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Supporting information for

# $Ba_3SnGa_{10-x}In_xO_{20}$ ($0 \leq x \leq 2$): Site-selective doping, band structure engineering and photocatalytic overall water splitting

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Table S1. Atomic coordinate, occupancy factor, isotropic thermal displacement factors for $Ba_3SnGa_{10}O_{20}$ obtained from Rietveld refinements

| atom | site | *x* | *y* | *z* | Occ. | $B_{eq}$ |
|---|---|---|---|---|---|---|
| Ba1 | 2a | 0 | 0 | 0 | 1 | 1.20(2) |
| Ba2 | 4i | 0.28026(3) | 0 | 0.0212(1) | 1 | 1.00(2) |
| Ga1 | 2b | 0 | 0.5 | 0 | 0.770(4) | 0.75(4) |
| Sn1 | 2b | 0 | 0.5 | 0 | 0.230(4) | 0.75(4) |
| Ga2 | 4h | 0 | 0.36382(6) | 0.5 | 0.615(2) | 0.58(2) |
| Sn2 | 4h | 0 | 0.36382(6) | 0.5 | 0.385(2) | 0.58(2) |
| Ga3 | 8j | 0.35398(5) | 0.36346(5) | 0.0113(1) | 1 | 0.72(2) |
| Ga4 | 8j | 0.13874(5) | 0.28522(5) | 0.9758(1) | 1 | 0.56(2) |
| O1 | 4i | 0.4357(3) | 0 | 0.8179(8) | 1 | 0.53(3) |
| O2 | 4i | 0.9018(3) | 0 | 0.4157(8) | 1 | 0.53(3) |
| O3 | 8j | 0.2384(2) | 0.3645(3) | 0.8988(6) | 1 | 0.53(3) |
| O4 | 8j | 0.4143(2) | 0.2501(2) | 0.8400(6) | 1 | 0.53(3) |
| O5 | 8j | 0.8610(2) | 0.1446(2) | 0.8640(6) | 1 | 0.53(3) |
| O6 | 8j | 0.0739(2) | 0.3797(3) | 0.1801(6) | 1 | 0.53(3) |

$a$ = 15.19472(3) Å, $b$ = 11.76213(3) Å, $c$ = 5.15730(1) Å, $\beta$ = 90.9765(1) Å, $V$ = 921.591(3) Å$^3$

$R_p$ = 3.211%, $R_{wp}$ = 4.221%, $R_{exp}$ = 2.156%, GOF = 1.958.

Definition of R factors and GOF:

$$R_p = \sum \left| Y_{o,m} - Y_{c,m} \right| / \sum Y_{o,m} \qquad R_{wp} = [\sum w_m (Y_{o,m} - Y_{c,m})^2 / \sum w_m Y_{o,m}^2]^{1/2}$$

$$R_{exp} = [(N\text{-}P) / \sum w_m Y_{o,m}^2]^{1/2} \qquad GOF = R_{wp} / R_{exp}$$

Table S2. Selected metal-oxygen bond distances (Å) for $Ba_3SnGa_{10-x}In_xO_{20}$ ($0 \leq x \leq 2.0$) obtained from Rietveld refinements

| **Bond** | ***x* = 0** | ***x* = 0.5** | ***x* = 1.0** | ***x* = 1.5** | ***x* = 2.0** |
|---|---|---|---|---|---|
| M1-O1 × 2 | 1.923(4) | 1.853(6) | 1.984(5) | 2.002(6) | 1.904(8) |
| M1-O6 × 4 | 2.022(3) | 2.037(4) | 2.052(3) | 2.066(4) | 2.146(6) |
| <M1-O> | 1.989 | 1.976 | 2.029 | 2.045 | 2.065 |
| | | | | | |
| M2-O1 × 2 | 2.091(3) | 2.124(4) | 2.165(3) | 2.220(4) | 2.210(5) |
| M2-O4 × 2 | 2.033(3) | 2.104(4) | 2.088(3) | 2.136(4) | 2.190(6) |
| M2-O6 × 2 | 2.020(3) | 2.037(4) | 2.113(3) | 2.153(4) | 2.147(6) |
| <M2-O> | 2.048 | 2.088 | 2.122 | 2.170 | 2.182 |
| | | | | | |
| Ga3-O2× 1 | 1.834(2) | 1.831(3) | 1.832(2) | 1.841(3) | 1.826(4) |
| Ga3-O3× 1 | 1.841(3) | 1.862(4) | 1.798(3) | 1.802(4) | 1.866(6) |
| Ga3-O4× 1 | 1.852(3) | 1.838(4) | 1.834(3) | 1.821(4) | 1.847(6) |
| Ga3-O5× 1 | 1.823(3) | 1.768(4) | 1.811(3) | 1.800(4) | 1.738(6) |
| <Ga3-O> | 1.838 | 1.825 | 1.819 | 1.816 | 1.819 |
| | | | | | |
| Ga4-O3 × 1 | 1.828(3) | 1.854(4) | 1.859(3) | 1.858(4) | 1.923(6) |
| Ga4-O4 × 1 | 1.852(3) | 1.812(4) | 1.869(3) | 1.855(4) | 1.782(6) |
| Ga4-O5 × 1 | 1.848(3) | 1.860(4) | 1.857(3) | 1.869(4) | 1.899(6) |
| Ga4-O6 × 1 | 1.831(3) | 1.843(4) | 1.806(3) | 1.802(4) | 1.795(6) |
| <Ga4-O> | 1.840 | 1.842 | 1.848 | 1.846 | 1.850 |

Table S3. Atomic coordinate, occupancy factor, isotropic thermal displacement factors for $Ba_3SnGa_{9.5}In_{0.5}O_{20}$ obtained from Rietveld refinements

| atom | site | *x* | *y* | *z* | Occ. | $B_{eq}$ |
|---|---|---|---|---|---|---|
| Ba1 | 2a | 0 | 0 | 0 | 1 | 1.49(3) |
| Ba2 | 4i | 0.27982(5) | 0 | 0.0188(1) | 1 | 1.19(2) |
| Ga1 | 2b | 0 | 0.5 | 0 | 0.656(5) | 0.98(5) |
| Sn1/In1 | 2b | 0 | 0.5 | 0 | 0.344(5) | 0.98(5) |
| Ga2 | 4h | 0 | 0.36130(7) | 0.5 | 0.422(2) | 0.81(3) |
| Sn2/In2 | 4h | 0 | 0.36130(7) | 0.5 | 0.578(2) | 0.81(3) |
| Ga3 | 8j | 0.35296(7) | 0.36508(7) | 0.0096(2) | 1 | 0.95(3) |
| Ga4 | 8j | 0.13967(7) | 0.28434(7) | 0.9744(2) | 1 | 0.54(3) |
| O1 | 4i | 0.4396(4) | 0 | 0.807(1) | 1 | 0.50(5) |
| O2 | 4i | 0.9010(4) | 0 | 0.411(1) | 1 | 0.50(5) |
| O3 | 8j | 0.2377(3) | 0.3676(4) | 0.8866(8) | 1 | 0.50(5) |
| O4 | 8j | 0.4105(3) | 0.2536(3) | 0.8323(8) | 1 | 0.50(5) |
| O5 | 8j | 0.8587(3) | 0.1473(3) | 0.8491(7) | 1 | 0.50(5) |
| O6 | 8j | 0.0734(3) | 0.3781(4) | 0.1779(8) | 1 | 0.50(5) |

$a$ = 15.26409(4) Å, $b$ = 11.81621(3) Å, $c$ = 5.18857(1) Å, $\beta$ = 90.9007(2) Å, $V$ = 935.715(5) Å$^3$

$R_p$ = 4.184%, $R_{wp}$ = 5.492%, $R_{exp}$ = 2.498%, GOF = 2.199.

Table S4. Atomic coordinate, occupancy factor, isotropic thermal displacement factors for $Ba_3SnGa_9InO_{20}$ obtained from Rietveld refinements

| atom | site | *x* | *y* | *z* | Occ. | $B_{eq}$ |
|---|---|---|---|---|---|---|
| Ba1 | 2a | 0 | 0 | 0 | 1 | 1.22(2) |
| Ba2 | 4i | 0.27980(4) | 0 | 0.0175(1) | 1 | 0.97(2) |
| Ga1 | 2b | 0 | 0.5 | 0 | 0.535(4) | 0.46(4) |
| Sn1 | 2b | 0 | 0.5 | 0 | 0.465(4) | 0.46(4) |
| Ga2 | 4h | 0 | 0.35937(5) | 0.5 | 0.233(2) | 0.70(2) |
| Sn2 | 4h | 0 | 0.35937(5) | 0.5 | 0.767(2) | 0.70(2) |
| Ga3 | 8j | 0.35242(5) | 0.36477(5) | 0.0093(2) | 1 | 0.56(2) |
| Ga4 | 8j | 0.14077(5) | 0.28291(5) | 0.9768(2) | 1 | 0.48(2) |
| O1 | 4i | 0.4324(3) | 0 | 0.8218(9) | 1 | 0.45(4) |
| O2 | 4i | 0.9008(3) | 0 | 0.4175(9) | 1 | 0.45(4) |
| O3 | 8j | 0.2406(2) | 0.3645(3) | 0.8997(6) | 1 | 0.45(4) |
| O4 | 8j | 0.4125(2) | 0.2557(3) | 0.8357(6) | 1 | 0.45(4) |
| O5 | 8j | 0.8582(2) | 0.1447(3) | 0.8557(6) | 1 | 0.45(4) |
| O6 | 8j | 0.0763(2) | 0.3776(3) | 0.1681(7) | 1 | 0.45(4) |

$a$ = 15.32033(4) Å, $b$ = 11.85491(3) Å, $c$ = 5.21515(1) Å, $\beta$ = 90.8105(2) Å, $V$ = 947.086(4) Å$^3$

$R_p$ = 3.140%, $R_{wp}$ = 4.092%, $R_{exp}$ = 2.220%, GOF = 1.844.

Table S5. Atomic coordinate, occupancy factor, isotropic thermal displacement factors for $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ obtained from Rietveld refinements

| atom | site | *x* | *y* | *z* | Occ. | $B_{eq}$ |
|---|---|---|---|---|---|---|
| Ba1 | 2a | 0 | 0 | 0 | 1 | 1.19(3) |
| Ba2 | 4i | 0.27946(5) | 0 | 0.0154(1) | 1 | 0.85(2) |
| Ga1 | 2b | 0 | 0.5 | 0 | 0.330(4) | 0.36(4) |
| Sn1 | 2b | 0 | 0.5 | 0 | 0.670(4) | 0.36(4) |
| Ga2 | 4h | 0 | 0.35732(6) | 0.5 | 0.085(2) | 0.70(2) |
| Sn2 | 4h | 0 | 0.35732(6) | 0.5 | 0.915(2) | 0.70(2) |
| Ga3 | 8j | 0.35190(6) | 0.36516(6) | 0.0089(2) | 1 | 0.47(2) |
| Ga4 | 8j | 0.14198(6) | 0.28126(6) | 0.9759(2) | 1 | 0.23(3) |
| O1 | 4i | 0.4296(4) | 0 | 0.819(1) | 1 | 0.33(4) |
| O2 | 4i | 0.9021(3) | 0 | 0.421(1) | 1 | 0.33(4) |
| O3 | 8j | 0.2405(3) | 0.3643(3) | 0.8980(8) | 1 | 0.33(4) |
| O4 | 8j | 0.4113(3) | 0.2595(3) | 0.8296(7) | 1 | 0.33(4) |
| O5 | 8j | 0.8584(2) | 0.1438(3) | 0.8513(7) | 1 | 0.33(4) |
| O6 | 8j | 0.0767(3) | 0.3759(3) | 0.1618(8) | 1 | 0.33(4) |

$a$ = 15.37493(5) Å, $b$ = 11.89386(4) Å, $c$ = 5.24437(2) Å, $\beta$ = 90.6945(2) Å, $V$ = 958.954(6) Å$^3$

$R_p$ = 3.518%, $R_{wp}$ = 4.563%, $R_{exp}$ = 2.253%, GOF = 2.025.

Table S6. Atomic coordinate, occupancy factor, isotropic thermal displacement factors for $Ba_3SnGa_8In_2O_{20}$ obtained from Rietveld refinements

| atom | site | *x* | *y* | *z* | Occ. | $B_{eq}$ |
|---|---|---|---|---|---|---|
| Ba1 | 2a | 0 | 0 | 0 | 1 | 1.63(5) |
| Ba2 | 4i | 0.27884(7) | 0 | 0.0127(2) | 1 | 1.09(3) |
| Ga1 | 2b | 0 | 0.5 | 0 | 0 | 1.19(5) |
| Sn1 | 2b | 0 | 0.5 | 0 | 1 | 1.19(5) |
| Ga2 | 4h | 0 | 0.35566(8) | 0.5 | 0 | 0.97(3) |
| Sn2 | 4h | 0 | 0.35566(8) | 0.5 | 1 | 0.97(3) |
| Ga3 | 8j | 0.35226(9) | 0.36605(9) | 0.0061(3) | 1 | 0.68(4) |
| Ga4 | 8j | 0.1434(1) | 0.28000(9) | 0.9729(3) | 1 | 0.14(4) |
| O1 | 4i | 0.4375(6) | 0 | 0.810(2) | 1 | 0.56(7) |
| O2 | 4i | 0.8997(6) | 0 | 0.414(2) | 1 | 0.56(7) |
| O3 | 8j | 0.2395(4) | 0.3724(5) | 0.874(1) | 1 | 0.56(7) |
| O4 | 8j | 0.4100(4) | 0.2609(5) | 0.814(1) | 1 | 0.56(7) |
| O5 | 8j | 0.8569(4) | 0.1456(5) | 0.835(1) | 1 | 0.56(7) |
| O6 | 8j | 0.0778(4) | 0.3696(5) | 0.166(1) | 1 | 0.56(7) |

$a$ = 15.41431(8) Å, $b$ = 11.93819(6) Å, $c$ = 5.27206(3) Å, $\beta$ = 90.5704(3) Å, $V$ = 970.112(9) Å$^3$

$R_p$ = 5.302%, $R_{wp}$ = 7.049%, $R_{exp}$ = 2.250%, GOF = 3.134.

Table S7. Bond valences sum of $In^{3+}$ and $Sn^{4+}$ located at M1 or M2 site in $Ba_3SnGa_{10-x}In_xO_{20}$ ($0 \leq x \leq 2.0$)

| | | | | |
|---|---|---|---|---|
| $x = 0$ | | | | |
| | In1 | In2 | Sn1 | Sn2 |
| Bond valence sum | / | / | 4.821 | 4.091 |
| $x = 0.5$ | | | | |
| | In1 | In2 | Sn1 | Sn2 |
| Bond valence sum | 5.060 | 3.645 | 5.102 | 3.674 |
| $x = 1.0$ | | | | |
| | In1 | In2 | Sn1 | Sn2 |
| Bond valence sum | 4.269 | 3.323 | 4.304 | 3.350 |
| $x = 1.5$ | | | | |
| | In1 | In2 | Sn1 | Sn2 |
| Bond valence sum | 4.094 | 2.924 | 4.127 | 2.948 |
| $x = 2.0$ | | | | |
| | In1 | In2 | Sn1 | Sn2 |
| Bond valence sum | 4.058 | 2.820 | 4.091 | 2.843 |

Table S8. Estimated band gap energy for $Ba_3SnGa_{10-x}In_xO_{20}$

| $Ba_3SnGa_{10-x}In_xO_{20}$ | $E_g$/ eV |
|---|---|
| $x = 0$ | 4.53 |
| $x = 0.5$ | 4.50 |
| $x = 1.0$ | 4.47 |
| $x = 1.5$ | 4.41 |
| $x = 2.0$ | 4.27 |

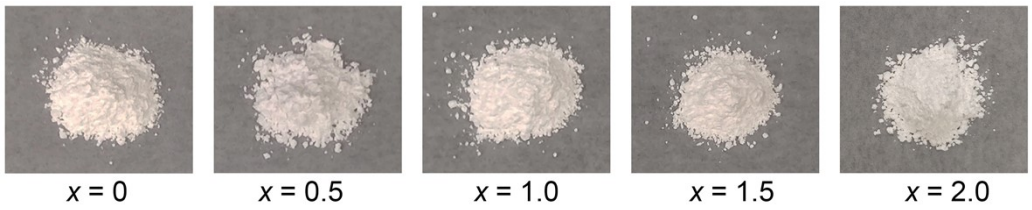


**Fig. S1**. Photographs of $Ba_3SnGa_{10-x}In_xO_{20}$ ($0 \leq x \leq 2.0$) samples.

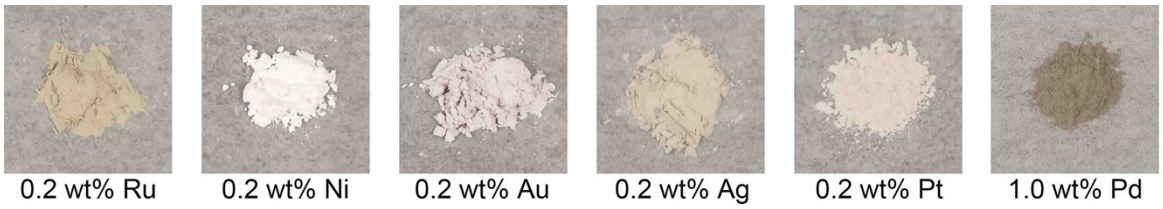


**Fig. S2**. Photographs for $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ loaded with different cocatalysts.

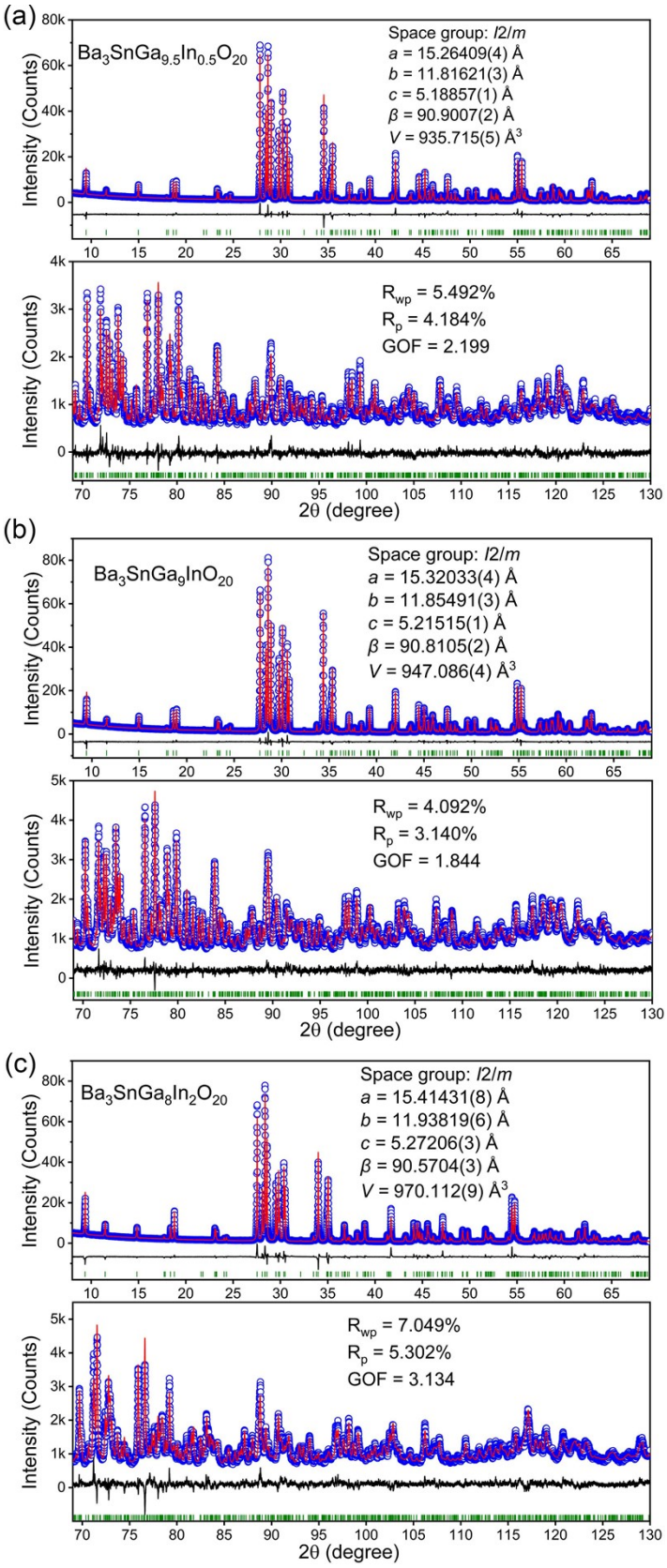


**Fig. S3**. Final convergence of the Rietveld refinements on high quality powder X-ray diffraction data for (a) $Ba_3SnGa_{9.5}In_{0.5}O_{20}$, (b) $Ba_3SnGa_9InO_{20}$, (c) $Ba_3SnGa_8In_2O_{20}$.

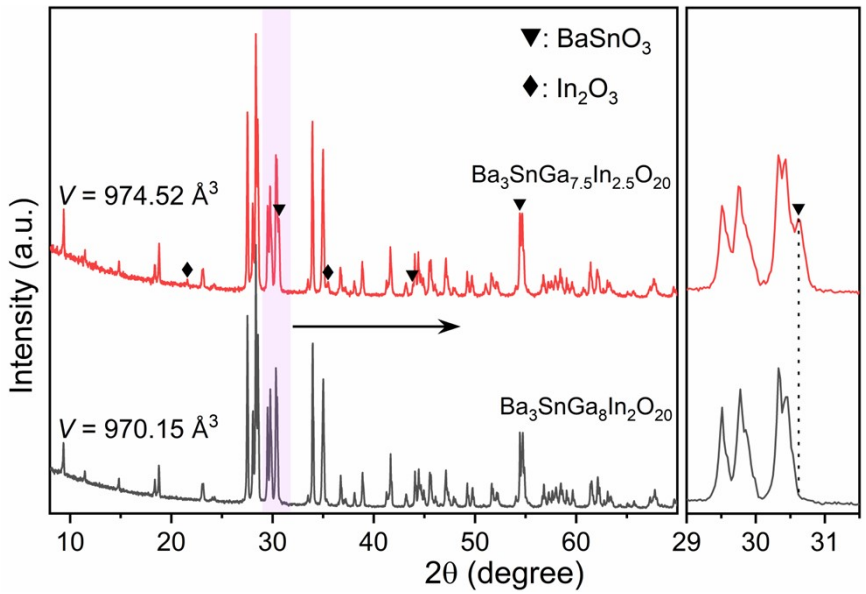


**Fig. S4**. Powder XRD patterns for phase-pure $Ba_3SnGa_8In_2O_{20}$ (gray line) and impure $Ba_3SnGa_{7.5}In_{2.5}O_{20}$ (red line). The impurity phases can be identified as $BaSnO_3$ and $In_2O_3$.

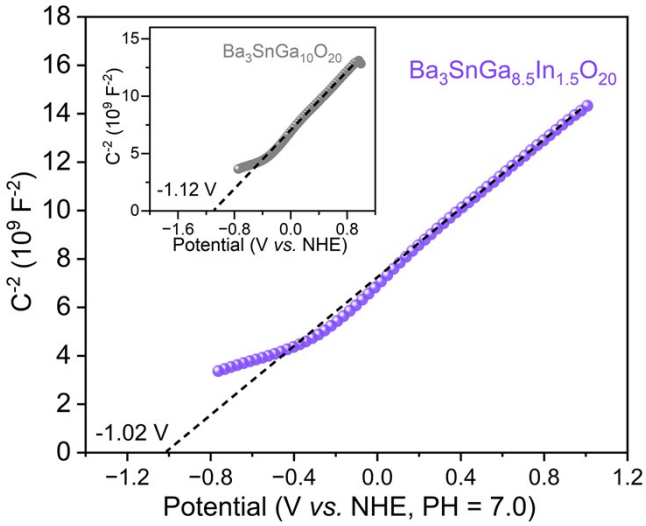


**Fig. S5**. Mott-Schottky plots for $Ba_3SnGa_{10}O_{20}$ (the inset) and $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ in a 0.3 M $Na_2SO_4$ aqueous solution (pH = 7.0).

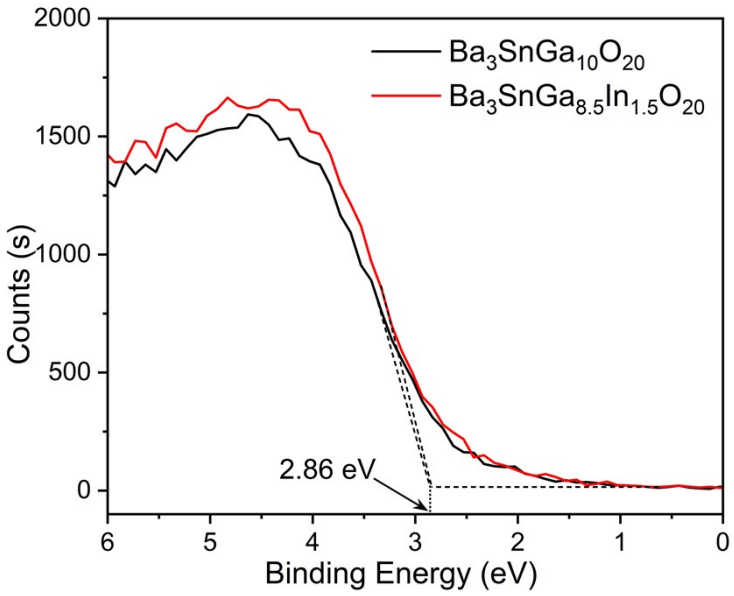


**Fig. S6**. Valence band-XPS curves for $Ba_3SnGa_{10-x}In_xO_{20}$ ($x$ = 0, 1.5).

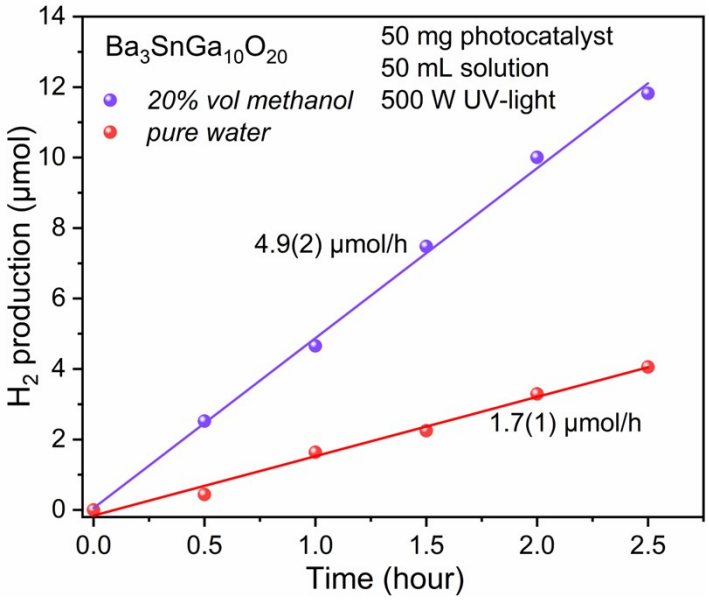


**Fig. S7**. Photocatalytic $H_2$ generation of $Ba_3SnGa_{10}O_{20}$ in 20 vol.% methanol aqueous solution (blue line) and in pure water (red line), respectively.

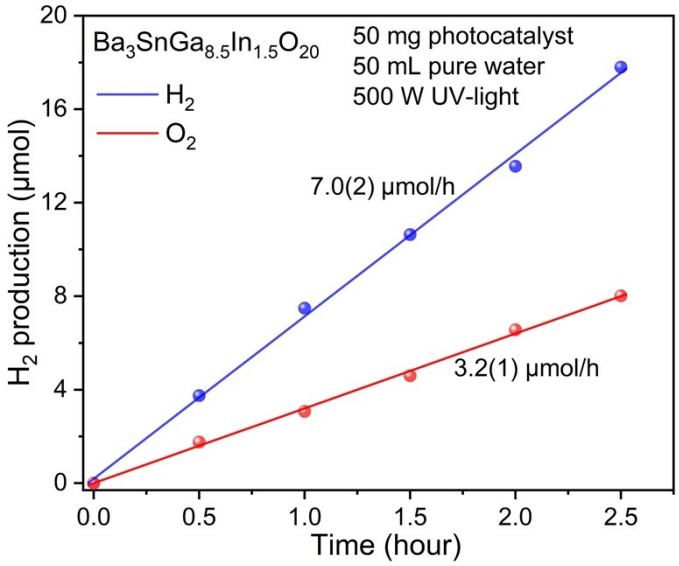


**Fig. S8**. Photocatalytic $H_2$ (blue line) and $O_2$ (red line) generation for $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ in pure water.

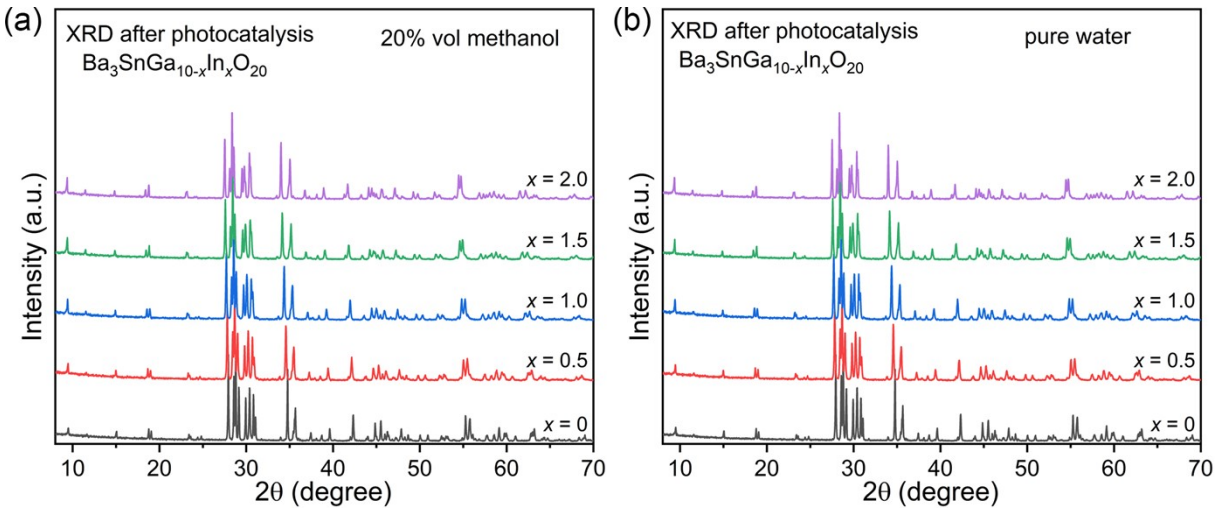


**Fig. S9**. Powder XRD patterns for $Ba_3SnGa_{10-x}In_xO_{20}$ ($0 \leq x \leq 2$) after photocatalytic reaction (a) in 20 vol.% methanol aqueous solution and (b) in pure water, respectively.

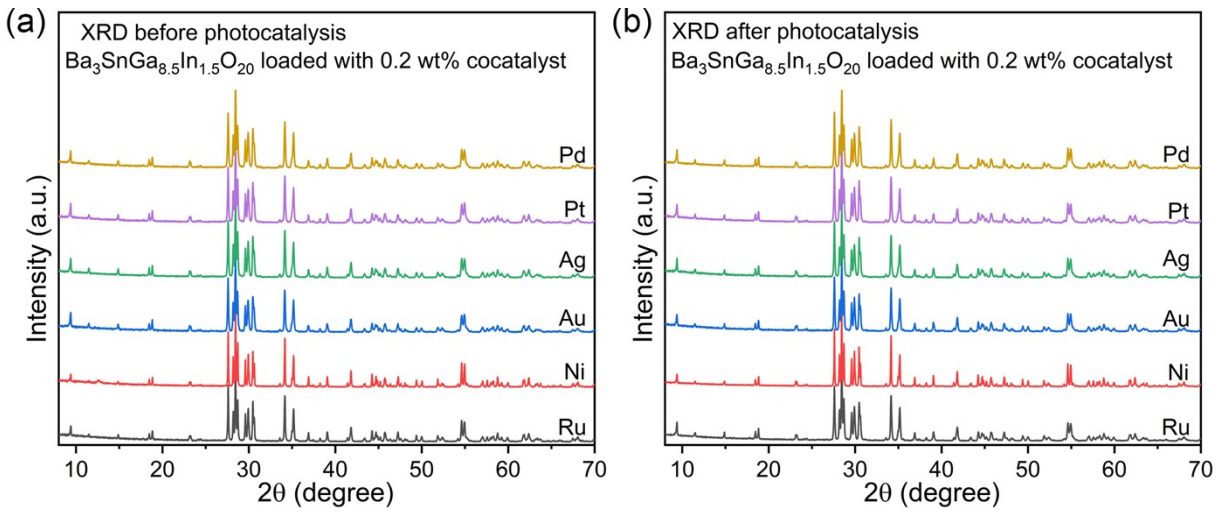


**Fig. S10**. Powder XRD patterns (a) before and (b) after photocatalytic reactions for $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ loaded with various cocatalysts.

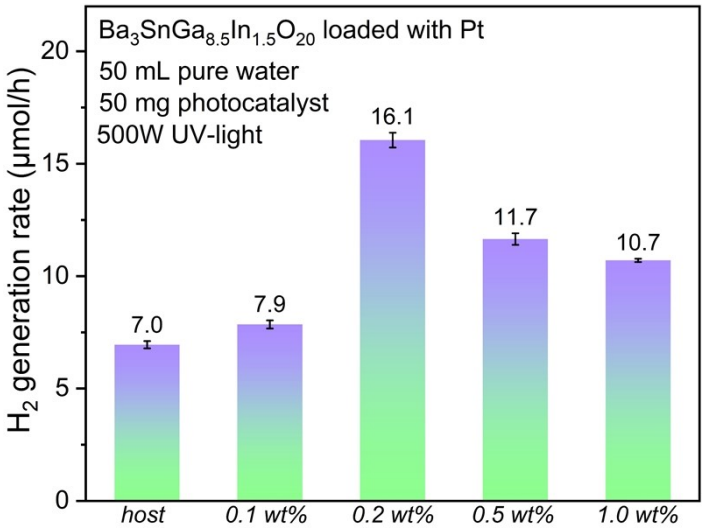


**Fig. S11**. Photocatalytic $H_2$ generation rates for $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ loaded with different amounts of Pt.

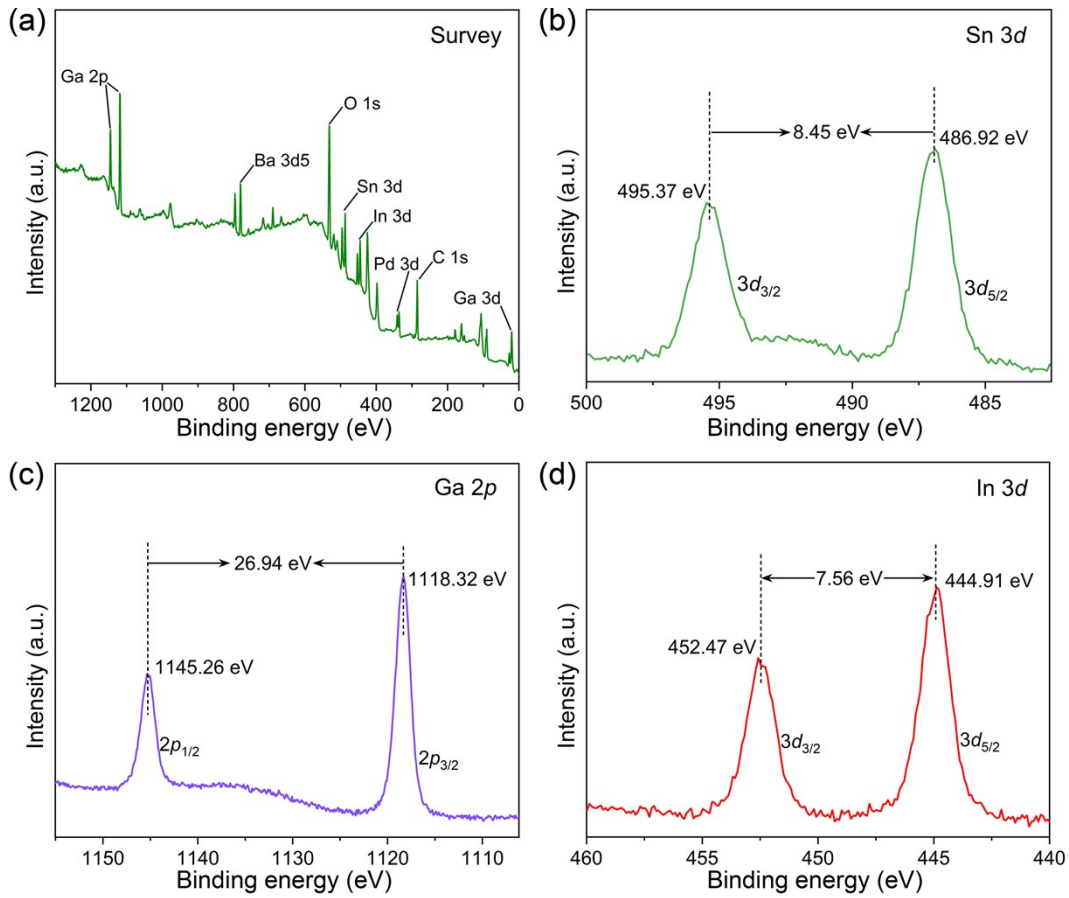


**Fig. S12**. (a) XPS survey scan of $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ loaded with 1 wt% Pd; (b) Sn 3d, (c) Ga 2p and (d) In 3d XPS spectra.

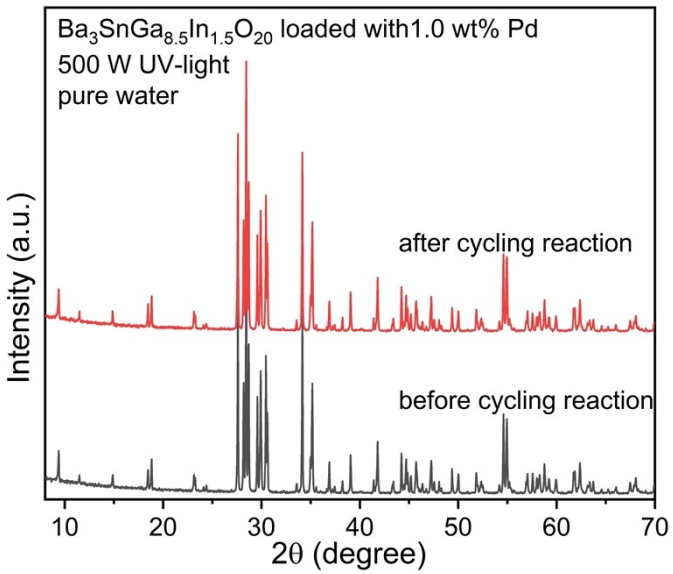


**Fig. S13**. Powder XRD patterns before (gray line) and after (red line) cyclic photocatalytic overall water splitting for $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ loaded with 1.0 wt% Pd.

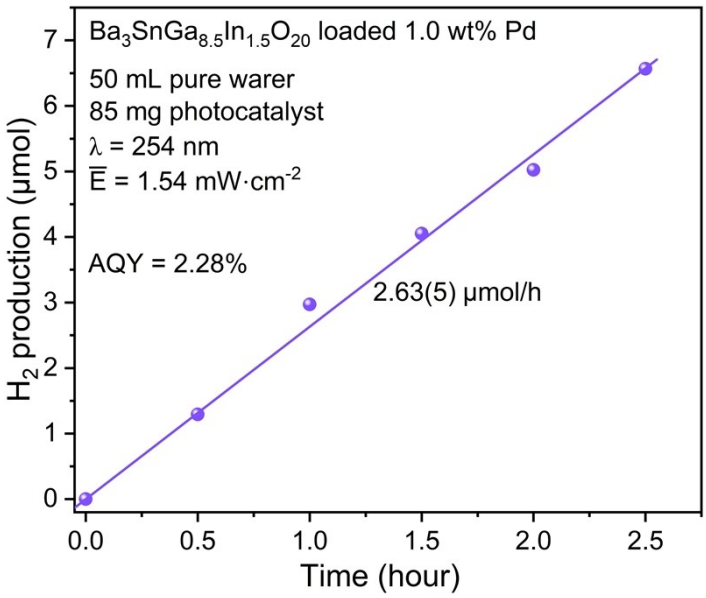


**Fig. S14**. Photocatalytic $H_2$ generation curve for $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ loaded with 1.0 wt% Pd. Photocatalytic condition: 85 mg of photocatalyst; 50 mL pure water; 500 W mercury lamp equipped with a 254 nm bandpass filter.

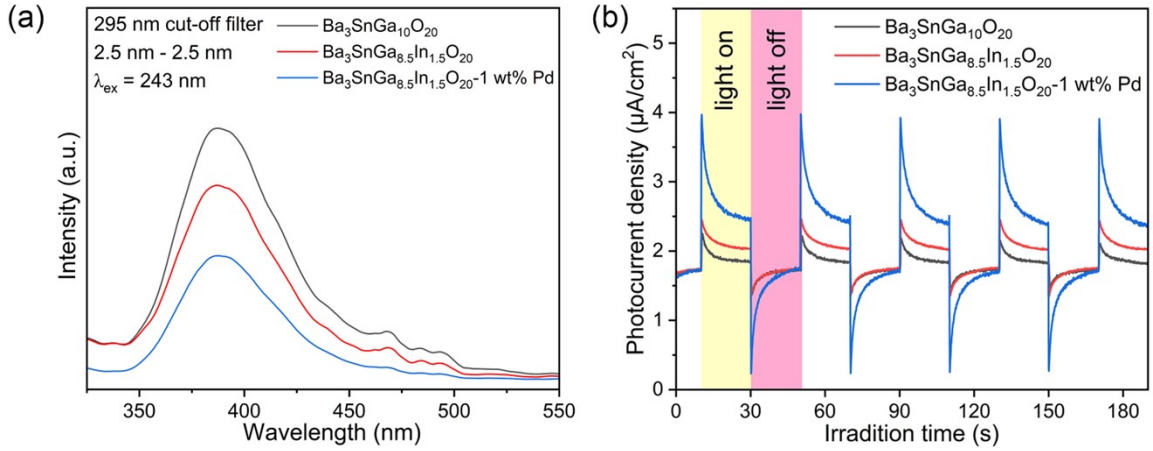


**Fig. S15**. (a) PL emission spectra and (b) transient photocurrent responses for $Ba_3SnGa_{10}O_{20}$ (gray lines), $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ (red lines), and $Ba_3SnGa_{8.5}In_{1.5}O_{20}$ loaded with 1.0 wt% Pd (blue lines), respectively.