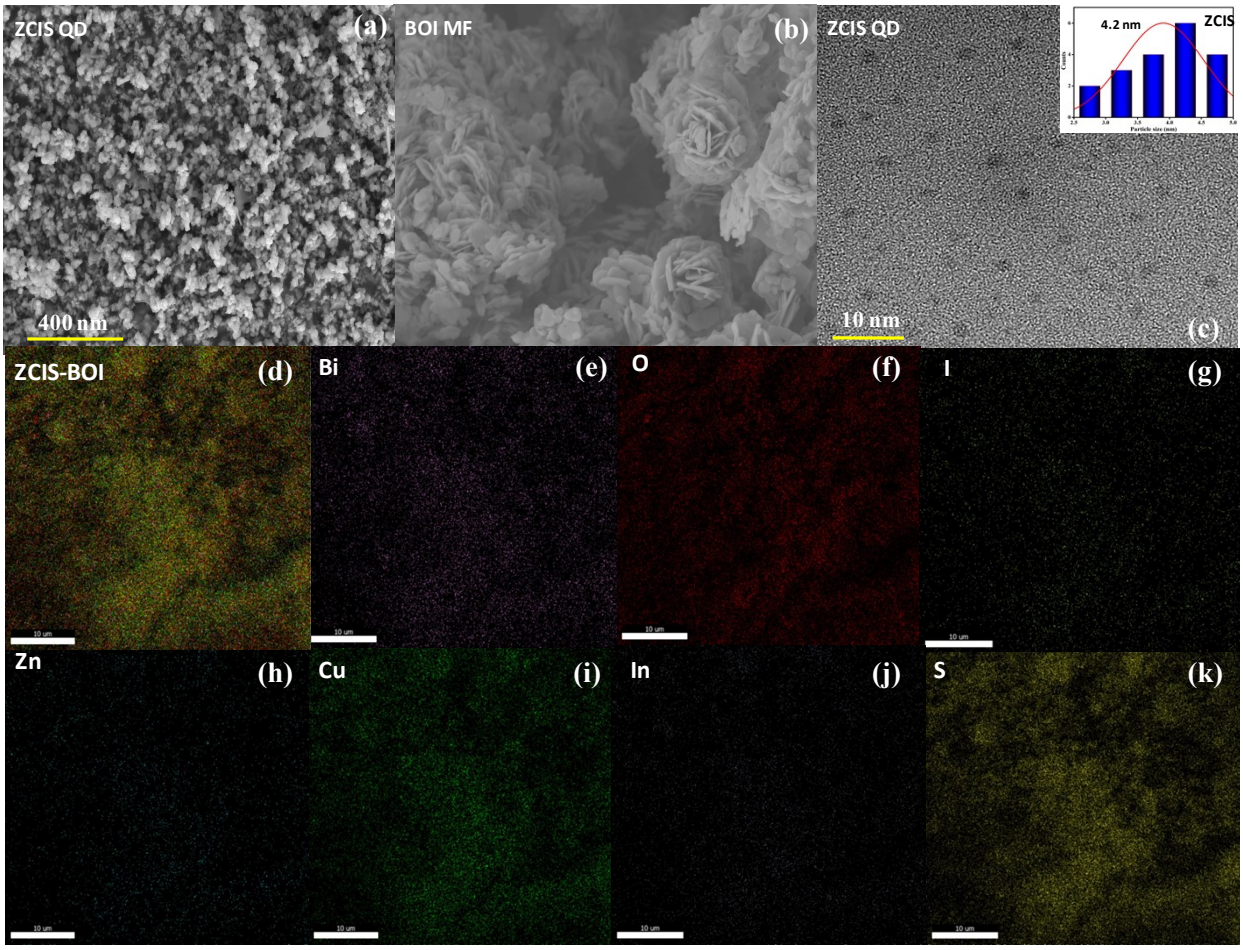

Fig. S1: FESEM image of (a) ZCIS, (b) BOI; (c) HRTEM image of ZCIS; and, color-mapping images of (d) ZCIS-BOI (1:1) composite, (e) Zn, (f) Cu, (g) In, (h) S, (i) Bi, (j) O, and (k) I.

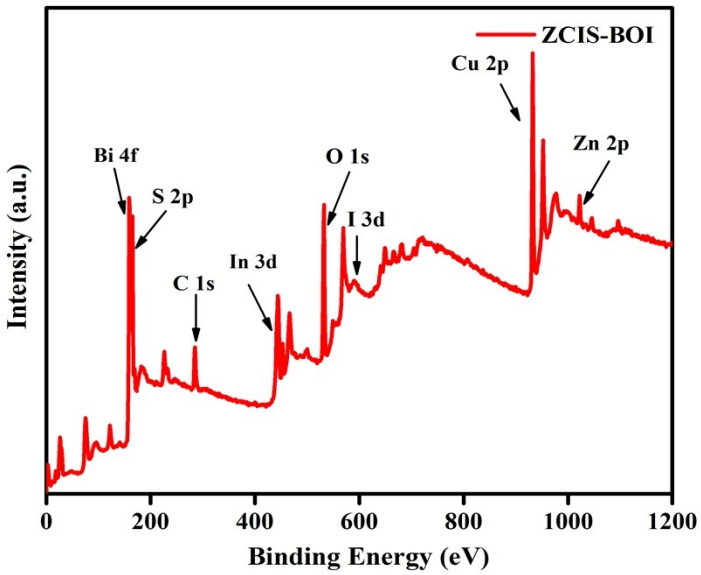

Fig. S2: XPS Survey of ZCIS-BOI(1:1).

Table-S1: Comparison table of binding energy in pristine BOI and ZCIS with ZCIS-BOI(1:1) composite.

Elements	Binding energy in BOI	Binding energy In ZCIS-BOI	Elements	Binding energy in ZCIS	Binding energy In ZCIS-BOI
Bi	158.8 eV 164.2 eV	159.4 eV 164.6 eV	Zn	1022.8 eV 1045.8 eV	1022.5 eV 1045.5 eV
O	529.6 eV 531.0 eV 532.5 eV	529.8 eV 531.3 eV 532.7 eV	Cu	932.4 eV 952.2 eV	932.1 eV 952.1 eV
I	618.5 eV 630.1 eV	618.8 eV 630.3 eV	In	445.3 eV 452.9 Ev	445.1 eV 452.8 eV
			S	158.9 eV 163.9 eV	158.7 eV 164.0 eV

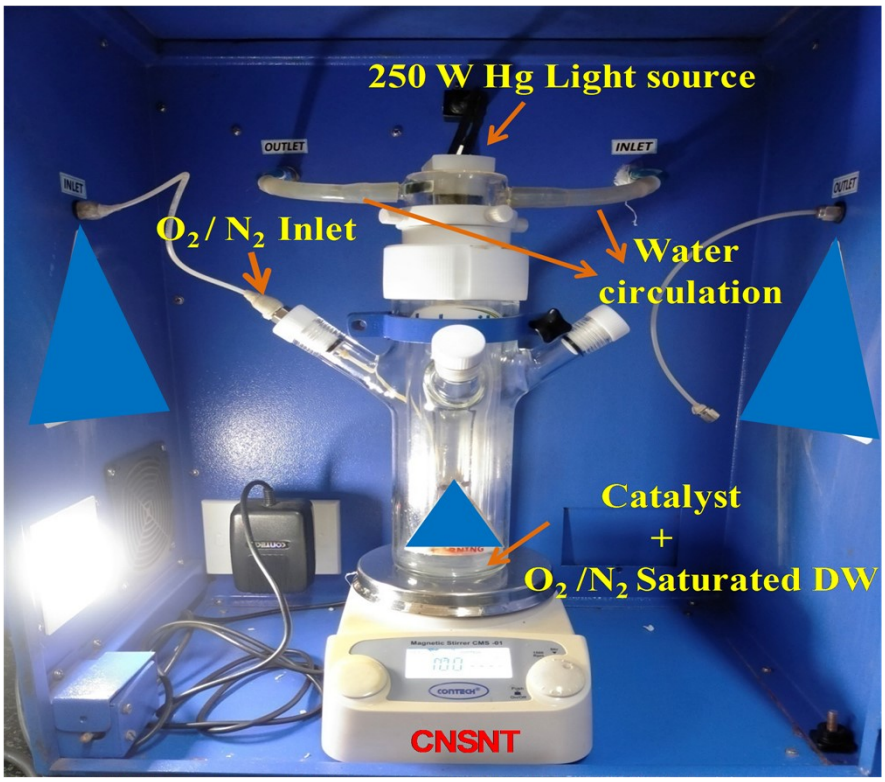

Fig. S3: H_2O_2/N_2 production reactor setup.

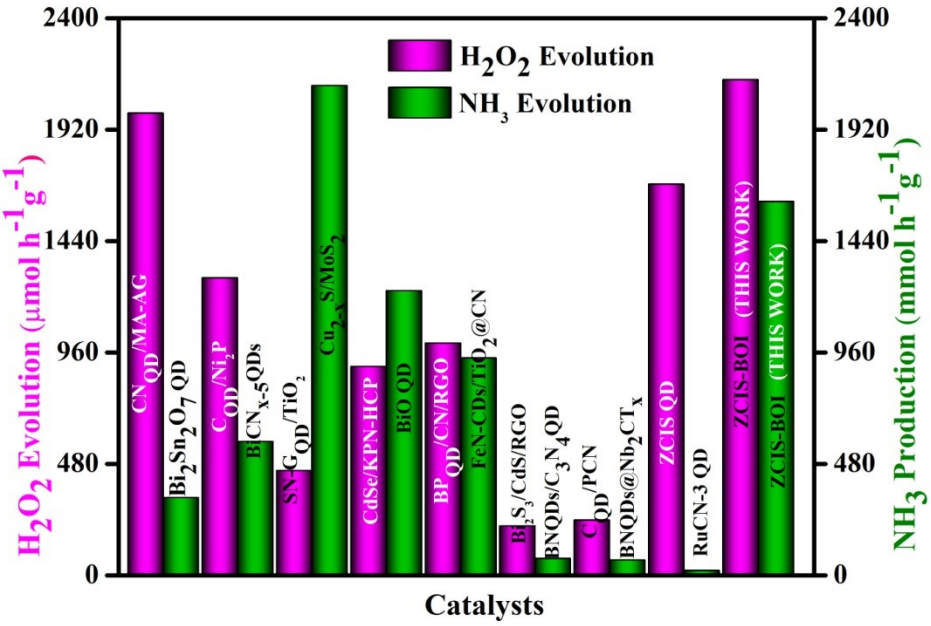

Fig. S4: Comparison study of H_2O_2 and NH_3 production over various reported photocatalyst catalysts.[2,4-17]

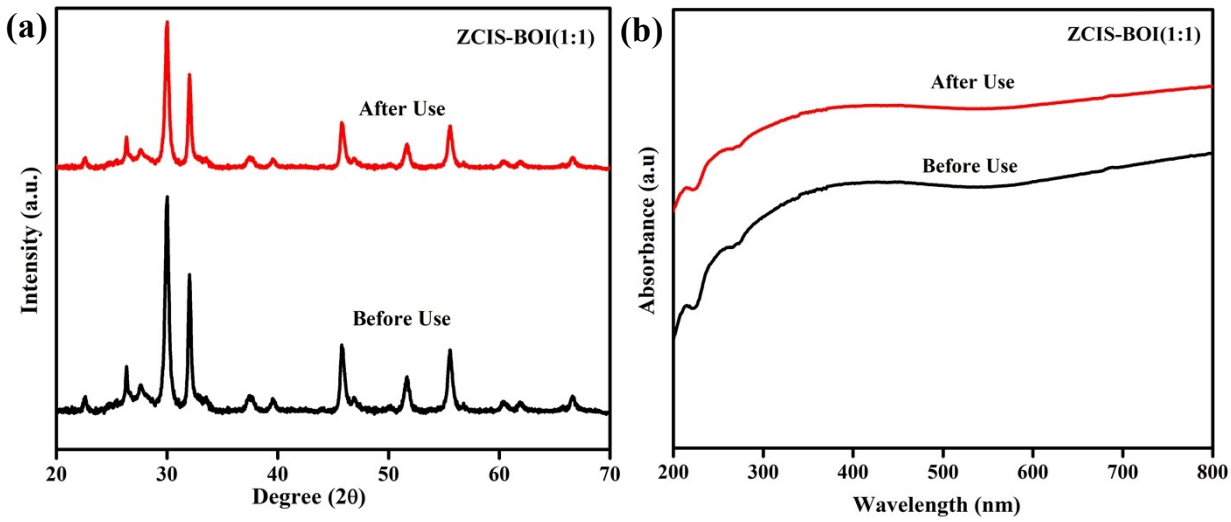

Fig. S5: XRD and UV of ZCIS-BOI(1:1) after and before use.

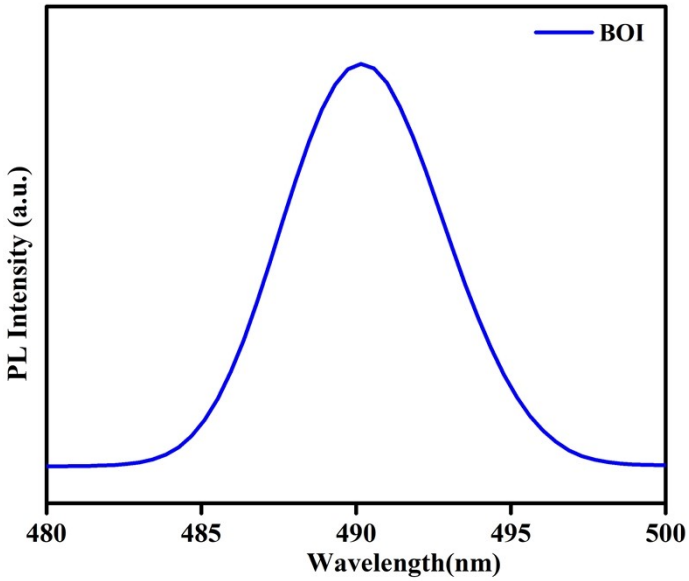

Fig. S6: PL plot of BOI.

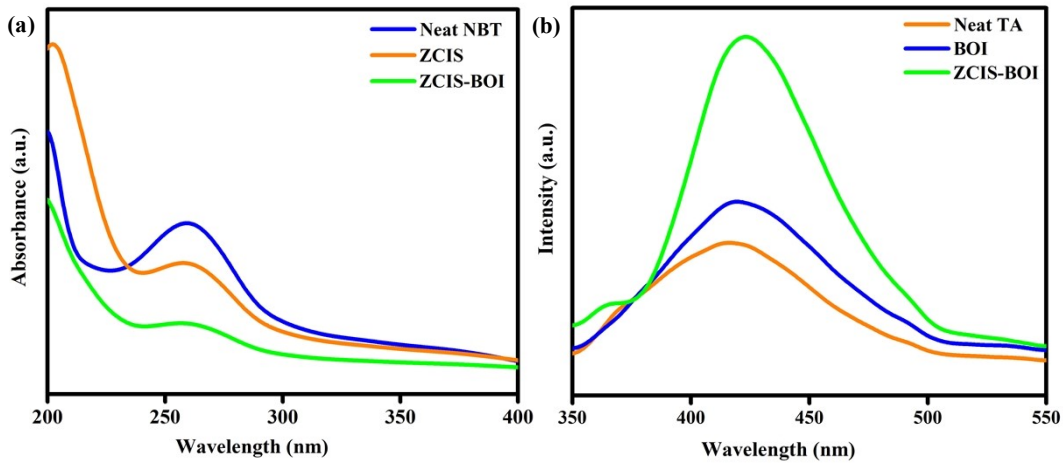

Fig. S7: (a) NBT analysis, (b) TA analysis.

H_2O_2 Evolution

Calculation of solar to chemical conversion efficiency (SCC %) for H_2O_2 production[2]

SCC % of ZCIS-BOI(1:1) towards H_2O_2 evolution under 250 W Hg-lamp can be calculated by following the equation below:

$$\text{SCC \%} = \frac{\Delta G^\circ \; for \; H2O2 \; generation \; (J/mol) \; \times \; H2O2 \; produced \; (mol)}{Input \; energy \; (W) \; \times \; reaction \; time(s)} \times 100 \text{ --------- (1)}$$

Further, ΔG° for H_2O_2 evolution is 117 KJ.mol^{-1}. The irradiance of 250 W Hg-lamp is 1.33 W.cm^{-2} and 84.78 cm^2 irradiated area. In a 1 h of reaction time, the amount of H_2O_2 produced is 85.4 μmol.

Input Energy (W) = $irradiance \; (Wcm^{-2}) \times irradiated \; area \; (cm^2)$

=1.33 × 84.78

= 112.75 W

Acc. to equation (1), the SCC efficiency is calculated to be 0.24%.

Calculation of solar to chemical conversion efficiency (SCC %) for NH_3 generation[3]

Solar to chemical conversion efficiency (SCC %) of ZCIS-BOI(1:1) heterojunction towards NH_3 evolution under 250 W Hg lamp was calculated by the following Eq[n]:

$$\text{SCC \%} = \frac{\Delta G^{\circ}\ for\ NH3\ production\ (J/mol)\ \times\ NH3\ produced\ (mol)}{Input\ energy\ (W)\ \times\ reaction\ time(s)} \times 100$$

$$= \frac{339000\ \times\ 0.032}{1330\ \times\ 3600} \times 100 = 0.36\%$$

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