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Electronic Supplementary Information

Graphene oxide supported cobalt phosphide nanorods designed from a molecular complex for efficient hydrogen evolution at low overpotential

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S1 Experimental details

S1.1 Characterization techniques

Co_2P nanorods and GO-Co_2P composites were characterized by powder X-ray diffraction (PXRD) using a Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.5406 Å). TEM measurements were carried out on a JEOL model JEM- 2100 transmission electron microscope operated at 200 kV.Samplefor TEMwas prepared by dispersing it in ethanol by sonication for 5 min. A small drop of slurry was poured onto a carbon-coated copper grid (200 mesh) and dried in air. The X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo Scientific ESCALAB-MkII photoelectron spectrometer at a pressure of about 1×10^{-9} mbar at room temperature using pellet sample. Shirley background was corrected before the peak deconvolution.

S1.2 Chemicals and reagents

Trioctylphosphine (TOP), triphenyl phosphine, and $CoCl_2$were procured from Sigma-Aldrich (USA) whereas H_2SO_4, acetone and ethanol procured from CDH Chemicals India. They were used as received. Nafion (Sigma-Aldrich) was used for electrode preparation. Water (double-distilled) was used in all of the experiments

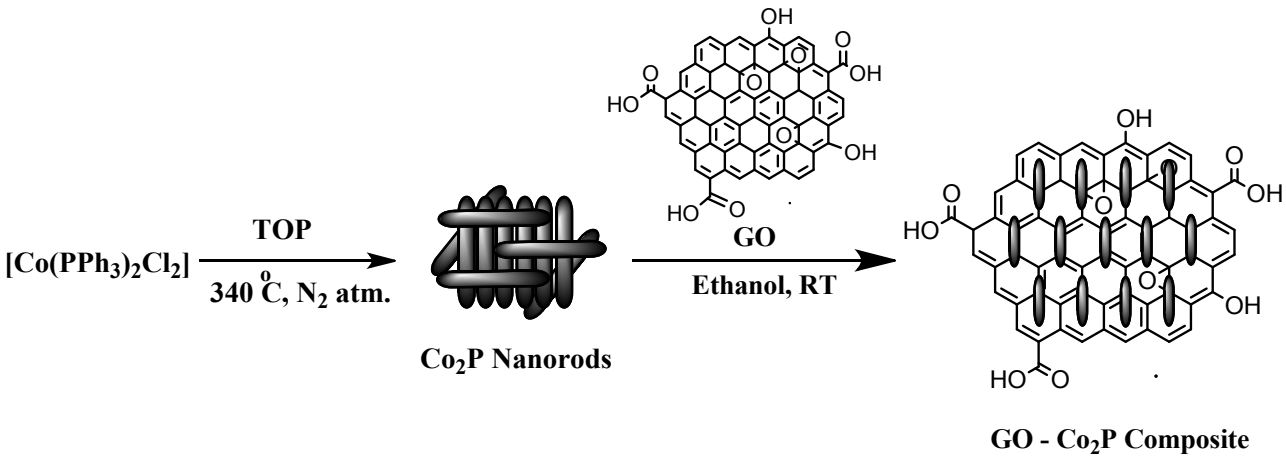
S1.3 Synthesis of cobalt phosphide (Co_2P)nano rods

A slurry containing 0.5 mmol of $[Co(PPh_3)_2Cl_2]$[13]complex in 4 mL of trioctylphosphine (TOP), prepared in a three necked flask (100 mL) was heated to 100 °C to remove water and oxygen. The resulting homogeneous blue solution was heated to 340 °C under N_2 and kept at the

same temperature for 120 min, affording a dark suspension. It was cooled to room temperature and resulting Co_2P nanorodswere washed by repeated centrifugation with an excess of acetoneand dried in *vacuo*.

S1.4 Synthesis of Co_2P nanorodsgrafted on graphene oxide (GO)

The GO (100 mg) was completely dispersed in 20 mL of de-ionized water by sonication. The 40 mg of Co_2Pnanorods dispersed in 20 mL of water by sonication were added to suspension of GO. The mixture was stirred for 24 h at room temperature. The particles were separated by centrifugation, washed with acetone (30 mL) and dried in *vacuo*. The composite so obtained was labeled as GO-Co_2P.



Scheme S1 Synthesis of GO-Co_2P Composite

S1.5 Electrochemical measurement

The electrochemical measurements were carried out using Autolab (PGSTAT302N) instrument with catalyst coated glassy carbon electrode (GCE), graphite rod and Ag/AgCl (saturated KCl) electrode as the working electrode, counter electrode and reference electrode

respectively. A mixture of ethanol (480 µL) and Nafion (20 µL) was used to disperse the catalyst (2 mg) for preparing the catalyst ink. In this way we used 5 wt% of Nafion solution to make the catalyst ink. A 10 µL drop of the ink was transferred to GCE (area = 0.03 cm^2) and allowed to dry for 5 min. In this way 1.33 $mg/cm^2$of catalyst was placed on electrode. All three electrodes were fixed in the cell consisting 0.5 M H_2SO_4 solution (electrolyte). Linear sweep voltammetry (LSV) data were recorded at a sweep rate of 5 mV/s. The same electrochemical setup was used to performed electrochemical impedance spectroscopic (EIS) studies at different applied potentials at an amplitude of 10 mV. All the potentials are reported with respect to the reversible hydrogen electrode (RHE).

S2 SEM–EDX Data

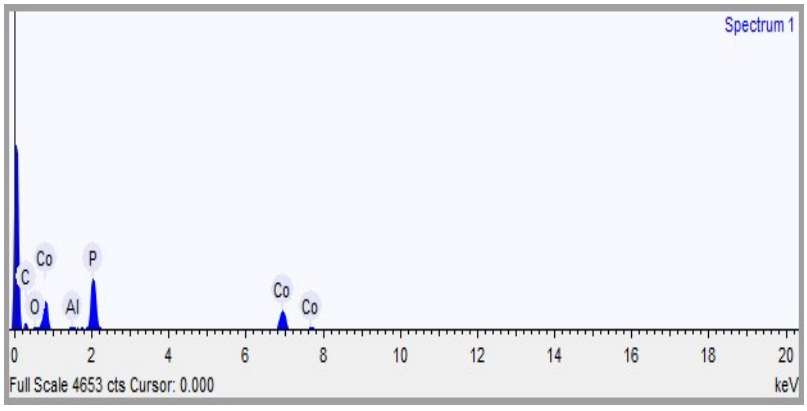


Fig. S1SEM-EDX of Co_2P nanorods

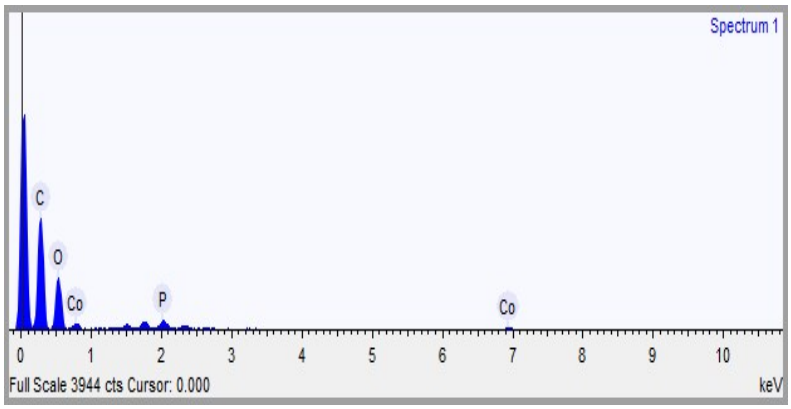


Fig. S2SEM-EDX of GO-Co_2P composite

S3 Raman spectrum of GO-Co_2P

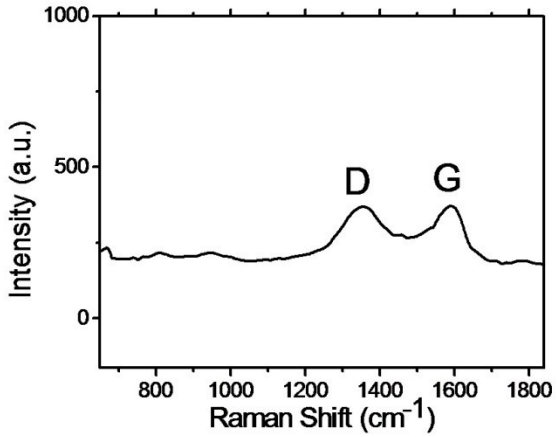


Fig. S3 Raman spectrum of Co_2P@GO

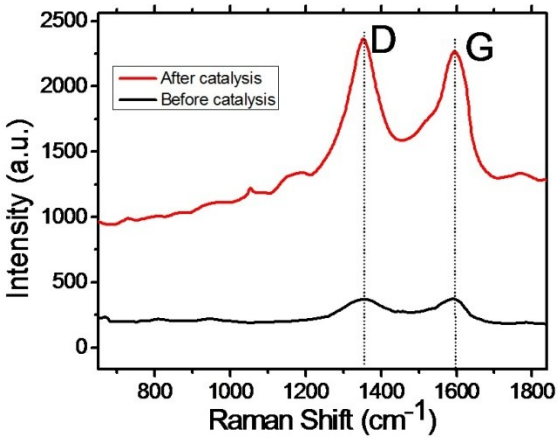


Fig. S4 Raman spectrum of GO-Co_2P before and after catalysis

S4. Supplementary figures of HER activity

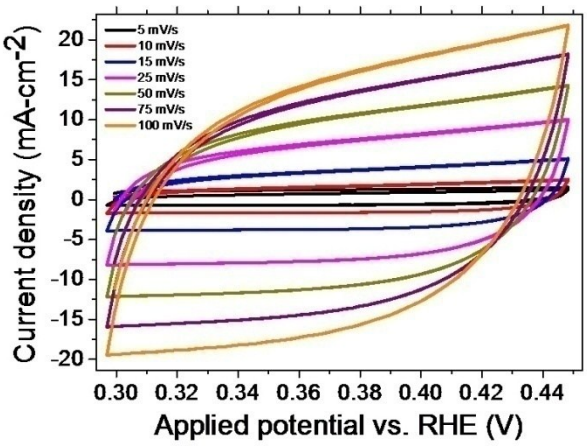


Fig. S5CV curves at various scan rates

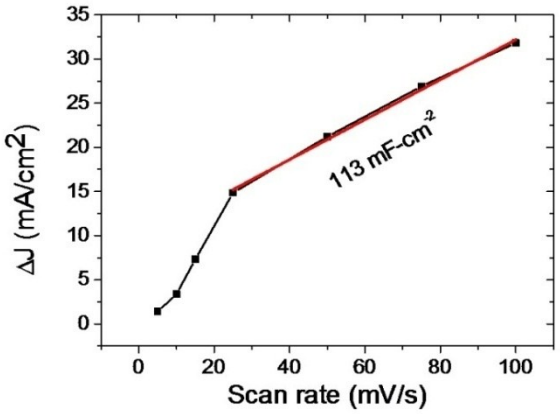


Fig. S6 Change in the current density ($\Delta J/mAcm^{-2}$) vs. scan rate to get the double layer capacitance

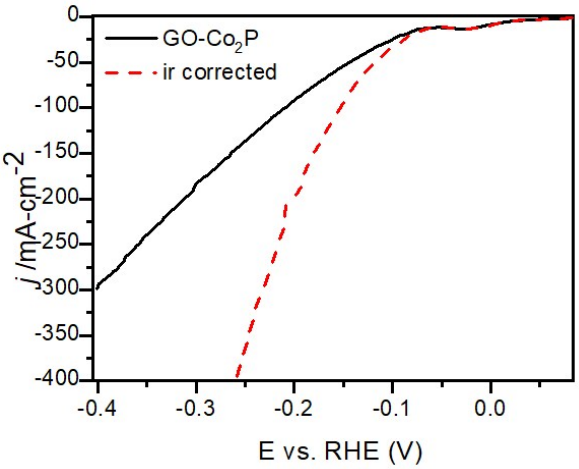


Fig. S7 Linear sweep voltammogram (LSV) at the scan rate of 5 mV/s of Go-Co_2P

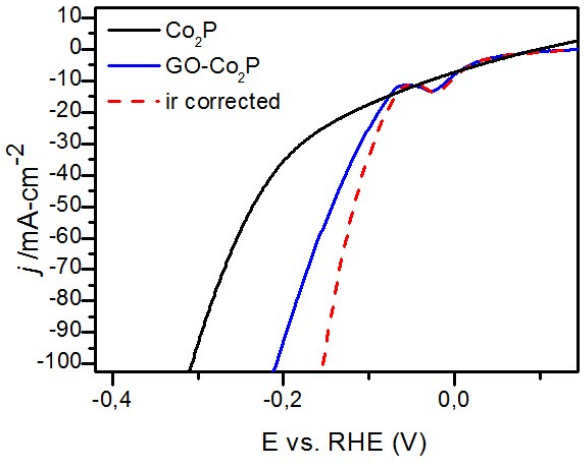


Fig. S8 Linear sweep voltammogram (LSV) at the scan rate of 5 mV/s of Go-Co_2P and Co_2P

Table S1Comparison of HER performance of some transition metal catalysts in 0.5 M H_2SO_4 solution

S. No.	Material	η_{20} (mV)	η_{100} (mV)	Tafel Slope (mV/dec)	Exchange current density (mA-cm^{-2})	Mass loading (mg/cm^2)	Reference
1	GO-Co_2P (This work)	62	137	83	3.48	1.33	-
2	MoPS	78	120			3	1
3	MoP		271	54	0.086	0.36	2

4	$CoSe_2$ NP@CP	150	181	40	0.049	2.8	3
5	Ni_2P@ Ti	130	180	46	3.3	1	4
6	CoP/NCNT	99		49	0.32	2	5
7	Co_2P/NCNT	171		62		2	5
8	CoP/CNT	198		68	0.13	2	5
9	Co_2P/CNT	219		74		2	5
10	CoP/Ti	95		50	.14	2	6
11	Co_2P/Ti (Hollow crystalline structure)	109		45		2	6
12	Co_2P/Ti	167		101		1	7
13	CoP–RGO	156 (η_{10})		70	0.057		8
14	CoP–CC	100	204	51	0.288	0.92	9
15	Ni–Co–S/FTO	280(η_{10})		93/70	0.74		10
16	Mo_3S_{13}/FTO	200 (η_{10})		37			11
18	MoB_2	230 ($\eta_{2.5}$)			100	0.3	12

S5 TOF (turn over frequency) calculation for electrocatalyst:

We calculated the TOF for the HER activity on GO-Co_2P as suggested by the reviewer. We added the TOF values in the main text. TOF values were calculated as mentioned earlier (*Energy Environ. Sci.,* 2015, 8, 3022-3029).

$$TOF = \frac{3.12 \times 10^{15}\left(\frac{H2}{\frac{s}{cm^2}}\right) \times |j| \times electrode\ area}{surface\ active\ sites \times surfcae\ area}$$

Our material is uniform Co_2P nanorods embedded on graphene surface. The main active materials is Co_2P. So, we calculated real surface area of the nanorods having diameter of 12 nm (2r) and length of 90 nm (h).

Area of the rod = $2\pi r^2 + h\ (2\pi r)$

= 0.3617×10^{-10} cm^2

Volume of the rod = $\pi r^2 h$

= 1.017×10^{-17} cm^3

Therefore, no. of rods in 1 cc volume = 0.9829×10^{17}

Now the density of Co2P is 7.74 g/cc.

The amount of the sample loaded on the electrode = 0.04×10^{-3} g (we consider whole amount is due to Co_2P as graphene oxide amount is very less.)

Therefore, no. of rods on the electrode = (0.9829 x 10^{17} x 0.04 x 10^{-3}) / 7.74

= 5 x 10^{11}

Effective Surface area = no. of rods on the electrode x area of one rod.

= 5 x 10^{11} x 0.3617 x 10^{-10} cm^2

= 18.085 cm^2

No. of surface active sites = 2.017 x 10^{15} atoms cm^{-2} as given in Energy Environ. Sci., 2015, 8, 3022—3029.

$$TOF(at\ 100\ mV) = \frac{3.12\ \times 10^{15}\left(\frac{\frac{H2}{s}}{cm^2}\right) \times\ 34.27 \times 0.1962\ cm^2}{2.017\ \times 10^{15}\frac{atoms}{cm^2} \times 18.085 cm^2}$$

Now,

= 0.57 H_2/s

Similarly, at 200 mV and 300 mV overpotentials, TOF values are 3.3 H_2/s and 9.69 H_2/s respectively. These values are quite high compared to the literature value (Energy Environ. Sci., 2015, 8, 3022--3029).

S5 References

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