$Bi_2Te_3@CoNiMo$ composite as a high performance bifunctional catalyst for the

hydrogen and oxygen evolution reactions

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Supplementary Figure S1. SEM images of Bi_2Te_3 nanosheets synthesized by adding different PVP concentrations (a) 3.13 uM, (b) 9.38 uM (c) 12.5 uM, (d) 18.75 uM and thicknesses of nanosheets for the four samples (e)

It can be seen from Fig. S1 that the surface morphology becomes more regular and thin with the increase of the PVP (W=40000) content. The above results indicate that the concentration of PVP plays an important role in determining the morphology and thickness. Distribution of the thickness of the as-formed Bi_2Te_3 nanosheets prepared with different PVP concentration is given in Fig. S2e. The result suggests that the thickness of Bi_2Te_3 nanosheets decreases from 23.4 to 8.51 nm with the PVP concentration rising. In the initial reaction stage, large amount of Bi_2Te_3 crystal nuclei are formed. Considering the special lattice structure of Bi_2Te_3 , it holds the layered-like rhombohedral structure where the c-axis is a Van der Waals force which is weak and

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fragile. When the nascent crystal nuclei start growing, the gravity between grains will increase. If the gravity increases to a certain value which exceeds Vander Waals force, the grains will break between Te1 atomic layers.^{S1,S2} During the reaction process, the PVP play an important role in the Bi_2Te_3 crystal assembling, which is apt to adsorb on the specific crystal plane of Bi_2Te_3 and assemble the tiny nascent crystal nuclei along the direction perpendicular to the c-axis, and then the nanosheets structure can be formed. With the content of PVP increasing, the number of PVP molecules absorbed around the tiny nascent crystal nuclei will increase, which prohibits the agglomeration of the crystals. As a consequence, the thickness of nanosheets will become thinner.



Supplementary Figure S2. EDS analyses of Bi₂Te₃ nanosheets modified by different Co content Fig. S2(a-d) shows the SEM images of different Co content modified Bi₂Te₃ nanosheets and their elements content tables. The Co contents in Fig. S1(a-d) are 3.47, 6.94, 34.7, and 69.4 mM, respectively. It can be seen that the size of the particles increases with the Co content.



Supplementary Figure S3. Raman spectra of modified Bi₂Te₃ nanosheets: (a) un-modified Bi₂Te₃,
(b) 3.47 mMCo-modified Bi₂Te₃, (c) 6.94 mMCo-modified Bi₂Te₃, (d) 34.7 mMCo-modified Bi₂Te₃, (e) 69.4 mMCo-modified Bi₂Te₃, (f) enlarged view of (e)

Fig. S3a shows the Raman of un-doped Bi_2Te_3 nanosheets, the peak position of 106 cm⁻¹ and 130 cm⁻¹ are assigned to Bi_2Te_3 nanosheets.^{S3} The mode above 320 and 745 cm⁻¹ from Fig. S3b to Fig. S3e are caused by MoO₃ and MoO₂, respectively. However, the peak intensity of the modes between 420 cm⁻¹ and 680 cm⁻¹ become higher with the increasing of Co content. Apparent variations are presented in the Raman spectra from 420 to 680 cm⁻¹ for the four samples with different Co content. For the sample of 3.47 mM Co-doped Bi2Te3, only one peak of around 580 cm⁻¹ can be observed in the figure S3b. When the Co content increases to 6.94 and 34.7 mM, the peak of 580 cm⁻¹ disappears. Another peak located at around 650 cm⁻¹ become more obvious with the Co concentration increasing. Further increasing the Co content to 69.4 mM, the Raman spectra has dramatically changed. Three peaks were obtained by peak fitting method in the scale of 420 to 680 cm⁻¹ (Fig. S3f). The first mode about 510 cm⁻¹ corresponds to CoO, the second mode about 580 cm⁻¹ closes to Co_2O_3 and the last mode about 650 cm⁻¹ relates to Co_3O_4 . All the changes indicate that the different Co oxides species can be formed at different Co content. At lower content, Co_2O_3 can be detected, major of which is transformed to Co_3O_4 by increasing Co content at the moderate concentration. Except for Co₂O₃ and Co₃O₄, CoO can also be obtained by adding to a higher Co content (69.4 mM).



Supplementary Figure S4. LSV curves of samples on Ni foam in 0.9 M KOH solution, scan rate $= 10 \text{ mV s}^{-1}$.

We also calculated the TON to measure the HER activity.

$$TON = \frac{H_2 \text{ (mol)}}{\text{catalyst (mol)}} = \frac{\frac{Q}{2 \times F}}{M}$$

Where Q is the electric quantities (C) at shaded area (see in Fig. S4), M (mol) is the number of moles of sample deposited onto the Ni foam, F is the Faraday constant (96500 C mol⁻¹)

The TON values of the Bi₂Te₃@CoNiMo-Ni foam and the Pt/C-Ni foam at shaded area is about 0.0068 and 0.0045, respectively. It can be seen that TON value of Bi₂Te₃@CoNiMo-Ni foam is slightly higher than that of Pt/C-Ni foam. Therefore, Bi₂Te₃@CoNiMo-Ni foam has favorable HER performance.

	R_s/Ω	R_f/Ω	C _f /mF	R_{ct}/Ω	C _{dl} /mF
Bi ₂ Te ₃ @Co _{3.47} NiMo	1.849	2.634	2.541	6.438M	321.9
Bi ₂ Te ₃ @Co _{6.94} NiMo	1.822	1.431	1.701	2.131M	116.6
Bi2Te3@Co34.7NiMo	1.732	0.766	2.121	1.124K	12.49
Bi ₂ Te ₃ @Co _{69.4} NiMo	1.874	0.386	0.2037	465.3	16.08

Supplementary Table S1

Supplementary Table S	52		
Catalysts	Current density j	Overpotential (vs. RHE)	Reference
Co ₃ O ₄ /N-rmGO	10 mA cm^{-2}	0.31 V	S2
CoO _x @CN	10 mA cm^{-2}	0.26 V	S 3
Ni ₃ S ₂ /Ni	10 mA cm^{-2}	0.187 V	30
NG-NiCo	~	onsetpotential (0.35 V)	31
N-CG-CoO	10 mA cm^{-2}	0.34 V	32
Ni-doped Co ₃ O ₄	10 mA cm^{-2}	~0.54 V	33
Bi ₂ Te ₃ @CoNiMo	10 mA cm^{-2}	0.08 V	this work



Supplementary Figure S5. Experimental configurations of the two-electrode water splitting measurement used for both the HER and OER driven by solar energy

The type of solar cells is Polycrystalline Silicon Solar Plates and we connect two panels together by using welding technique. The output voltage of the assembled solar cell is about 2.2 V.



Supplementary Figure S6. Crystal structure of Bi_2Te_3 ^{S4}



Supplementary Figure S7. Wetting ability test of (a) un-modified Bi_2Te_3 nanosheets (b) 69.4 mM Co-modified Bi_2Te_3 nanosheets, (c) the contact angles of these two samples

Fig. S7c shows the contact angle of un-modified Bi_2Te_3 nanosheets is about 69° and that of 69.4 mM Co-modified Bi_2Te_3 nanosheets is about 47.6°. From the whole images of Fig. S7(a-c), we can draw a conclusion that doped Bi_2Te_3 nanosheets are much more hydrophilous.



Supplementary Figure S8. UV-vis absorption spectra of un-modified Bi₂Te₃ nanosheets and 69.4 mM Co-modified Bi₂Te₃ nanosheets

The UV-vis absorption spectra of Bi_2Te_3 and CoNiMo nanoparticle-loaded Bi_2Te_3 are given in Fig. S8. Their band gap absorption edges were around 300 and 350 nm, and that of the CoNiMo nanoparticle-loaded Bi_2Te_3 had shifted into the visible spectrum. Besides, the band gap of the samples could be confirmed by the formula $\alpha hv = A(hv - Eg)n/2$ (inset in Fig. S8), where α , h, v, A, Eg and n are the absorption coefficient, Planck constant, incident light frequency, a constant, band gap and an integer, respectively.^{S4} It is found that CoNiMo nanoparticles loaded Bi₂Te₃ reduced the band gap energy. It is reported the band gap of bulk Bi₂Te₃ is smaller than 0.34 eV.^{S5} while the band gap of ultra-small Bi₂Te₃ nanosheets increase to 2.14 eV due to the size effects. Highly dispersed CoNiMo nanoparticle in the Bi₂Te₃ matrix may lead to fast electron transfer in electro-induced water splitting reactions.



Supplementary Figure S9. Chronoamperometric response at a constant potential of 2 V. As shown in Fig. S9, a series of current density-time curves is detected. The overall decrease of the current at the beginning is caused by rapid bubbles formation on the surface.





Fig. S10 show typical FT-IR spectra of the electrolyte solution. The blue line is detected before electrochemical reaction, and the red line is detected under OER in the same electrolyte solution. A series of the absorption peaks in the Fig. S10a and Fig. S10b corresponds to vaporous water attached on the surface of electrodes. These typical peaks become more intense under OER due to the fluctuation of generated oxygen on the interface between electrolyte and catalysts.



Supplementary Figure S11. LSV curves of Pt net in 0.5 M H_2SO_4 and 1.0 M KOH solution, scan rate = 10 mV s⁻¹.

We used Ag/AgCl in 4 M KCl solution (Ag/AgCl) as the reference electrode in all measurements. It was calibrated with respect to reversible hydrogen electrode (RHE). The calibration was performed in the high purity hydrogen saturated electrolyte with a Pt net as the working electrode. LSVs were run at a scan rate of 10 mV s⁻¹, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the electrode reactions (see in Fig. S11).^{S6}

So, in our manuscript, the current density was normalized to the geometrical surface area and the measured potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation:

 $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.205$

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