

Supporting Information for  
Construction of 2D-composite  $\text{HCa}_2\text{Nb}_3\text{O}_{10}/\text{CaNb}_2\text{O}_6$  Heterostructured Photocatalysts with  
Enhanced Hydrogen Production Performance  
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Fig. S1 shows the XRD patterns of samples with different ratio of potassium and calcium, with the increasing of molar ratio, the diffraction peaks intensity of CNO weakens but which of the HCNO increases to the contrary for crystallinity rises and the peaks of CNO disappears as the molar ratio of potassium and calcium is 0.6 that means pure HCNO was obtained at this condition.

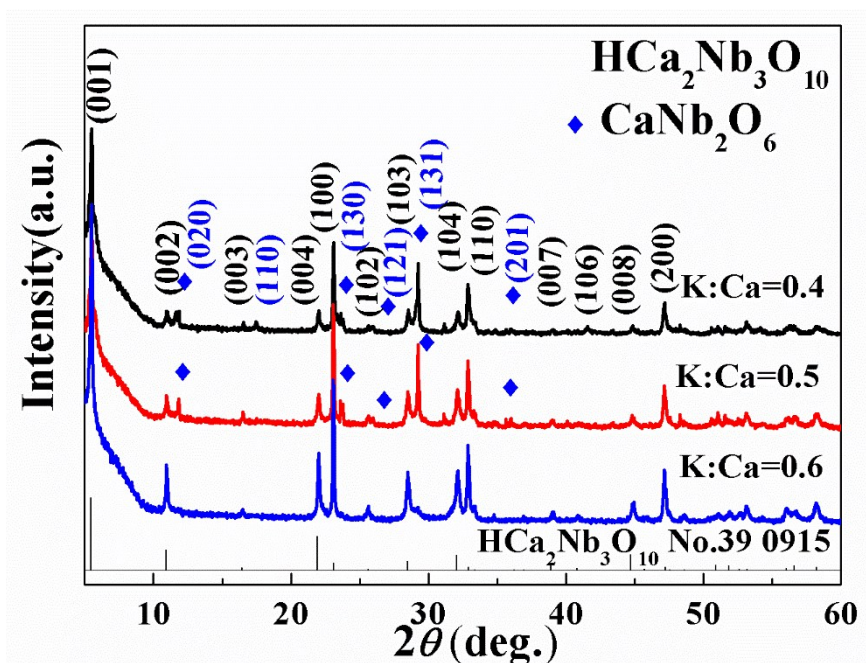


Fig. S1 XRD patterns of samples with different molar ratio of reactants

In order to identify the morphology of the samples, the SEM micrographs of samples with different molar ratio of reactants at the same magnification are shown in Fig. S2. All samples are in the same morphology of layered nanoplates and no significant change occurred as the molar ratio increasing.

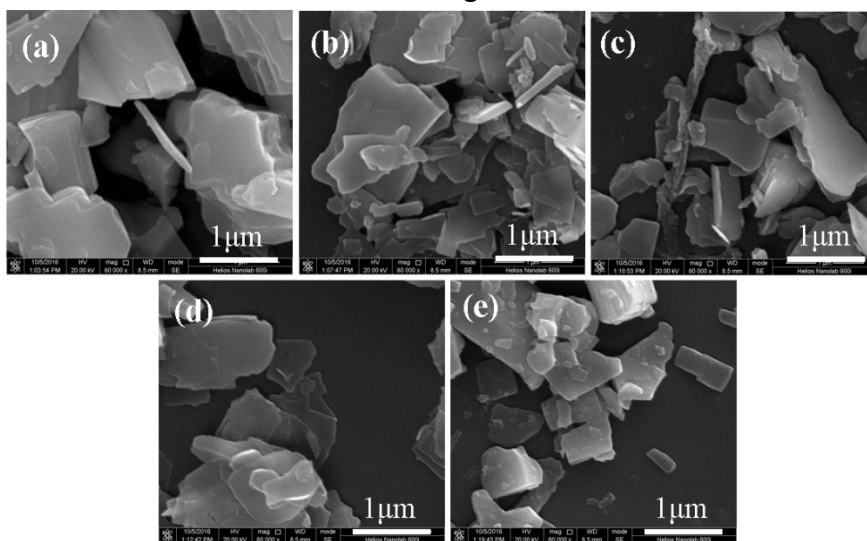


Fig. S2 SEM images of samples with different molar ratio of reactants.

a) 0.6; b) 0.55; c) 0.5; d) 0.45; e) 0.4

The rate of the sample 0.6 molar ratio of K/Ca (pure HCNO) is  $0.53 \text{ mmol h}^{-1}$ , while the sample with K/Ca molar ratio of 0.5 (HCNO/CNO) is about 2 times increased than HCNO up to  $1.5 \text{ mmol h}^{-1}$ . However, when the molar ratio of K/Ca is higher than 0.5, the photocatalytic activity decrease. A gradient trend of the photocatalytic activity can be found when the complex quantity of CNO is less or more than the optimal amount. There are two possible reasons taking into account for this. On the one hand, as the formation of heterostructure of HCNO/CNO, the rapid separation of the photogenerated holes and electrons is promoted resulting in the enhancement of the photo-catalytic efficiency. On the other hand, the surface active centers may be destroyed by the extra CNO covering on the surface of HCNO photocatalysts and excessive CNO may shield HCNO from the incident light which are bad for hydrogen production.

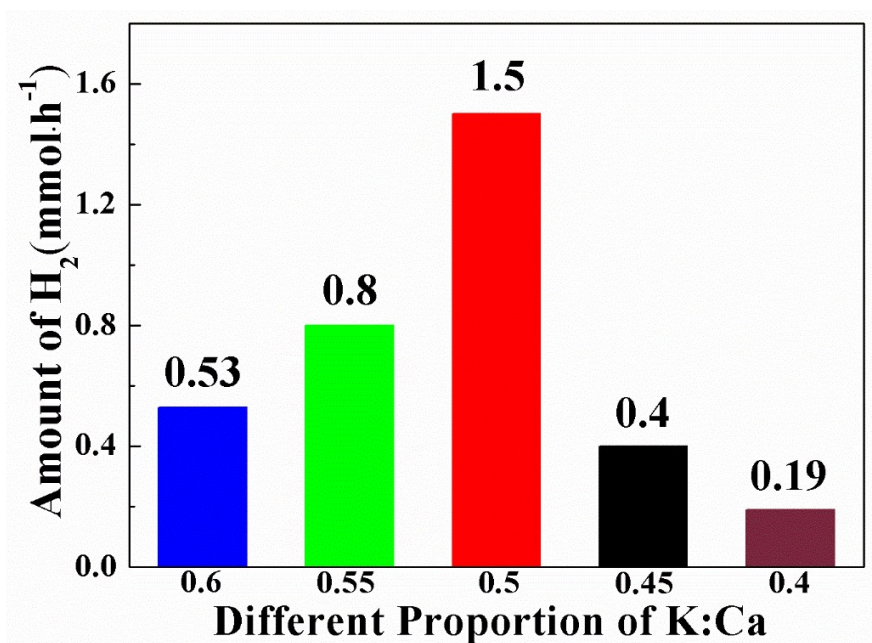


Fig. S3 The photocatalytic activity of samples with different molar ratio of reactants.

It can be confirmed that all the optical absorption edges of samples are about 370 nm but the intensity of composite samples enhanced slightly.

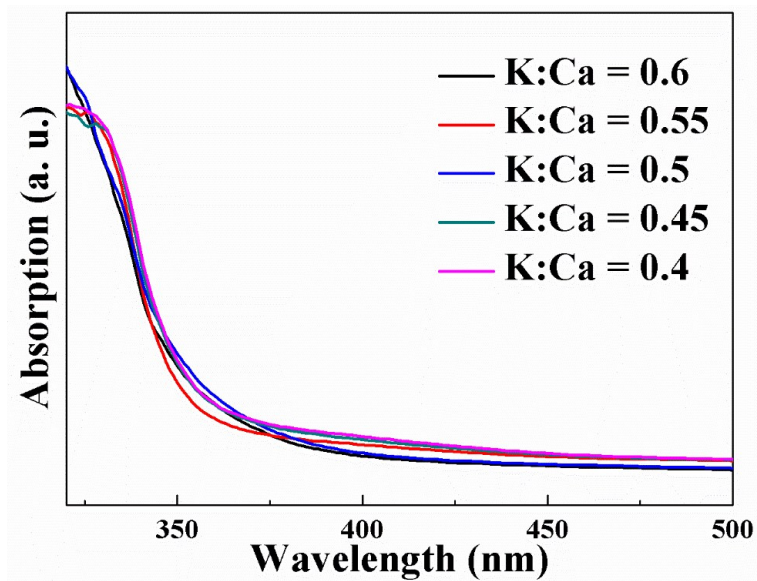


Fig. S4 The UV-vis spectra of samples with different molar ratio of reactants.

The longer lifetimes of photoinduced charge carriers was further examined by time-resolved fluorescence decay spectra in Fig. S5. Compared with HCNO, HCNO/CNO shows slow the decay kinetic characteristic with the help of 2D-composite heterostructure.

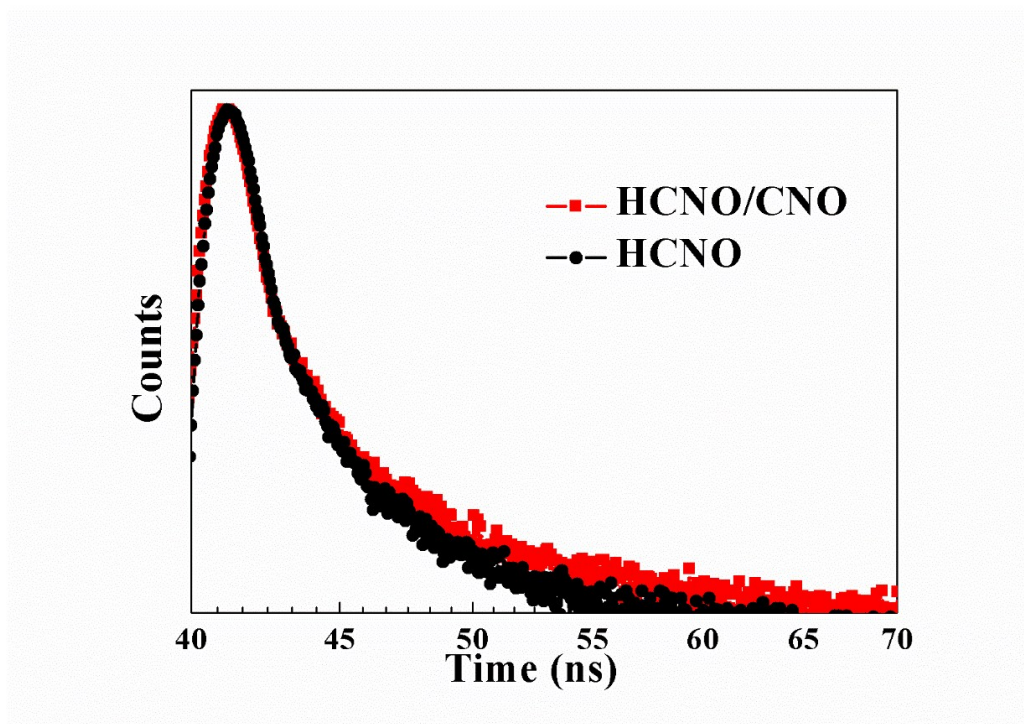


Fig. S5 Time-resolved fluorescence decay spectra of pure HCNO and HCNO/CNO.

Fig. S6 shows the electrochemical impedance spectra (EIS) of HCNO/CNO and CNO, the HCNO/CNO shows the smallest arc radii due to efficient charge separation and high interfacial electron conductivity profiting from the 2D-composite heterostructure.

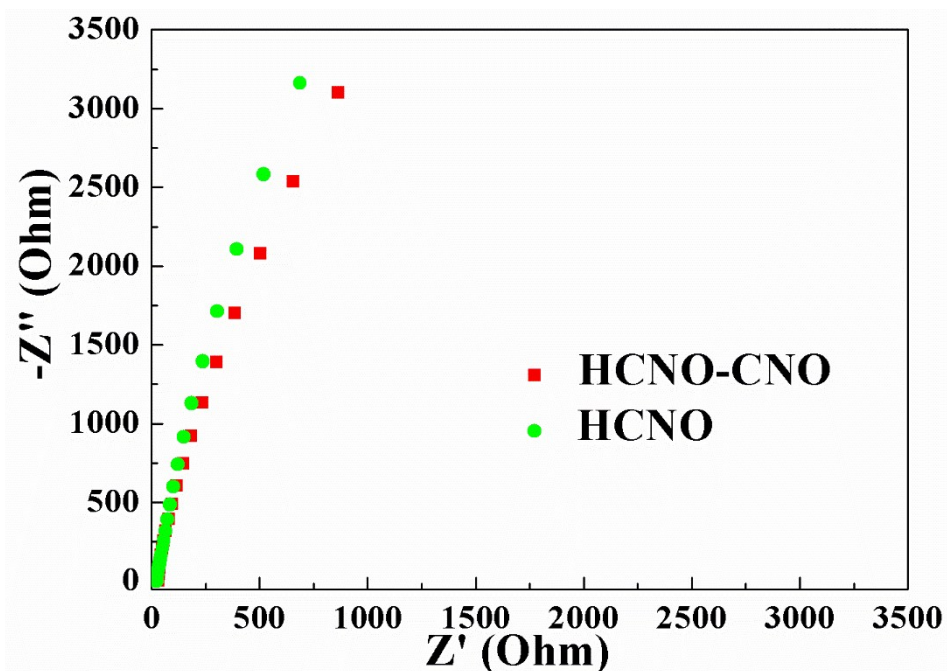


Fig. S6 EIS of HCNO/CNO and CNO.

As displayed in Figure S7, the atomic force microscopy (AFM) images and the corresponding height profiles show that the sample has an average thickness of 15-20 nm.

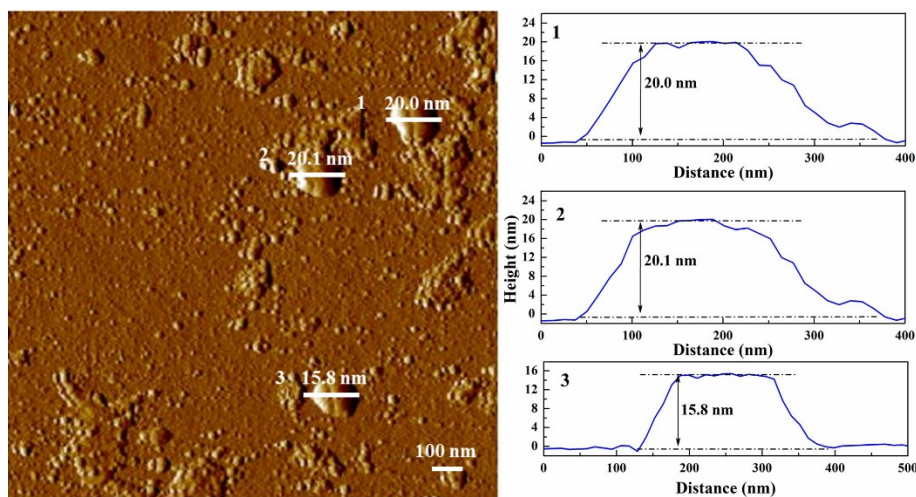


Fig. S7 Atomic force microscope (AFM) image and corresponding height profiles.

As shown in Fig. S8, hydrogen production of HCNO/CNO remains around  $1.45 \text{ mmol h}^{-1}$ . After 3 times circulation for 12 hours, the rate of nanosheets have no obvious decreasing tendency exhibiting a better stability.

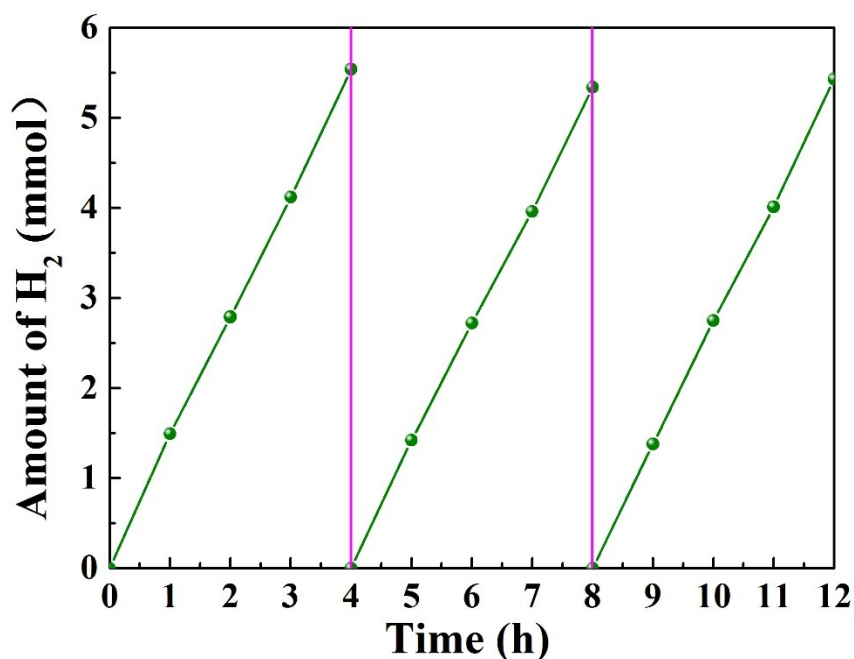


Fig. S8 Cycle performance of HCNO/CNO nanosheets for 12 hours

The apparent quantum yields (AQE) of the HCNO/CNO photocatalyst for H<sub>2</sub> evolution was measured under the illumination of monochromatic lights. The measured AQE for HCNO/CNO nanosheets at 350 nm is 14.3%, respectively, which is much larger than that measured for HCNO under the same conditions. This result suggests that HCNO/CNO has a much greater H<sub>2</sub> evolution capacity than HCNO.

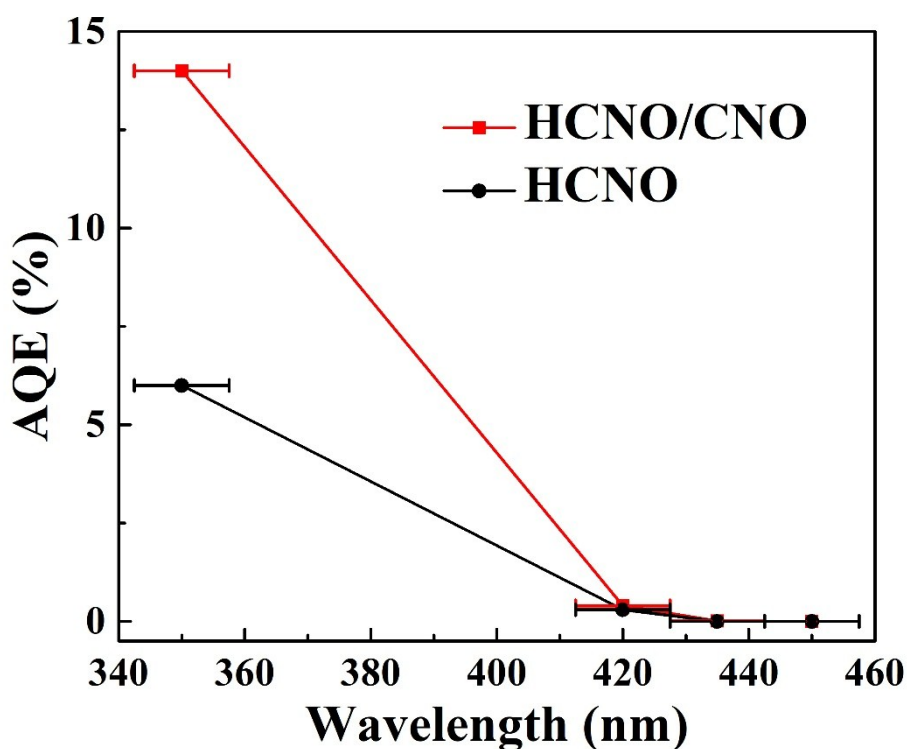


Fig. S9 The apparent quantum yields (AQE) of HCNO/CNO under monochromatic lights irradiation.