Electronic Supplementary Information

Reduced graphene oxide modified $CuBi_2O_4$ as an efficient and noble metal free photocathode for superior photo electrochemical hydrogen production

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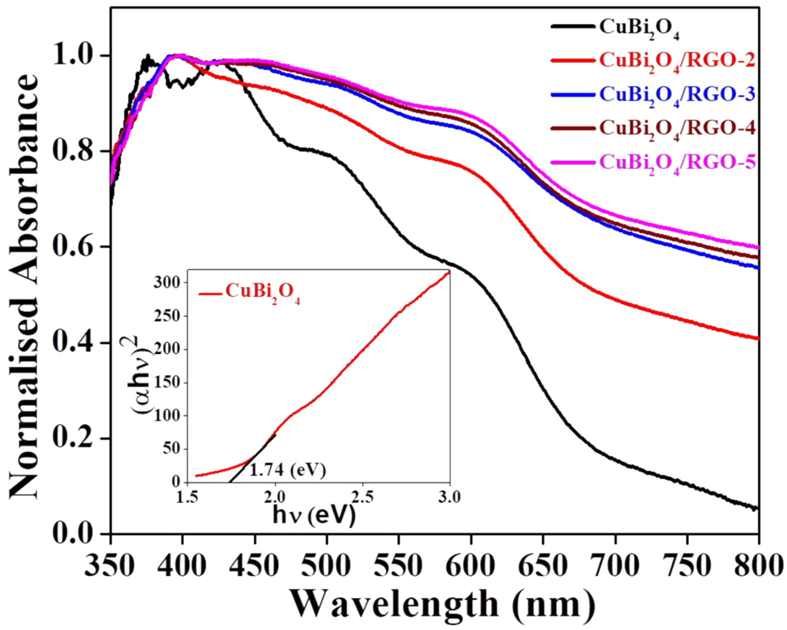

Figure S1. UV-Visible diffuse reflectance spectra of $CuBi_2O_4$ and $CuBi_2O_4$/RGO-X photocathodes and tauc plot in the inset shows estimated band gap of $CuBi_2O_4$.

Figure S1 Shows the UV-Visible spectra of $CuBi_2O_4$ and $CuBi_2O_4$/RGO-X (X=2-5) photocathode with different number of cycles of RGO deposited over $CuBi_2O_4$. It can be seen that the absorbance throughout the visible range gradually increases with the increase in the number of cycles of RGO and $CuBi_2O_4$/RGO-5 shows the highest absorbance in the visible region. The increase in the absorbance is attributed to the presence and increase in RGO concentration over the surface of $CuBi_2O_4$. The band gap of $CuBi_2O_4$ estimated by tauc plot is 1.74 (eV), which is in good agreement with the earlier reports.[S1, S2]

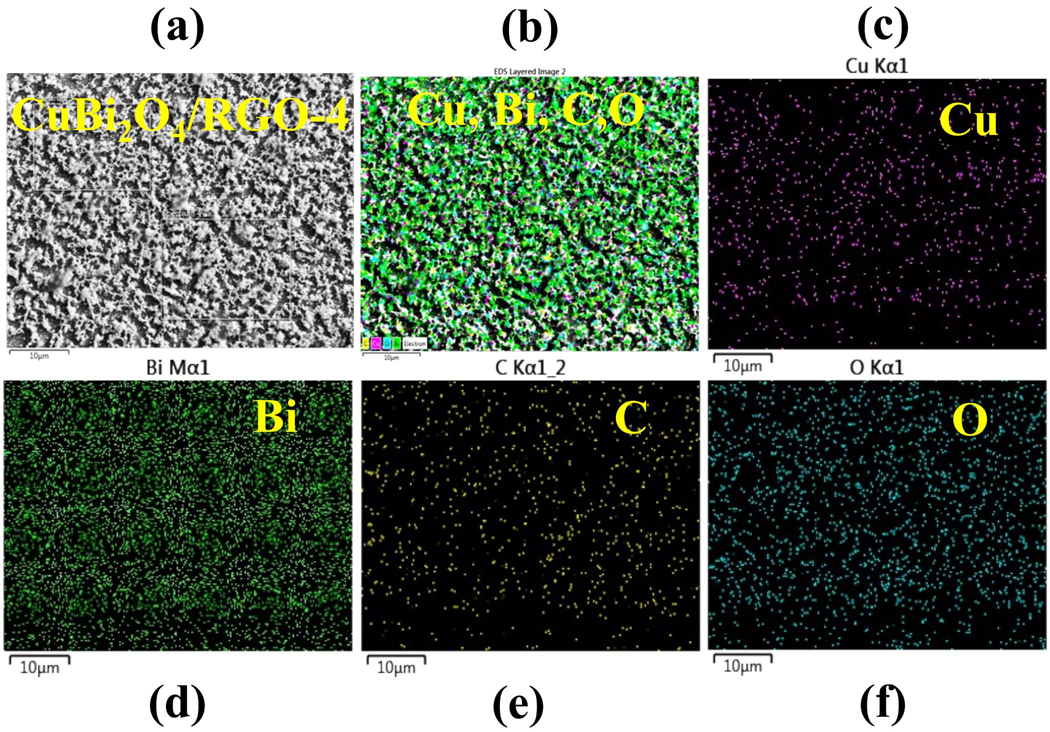

Figure S2. FESEM and corresponding Energy dispersive X-ray spectroscopic (EDX) image of $CuBi_2O_4$/RGO-4, (a, b), Elemental mapping shows uniform distribution of all the elements present in $CuBi_2O_4$/RGO-4 photocathode. (c), (d), (e), (f) Showing uniform distribution of Cu, Bi, C, and O respectively in $CuBi_2O_4$/RGO-4 photocathode.

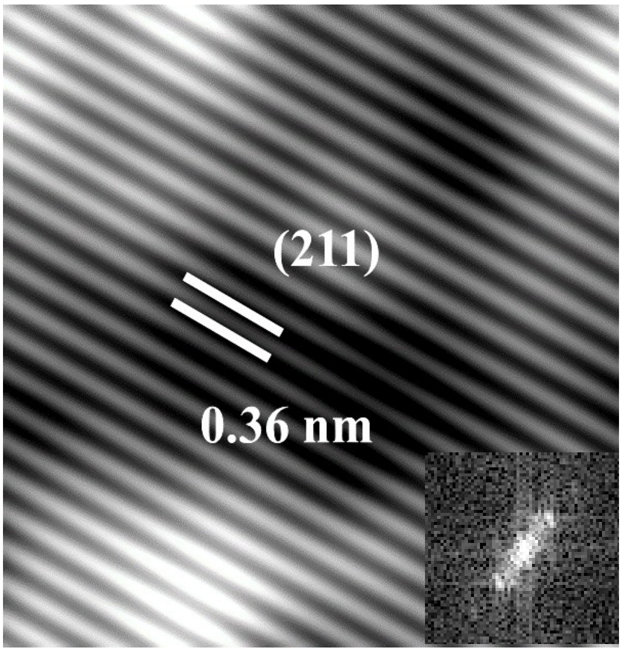

Figure S3. Inverse fast Fourier transformed (IFFT) image showing interplanar spacing of 0.36 nm corresponding to (211) lattice plane of $CuBi_2O_4$.[S3]

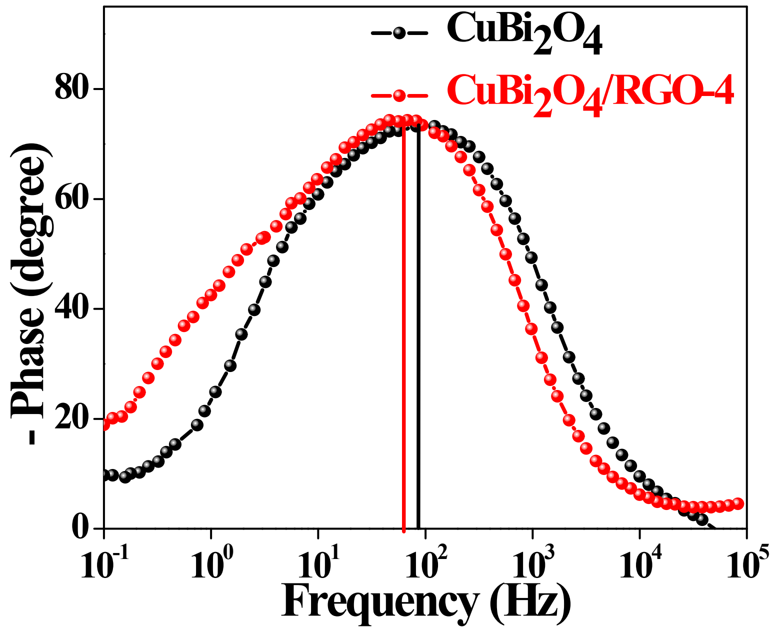

Figure S4. Bode phase plot of $CuBi_2O_4$ and $CuBi_2O_4$/RGO-4 showing enhanced life time of photo excited electrons in $CuBi_2O_4$/RGO-4 then bare $CuBi_2O_4$.

Figure S4. Shows Bode phase plot of $CuBi_2O_4$ and $CuBi_2O_4$/RGO-4 using which life time of photo excited electron can be calculated by using the formula [S4]

$$\tau_e = 1/(2\pi f_{max})$$

τ_e is the life time of photo excited electron, f_{max} is the maximum pick frequency. In figure S5 the f_{max} for $CuBi_2O_4$/RGO-4 and $CuBi_2O_4$ is 60.26 and 82.67 and life time of photo excited electrons were calculated to be 2.6 msec and 1.9 msec respectively. RGO acting as electron sink suppress electron hole recombination by rapidly accepting photoinduced electron from $CuBi_2O_4$ surface, improving electron life time.

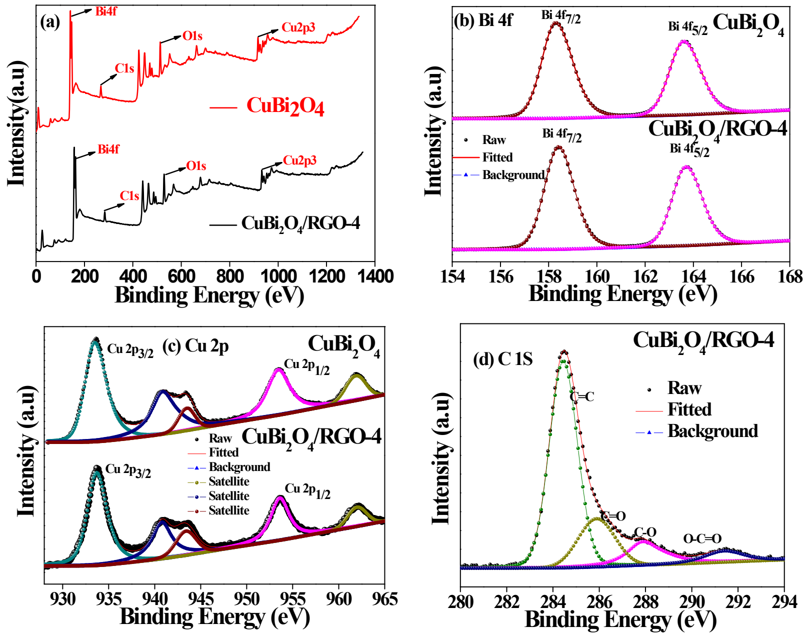

Figure S5. XPS (a) Survey spectra, core-level spectra of(b) Bi4f, (c) Cu2p, (d) C1s, showing presence of Bi^{3+} and Cu^{2+} in $CuBi_2O_4$ and $CuBi_2O_4$/RGO-4.

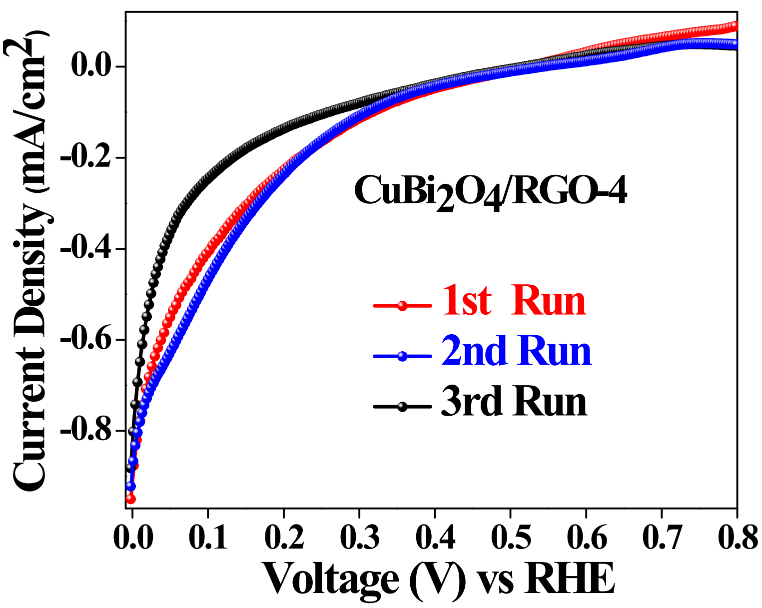

Figure S6. Reusability test for $CuBi_2O_4$/RGO-4.

To examine the reusability, we have chosen our best performing device namely, $CuBi_2O_4$/RGO-4, and three measurements of linear sweep voltammetry measurement of $CuBi_2O_4$/RGO-4 was carried out under 1 Sun illumination by sweeping potential from -0.6 to 0.2 V vs Ag/AgCl in neutral 0.5 M Na_2SO_4 (pH ~ 6.8) solution. After first linear sweep scan $CuBi_2O_4$/RGO-4 photocathode was washed with distilled water and dried, similar procedure was repeated with a fresh electrolyte. The experiment was repeated for consecutive three measurements. The photocurrent density of $CuBi_2O_4$/RGO-4 photocathode in the first two measurements remains constant within the error limits. In the third measurement, we have observed a slight change in the current characteristics, possible due to the washing and drying of the photocathode leading to some loss of the active material, as shown in Figure S6.

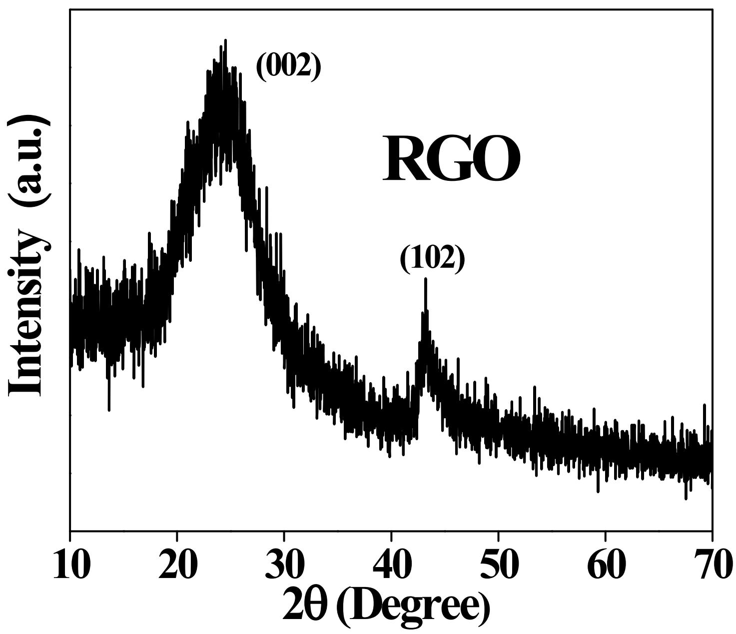

Figure S7. Powder X- ray diffraction (P-XRD) pattern of reduced graphene oxide (RGO).

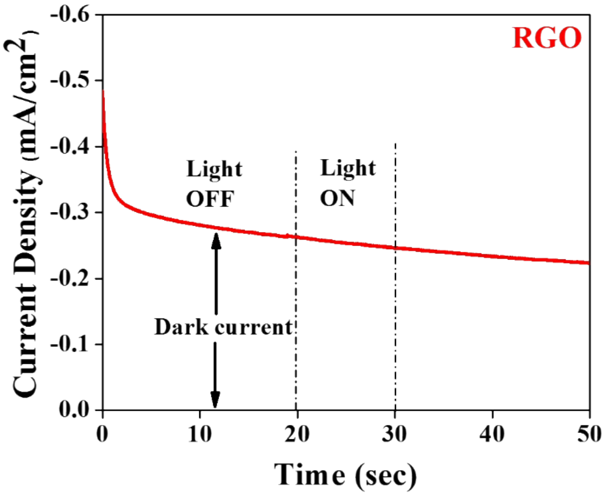

Figure S8. Chronoamperometry measurement of bare RGO on FTO at -0.6 V vs Ag/AgCl in neutral 0.5 M Na_2SO_4 (pH ~ 6.8) solution, showing electrochemical behaviour of RGO.

Table S1: A comparative study of various $CuBi_2O_4$ based Photocathodes.

Photocathode	**Photocurrent @ Potential (mA/cm²)**	**Preparation Technique**	**References**
$CuBi_2O_4$/Au/N,Cu–C	-0.5 @ 0.2 V RHE	Dropcasting	S5
$CuBi_2O_4/BiVO_4$	-0.5 @ -0.6V vs Ag/AgCl	electrodeposition	S6
$CuBi_2O_4$/Pt	-0.15@ 0V RHE	Drop-casting	S7
$CuO/CuBi_2O_4$ /Pt	-0.7 @ 0 V RHE	Drop-casting	S7
Au/ $CuBi_2O_4$	-0.5 @ 0.1V vs RHE	Cathodically electrochemical deposition	S4
Au/ $CuBi_2O_4$/Pt	-1.24 @ 0.1V vs RHE	Cathodically electrochemical deposition	S3
$CuBi_2O_4$/Pt	-0.8 @0.6 V RHE	Electrodeposition	S2
Ag- $CuBi_2O_4$/Pt	-1.0@0.6 V RHE	Electrodeposition	S2
$CuBi_2O_4$	-0.02 @ -0.25V vs	Hydrothermal	S8

	Ag/AgCl		
$CuBi_2O_4$/Pt	-0.5 @ 0.4 V RHE	Drop-casting	S9
$CuBi_2O_4$	-0.07@ 0.6V vs RHE	Electrochemical Synthesis	S10
$CuBi_2O_4$	-0.05 @ -0.4V vs Ag/AgCl	Spray-coating	S11
$CuBi_2O_4$/CuO	-0.28 @ -0.4V vs Ag/AgCl	Spray-coating	S11
$CuBi_2O_4$	-0.03 @ -0.4V vs Ag/AgCl	Electrodeposition	S12
$CuBi_2O_4$	-0.12@ -0.3V vs Ag/AgCl	Flux-mediated onepot solution process	S13
Textured $CuBi_2O_4$	-0.72 @ -0.6V vs Ag/AgCl	Dropcasting	S14
$CuBi_2O_4$	-0.48@ 0V RHE	Dropcasting	This work
$CuBi_2O_4$/RG0	-0.94@ 0V RHE	Dropcasting	This work

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