Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Supporting Information

## Benign Role of Bi on Electrodeposited $Cu_2O$ Semiconductor towards Photo-Assisted $H_2$ Generation from Water

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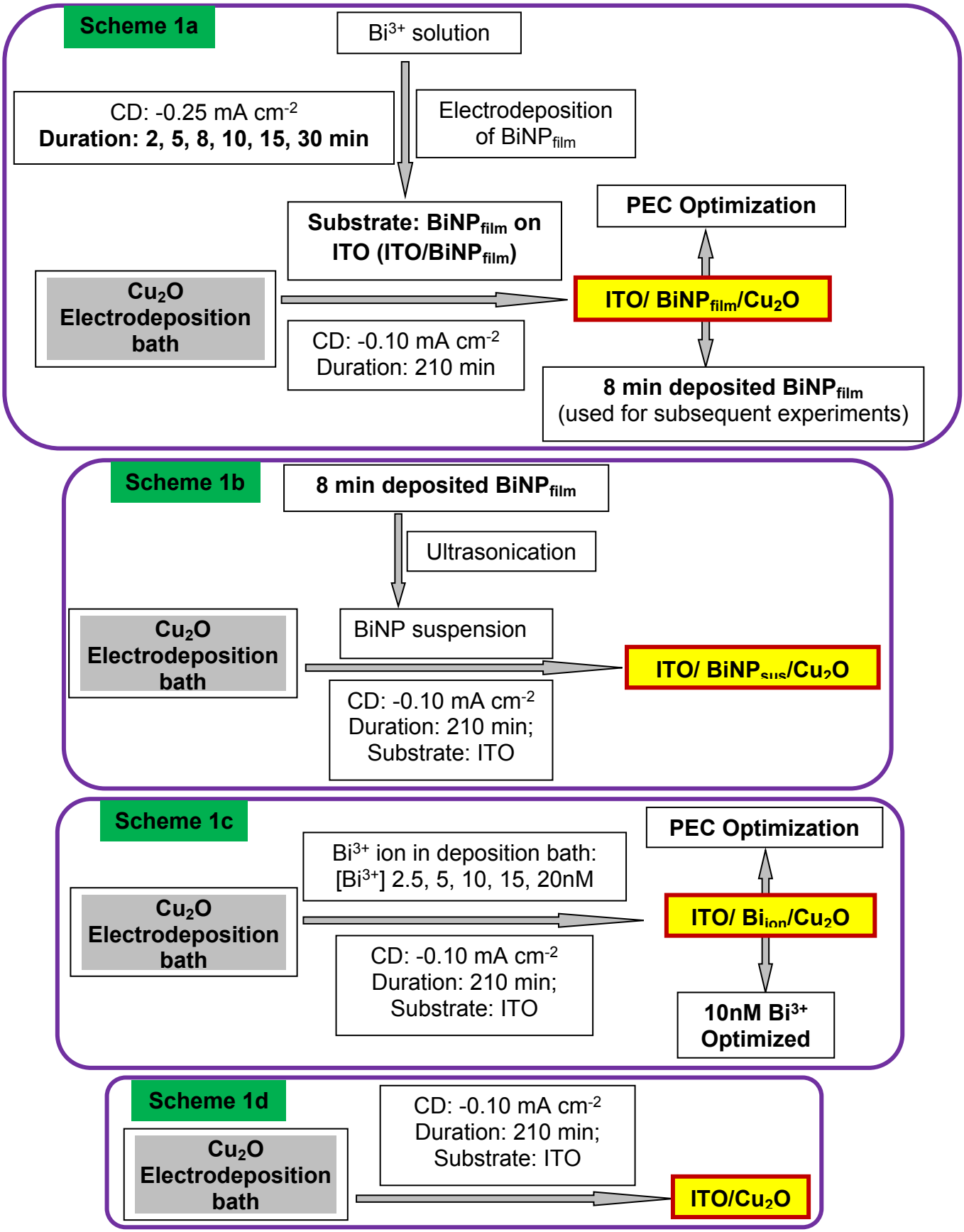


**Scheme 1(a-d):** Electrodeposition of $Cu_2O$ from different conditions.

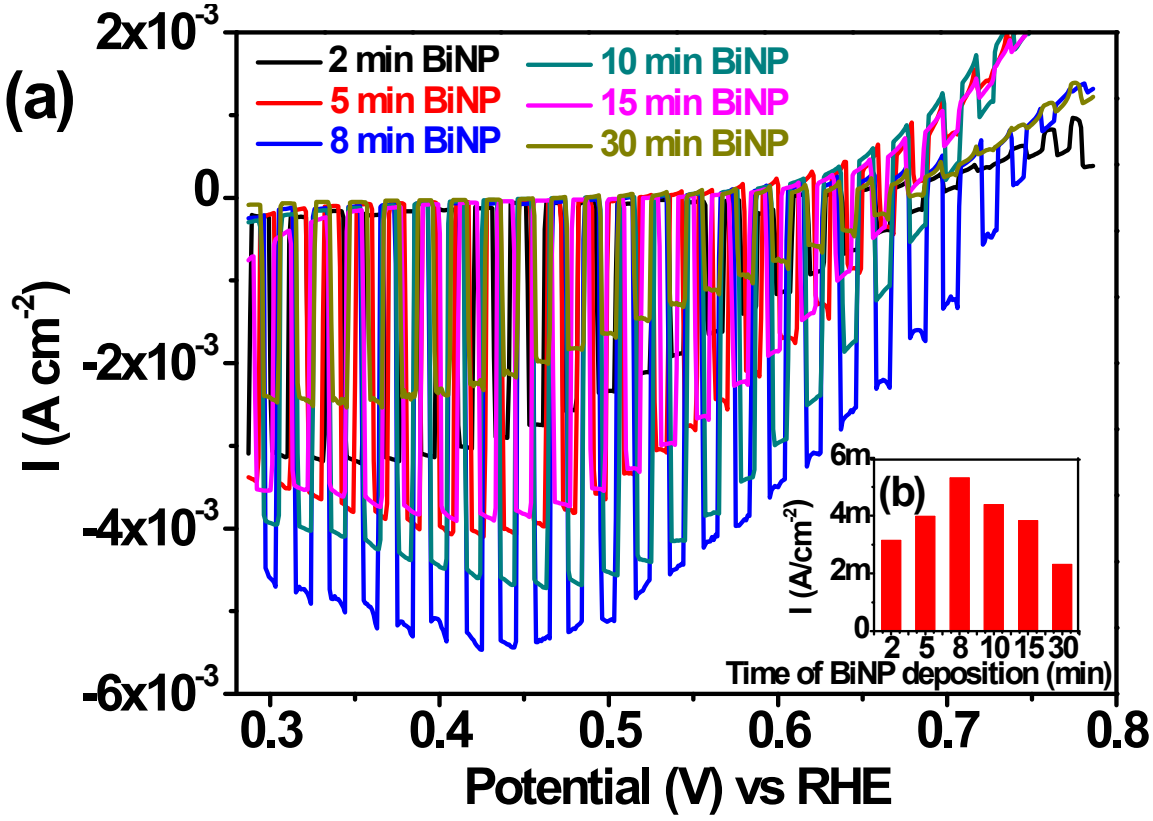


**Fig. S1. (a)** LSV plot in presence of 0.1 M $Na_2SO_4$ electrolyte (pH 4.9) under chopped light illumination of 35 mW $cm^{-2}$ at a scan rate of 10mV $s^{-1}$ for optimization of deposition time of BiNPs film followed by $Cu_2O$ deposition; **(b,** Bar plot**)** Variation of photo-generated current densities measured at a potential of 0.4 V vs RHE.

The optimized deposition time for BiNP film is 8 min. $Cu_2O$ film developed over this film shows maximum photocurrent in photoelectrochemical reduction of water under illumination.

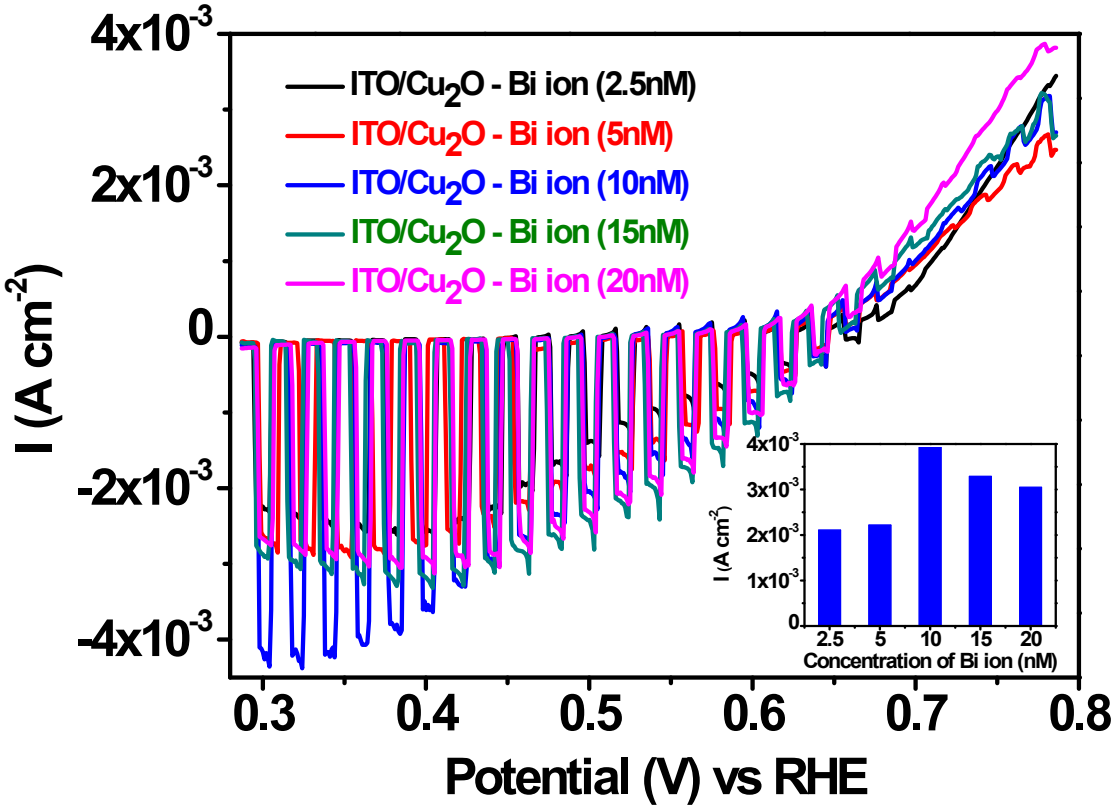


**Fig. S2. (a)** LSV plot in presence of 0.1 M $Na_2SO_4$ electrolyte (pH 4.9) under chopped light illumination of 35 mW $cm^{-2}$ at a scan rate of 10mV $s^{-1}$ for optimization of $Bi^{3+}$ ions concentration in the $Cu_2O$ electrodeposition bath. **(b,** Bar plot**)** Variation of photo-generated current densities measured at a potential of 0.4 V vs RHE.

The optimized $Bi^{3+}$ ions concentration in $Cu_2O$ electrodeposition bath is 10nmM. $Cu_2O$ film developed over this film shows maximum photocurrent in photoelectrochemical reduction of water under illumination.

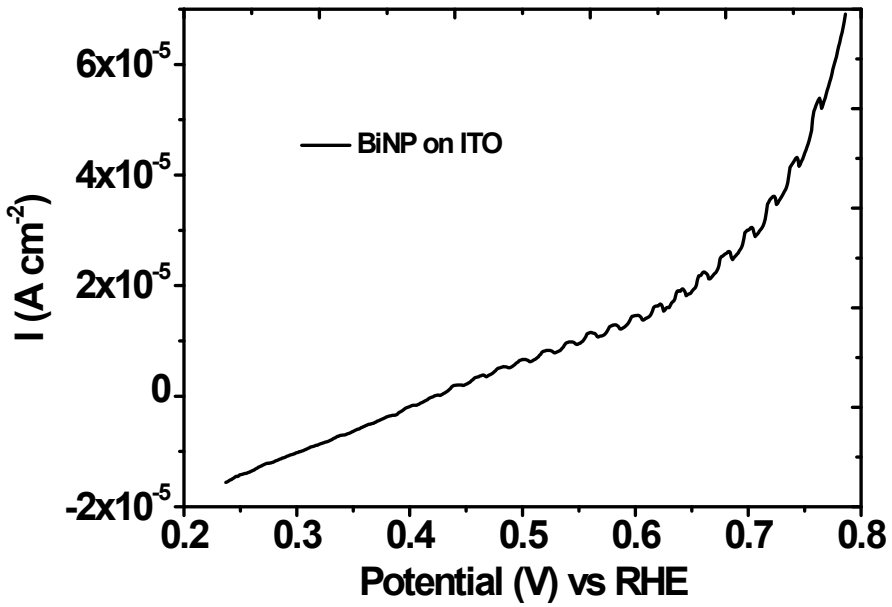


**Fig. S3.** LSV plot of BiNP on ITO in presence of 0.1 M $Na_2SO_4$ electrolyte (pH 4.9) under chopped light illumination of 35 mW $cm^{-2}$ at a scan rate of 10mV $s^{-1}$.

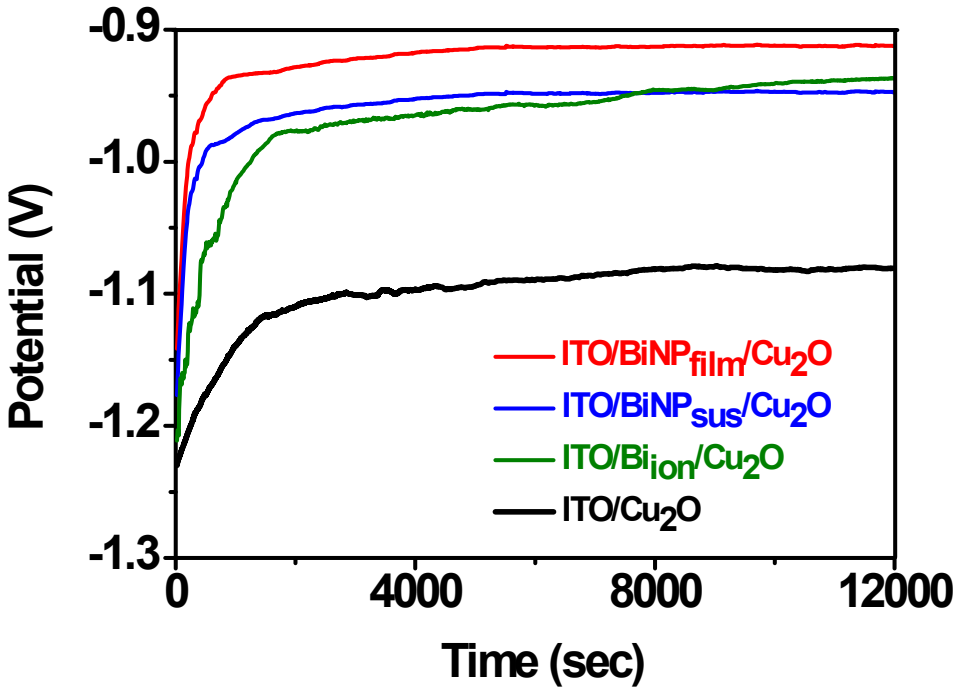


**Fig. S4.** Potential – Time curve during the deposition process of $Cu_2O$ in different condition.

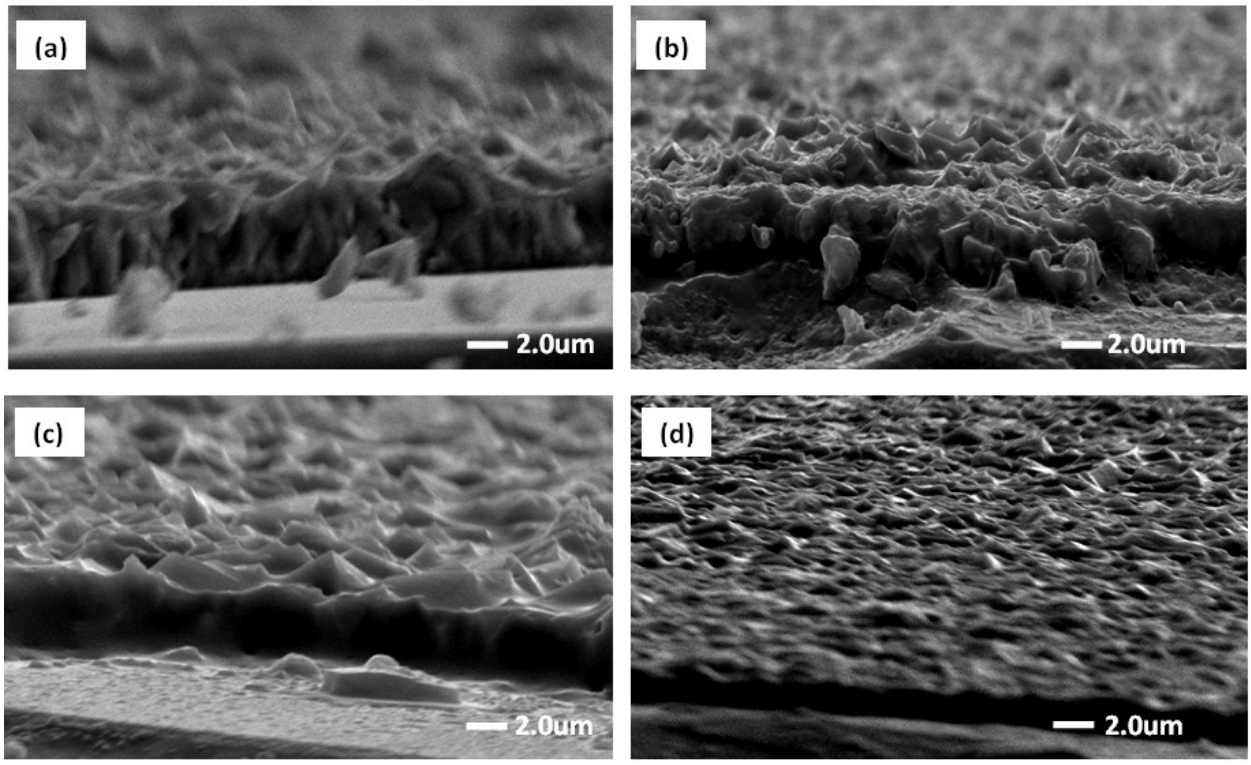


**Fig. S5.** Cross sectional SEM images of thin film semiconductor **(a)** ITO/$BiNP_{film}$/$Cu_2O$, **(b)** ITO/$BiNP_{sus}$/$Cu_2O$, **(c)** ITO/$Bi_{ion}$/$Cu_2O$, and **(d)** ITO/$Cu_2O$.

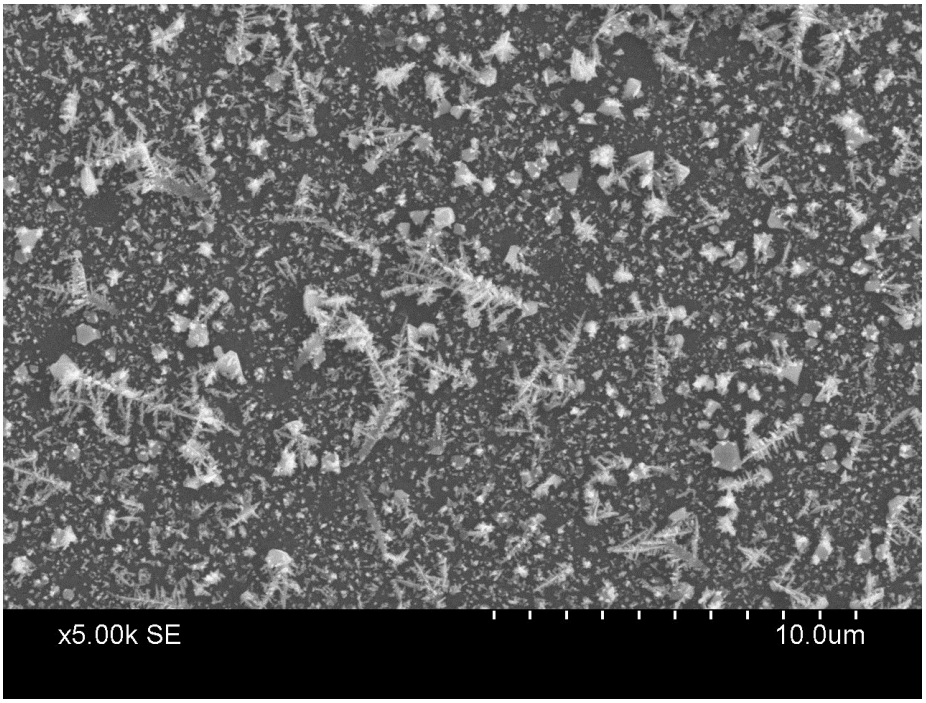


**Fig. S6.** SEM image of the BiNP film on ITO glass substrate.

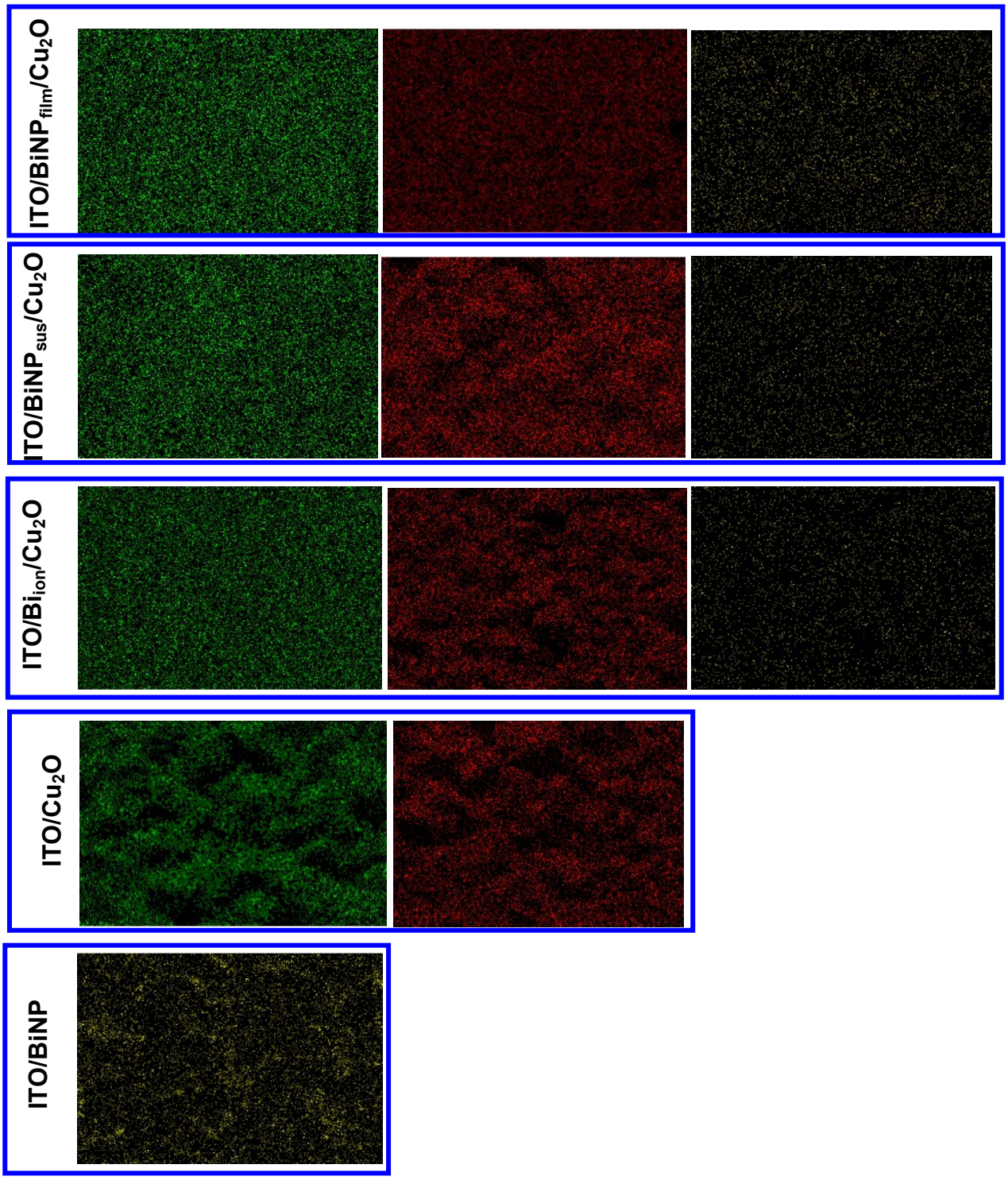


**Fig. S7.** Elemental mapping of Cu (Green), O (Red), and Bi (Yellow) obtained from different samples.

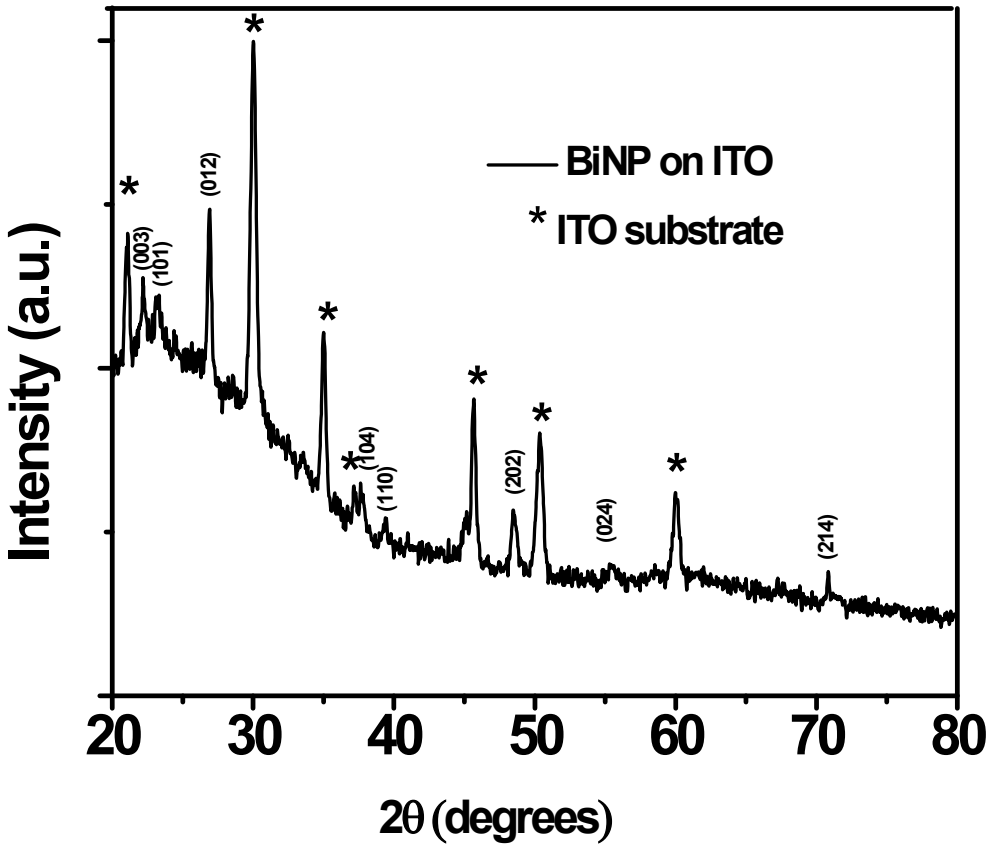


**Fig. S8.** XRD pattern of BiNP thin film on ITO substrate.

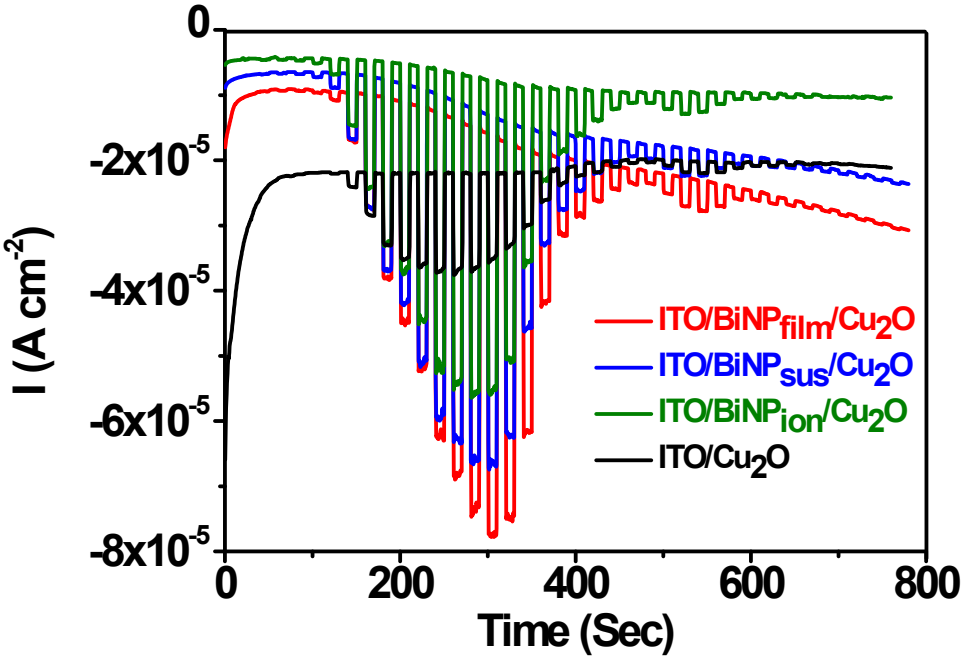


**Fig. S9.** Photoelectrochemical Action spectrum of $Cu_2O$ thin films on ITO substrates in presence of BiNPs and Bi ion using 0.1 M $Na_2SO_4$ electrolyte (pH 4.9) at an applied potential of 0.4 V vs RHE.

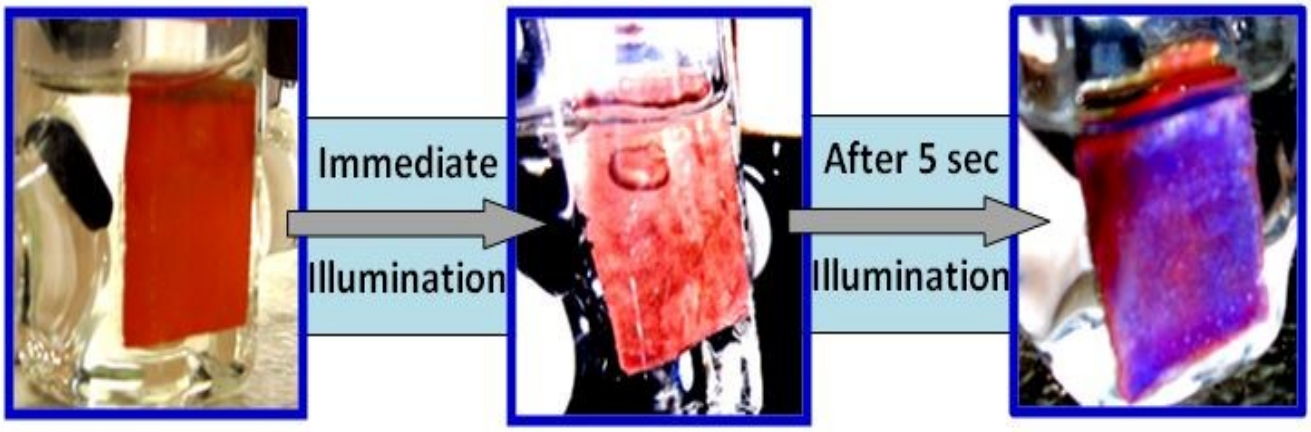


**Fig. S10.** Photoelectrochemical reduction of methyl viologen (sacrificial reagent) [$MV^{2+}_{colorless} \rightarrow MV^{+\bullet}_{deep\ blue}$] over ITO/$BiNP_{film}$/$Cu_2O$ electrodes under illumination.

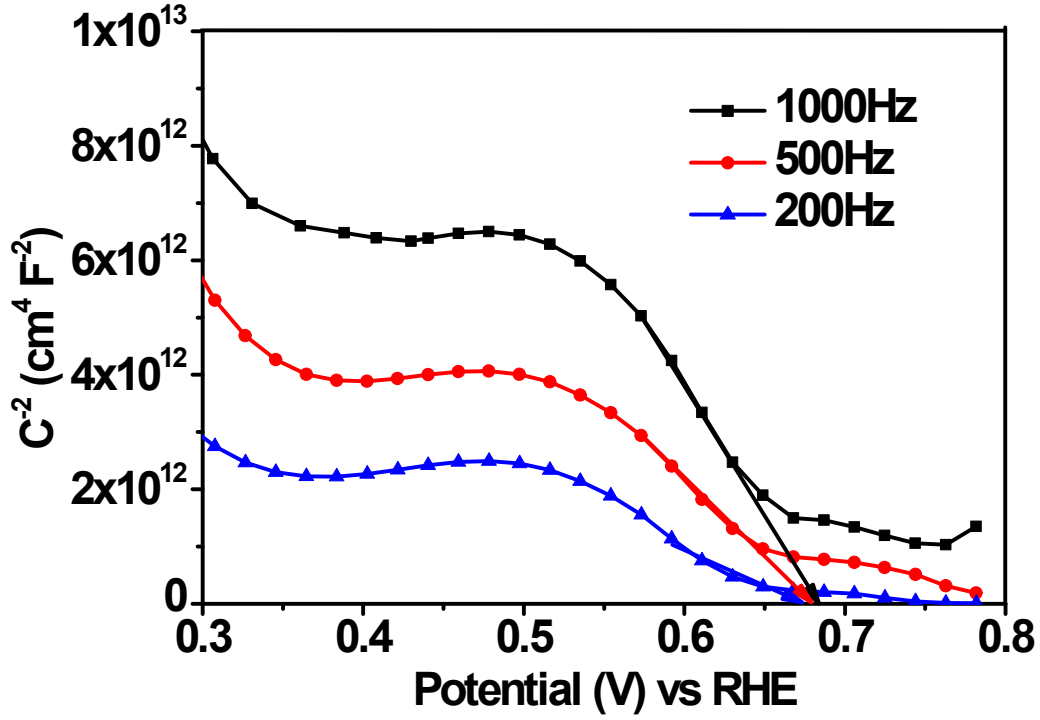


**Fig. S11.** Mott-Schottky plots of ITO/$BiNP_{film}$/$Cu_2O$ sample in presence of 0.1 M $Na_2SO_4$ electrolytes (pH 4.9) using an ac frequencies of 200, 500, and 1000 Hz.

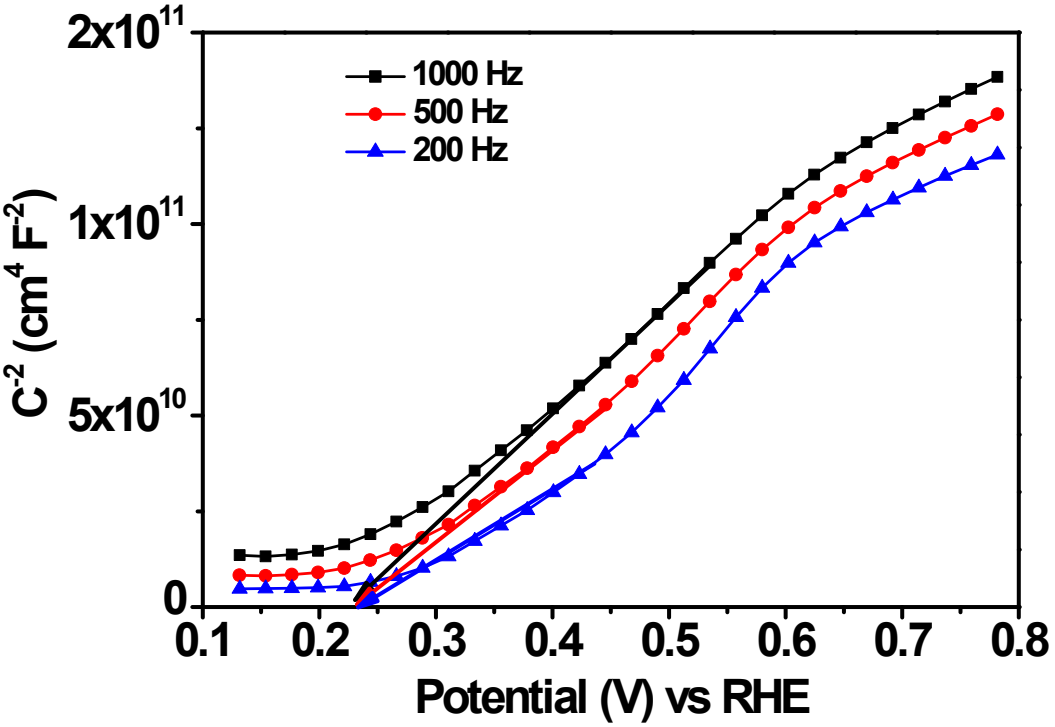


**Fig. S12.** Mott-Schottky plots of BiNP thin film on ITO in presence of 0.1 M $Na_2SO_4$ electrolytes (pH 4.9) using an ac frequencies of 200, 500, and 1000 Hz.

**Table S1.** Variation of atomic percentage of the constituent elements in the $Cu_2O$ thin films developed in presence of BiNP and $Bi^{3+}$ ions.

| Sample description | Elements | Atomic% |
|---|---|---|
| **ITO/BiNP$_{film}$/Cu$_2$O** | Cu | 64.34 |
| | O | 35.43 |
| | Bi | 0.23 |
| **ITO/BiNP$_{sus}$/Cu$_2$O** | Cu | 64.23 |
| | O | 35.56 |
| | Bi | 0.21 |
| **ITO/Bi$_{ion}$/Cu$_2$O** | Cu | 65.49 |
| | O | 34.30 |
| | Bi | 0.21 |
| **ITO/Cu$_2$O** | Cu | 57.19 |
| | O | 42.81 |
| **ITO/BiNP** | Bi | 100 |

**Table S2.** Variation of equivalent circuit (EC) parameters of the $Cu_2O$ thin films developed in presence of BiNP and $Bi^{3+}$ ions.

| Sample | $R_s$ (Ω) | $R_{ct}$ (Ω) | $C_{ct}$ (F) | Error |
|---|---|---|---|---|
| **ITO/BiNP$_{film}$/Cu$_2$O** | 73.28 | 30.61 | $2.4 \times 10^{-4}$ | $1.51 \times 10^{-9}$ |
| **ITO/BiNP$_{sus}$/Cu$_2$O** | 81.14 | 56.68 | $9.6 \times 10^{-5}$ | $1.60 \times 10^{-9}$ |
| **ITO/Bi$_{ion}$/Cu$_2$O** | 86.43 | 78.84 | $8.7 \times 10^{-5}$ | $1.52 \times 10^{-9}$ |
| **ITO/Cu$_2$O** | 91.73 | 128.7 | $2.3 \times 10^{-5}$ | $4.64 \times 10^{-9}$ |

**Table S.3.:** Comparison of photoelectrochemical reduction of water over $Cu_2O$ thin film on conducting glass substrates prepared under different deposition conditions, as available in literature to that with the as prepared $Cu_2O$, demonstrated in the present report.

| Sl. No | References | Substrates | $Cu_2O$ synthesized through | Electrolyte for characterization | Light intensity used | Maximum photocurrent density obtained for $H_2O \rightarrow H_2$ reaction |
|---|---|---|---|---|---|---|
| 01 | **Present work:** $Cu_2O$ film developed in presence of **(a) BiNP film (b) BiNP suspension (c) $Bi^{3+}$ ion** | ITO glass | Electrodeposition | 0.1 (M) $Na_2SO_4$ at pH ~ 4.9 | 35 mW $cm^{-2}$ | **a) -5.2 mA $cm^{-2}$ b) -4.9 mA $cm^{-2}$ c) -3.7 mA $cm^{-2}$** |
| 02 | J. Phys. Chem. C, 2012, 116, 7341−7350 | 100 nm Au and 10 nm Cr adhesion layer coated FTO glass | Electrodeposition | 1.0 (M) $Na_2SO_4$ at pH ~ 4.9 | 100 mW $cm^{-2}$ | -2.4 mA $cm^{-2}$ |
| 03 | J. Mater. Chem., 2012, 22, 2456–2464 | Cu coated ITO glass | Electrodeposition followed by anodization | 0.5(M) $Na_2SO_4$ at pH ~ 6.82 | 100 mW $cm^{-2}$ | -0.37 mA $cm^{-2}$ |
| 04 | Int. Journal of Hydrogen Energy, 2008, 33,2897 – 2903 | ITO glass | Electrodeposition | 0.5 (M) $Na_2SO_4$ | 50 mW $cm^{-2}$ | -0.025 mA $cm^{-2}$ |
| 05 | Electrochimica Acta, 2012, 62, 1– 7 | FTO glass | Electrodeposition | 0.1 (M) $Na_2SO_4$ | 100 mW $cm^{-2}$ | -0.06 mA $cm^{-2}$ |
| 06 | *ACS Appl. Mater. Interfaces,* 2015, 7, 18344−18352 | ITO Glass | Electrodeposition | 0.1 (M) $Na_2SO_4$ at pH ~ 4.9 | 35 mW $cm^{-2}$ | -2.6 mA $cm^{-2}$ |