Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

1. Supplementary methods

- **Supplementary method 1, The detailed process for preparing BCN nanosheets**

- Mixing and drying

  Boric acid (1g), urea (4g), alkaline earth metal compound (1.3 mmol) and a certain amount of glucose are mixed in aqueous solution. It is important to use water soluble alkaline earth metal compounds for homogenous mixing and the metal nitrates were used. And then this true solution is dried at 70 ℃ under stirring in oil bath to form a white solid. At this time, the drying temperature should be below 80 ℃ to inhibit the hydrolysis of urea.

$$NH_2CONH_2 + H_2O \leftrightarrow 2NH_3 + CO_2 \qquad (1)$$

- Drying and grinding

  The dried samples were again dried at 200 ℃ for 1 hour to form dehydrated condensate and then grinded fully in agate mortar.

  The dehydrated condensate is a mixture of ammonium polyborate and partly-dehydrated glucose.

$$aNH_2CONH_2 + 4H_3BO_3 = (NH_4)_{a/2}B_4O_7 + CO_2 + 4H_2O \qquad (2)$$

$$C_6H_{12}O_6 = C_6(H_2O)_{6-b} + bH_2O \qquad (3)$$

  Here it is important to take an appropriate drying time for avoiding phase separation of carbon due to excess dehydration of glucose.

- Annealing

  Then the samples are put in horizontal tubular furnace and, before heating up the system was degassed by vacuum pump and backfilled with pure N_2 gas. The temperature is increased with a rate of 2~4 °C/min.

  At > 500 ℃, the added nitrates are composed to form the metal oxide, which reacts with boron oxide to form metal borate. (Me=alkaline earth metals)

In heating process, raw materials were dehydrated and condensed to form complex compounds with different bonds

$$2H_3BO_3 = B_2O_3 + 3H_2O \quad (4)$$

$$2Me(NO_3)_2 = 2MeO + 4NO_2 + O_2 \quad (5)$$

Samples were then annealed at 1,000 ℃ for 4 hours under N_2 flow of 100 ml/min.

$$MeO + 2B_2O_3 = MeB_4O_7 \quad (6)$$

$$(NH_4)_{x/2}B_4O_7 + C_6(H_2O)_{6-y} \rightarrow B_xC_yN_zO + NH_3 + CO_2 \quad (7)$$

Here, the metal borates promote the formation of BCN nanosheets by improving solubility of B, C and N in melt phase. Also, the borates increase the rate of BCN formation by easing the access of N_2 into the reaction mixture.

- Washing

  After annealing, samples are cooled to room temperature and then treated with 10% HCl solution at 80 ℃ and washed in water and ethanol.

$$MeB_4O_7 + 2HCl + 5H_2O = MeCl_2 + 4H_3BO_3 \quad (8)$$

- Exfoliation and drying

  Samples are exfoliated by ultrasonic and then dried at 100℃ overnight.

- **Supplementary method 2. Preparation of Ni-Co LDHs/BCN as a cocatalyst for water oxidation.**

$Co(NO)_2 \cdot 6H_2O$ (0.2 g), $Ni(NO_3)_2 \cdot 6H_2O$ (0.1 g) and NH_4NO_3 (0.04 g) were dissolved in H_2O (3.5 ml) and 30 wt. % ammonia (1.5 ml) to form clear solution, named as Ni-Co LDHs. 200 mg BCN powder was dispersed in water (20 ml), which was then subject to ultrasonic treatment for 10 min to promote the dispersion of BCN in the solution. A certain amount of the Ni-Co LDHs solution (400 μl) was added to the mixture. After stirring for 3 h, the mixture was washed by filtering with distilled water and dried at 343 K to obtain Ni-Co LDHs/BCN.

- **Supplementary method 3. Photocatalytic redox of water.**

Reactions were experimented with a Pyrex top irradiation reactor connected to a glass closed gas-circulation system. Photoreduction to H_2 and photooxidation to O_2 were performed separately in aqueous solutions containing triethanolamine or silver nitrate as sacrificial reagents, respectively. To study the H_2 production ability, 50 mg catalyst was dispersed into 100 ml aqueous containing triethanolamine solution (10 vol.%). In the case of deposition of Pt, an appropriate amount of H_2PtCl_6 aqueous was added to the reactant solution before irradiation. Water photooxidation was carried out by dispersing the catalyst (50 mg) in 100 ml aqueous solution containing silver nitrate (0.01 M) as the electron acceptor and La_2O_3 (0.2 g) as the pH buffer agent (pH 8~9). The reactant solution was evacuated several times to remove air completely before irradiation under a 300W xenon lamp with an appropriate cutoff filter. The temperature of the solution was maintained at 12 ℃ by a flow of cooling water during the reaction. The evolved gases were analysed by a GC-7900 gas chromatograph with the thermal conductive detector, a 5Å molecular sieve column and using argon as the carrier gas.

For quantitative analysis, before reaction, we injected several times pure hydrogen or oxygen with different amounts (1, 2, 5, 10, 20 ml) to system at -100 kPa and analysed by GC-7900 gas chromatograph.

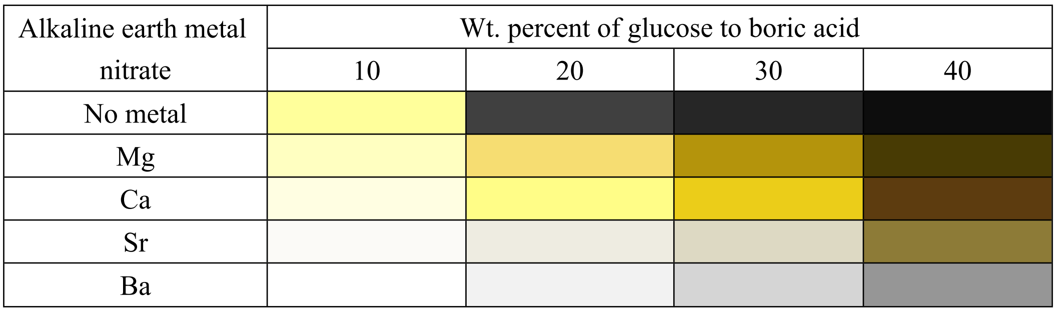
From the relation between the injected gas amounts and areas by GC, we obtained the mean value of area per unit gas volume (1 ml). By this value, we could calculate the amount of the evolved gas from the reaction system.

- **Supplementary method 4. Photocatalytic reduction of CO_2.**

The test was conducted at atmospheric pressure of CO_2 in a two neck flask (50 ml) at 30 ℃ as controlled by water with a constant temperature. The photocatalytic CO_2 reduction reaction was carried out by dispersing 50 mg catalyst in a solution containing solvent of 2ml H_2O and 4ml acetonitrile, 1ml triethanolamine, 1 μmol $CoCl_2$, 20mg 2, 2-bipyridine. This mixture system was subjected to vacuum degassing and backfilling with pure CO_2 gas (1 bar). Then the reaction flask was performed under an irradiation of 300 W xenon lamp with 420nm cutoff filter. The produced gases (CO and H2) were detecte d using a gas chromatography equipped with a packed molecular sieve column (TDX-01). Argon was used as the carrier gas.

2. Supplementary tables

- **Supplementary table 1.** Changes in colors of xGlu-Me samples after annealed at 1,000 ℃



Alkaline earth metal nitrate	Wt. percent of glucose to boric acid			
	10	20	30	40
No metal	🟨	⬛	⬛	⬛
Mg	🟨	🟨	🟨	🟫
Ca	⬜	🟨	🟨	🟫
Sr	⬜	⬜	⬜	🟫
Ba	⬜	⬜	⬜	▨

- **Supplementary table 2.** H_2 production rate according to the amount of 30Glu-Ca sample

The weight of catalyst, mg	0	50	100	150	200
HER, μmol·h^{-1}	0	8.30	13.26	14.68	14.91

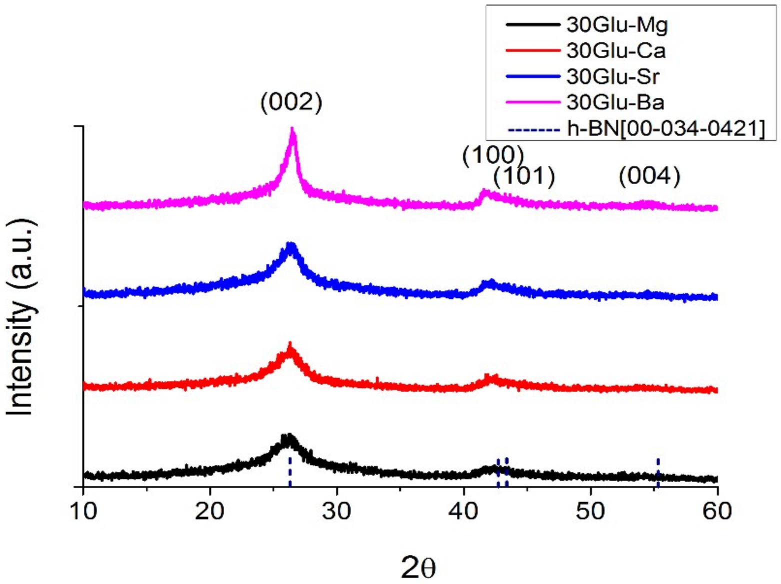
- **Supplementary table 3.** The specific surface area and HER of xGlu-Ca samples

Sample	20Glu-Ca	30Glu-Ca	40Glu-Ca
BET surface area, m2/g	358.10	383.07	403.81
HER, μmol·h^{-1}	6.06	15.35	9.38

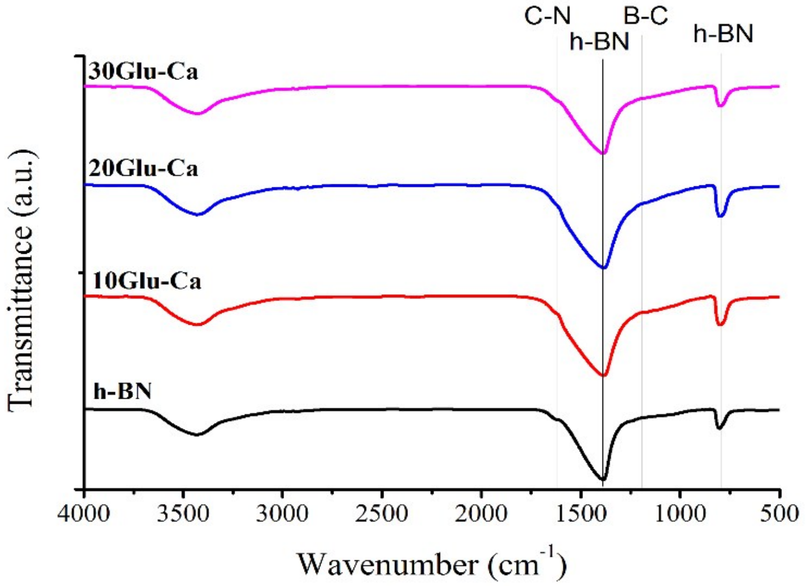
- **Supplementary table 4.** Band gap energies of xGlu-Me samples

x	**xGlu-Mg**	**xGlu-Ca**	**xGlu-Sr**	**xGlu-Ba**
20	2.70	2.85	2.75	2.83
30	2.40	2.53	2.56	2.67
40	1.89	1.91	2.08	2.22

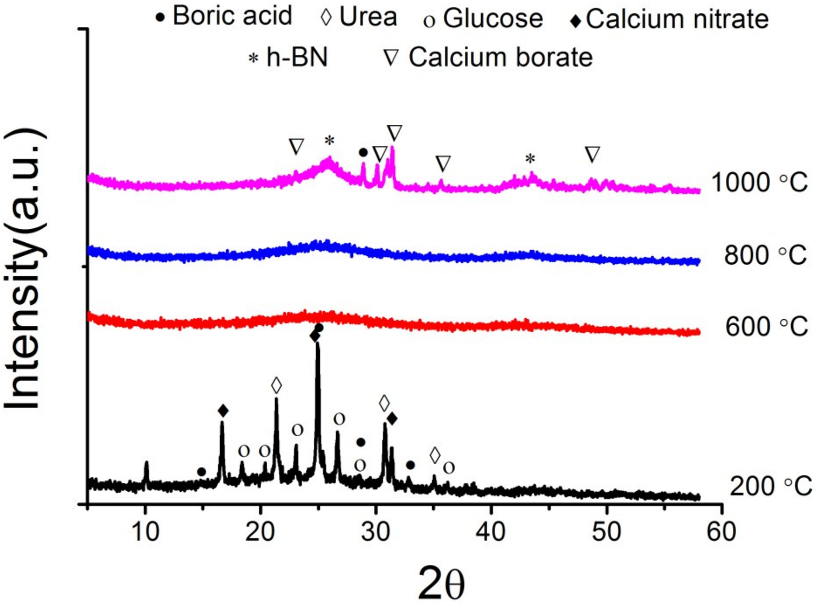
3. Supplementary Figures



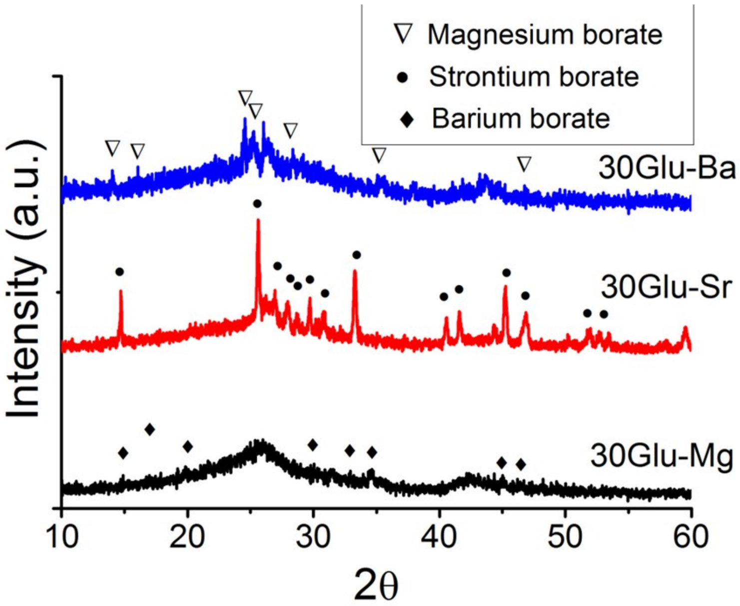
Supplementary Figure 1. XRD patterns of 30Glu-Me (Me=Mg, Ca, Sr, Ba) samples. All samples showed two characteristic XRD peaks at ~26 º and ~43 º , which are attributable to the (002) and (100) planes of graphitic h-BN



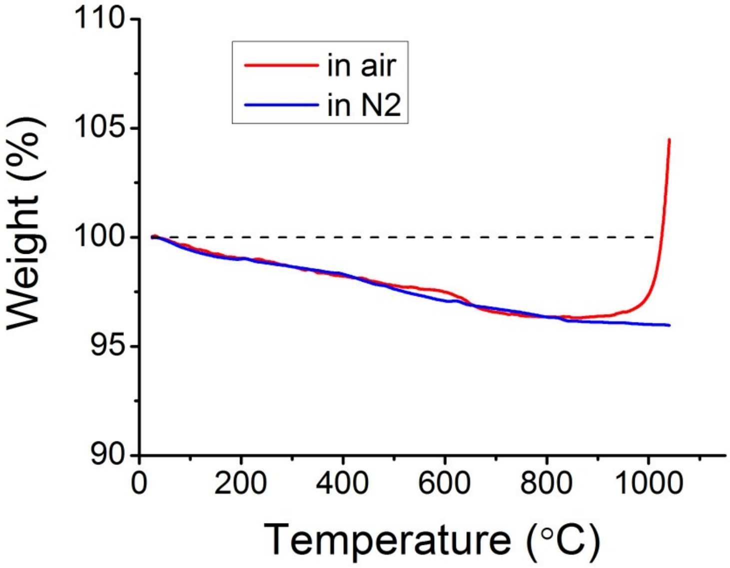
Supplementary Figure 2. FT-IR spectra of xGlu-Ca samples. Samples were mainly featured by two bands of 1,380 cm^{-1} and 780 cm^{-1}, which correspond to the in-plane B-N transverse stretching vibration and the out-of-plane B–N–B bending vibration, respectively



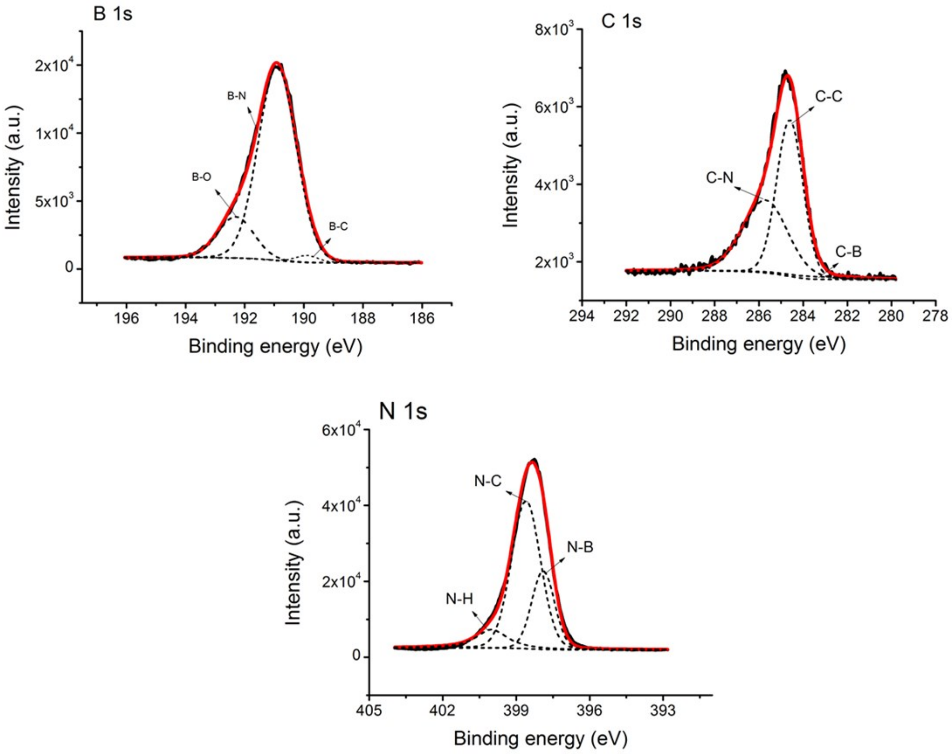
Supplementary Figure 3. XRD patterns of 30Glu-Ca sample at different annealing temperature.



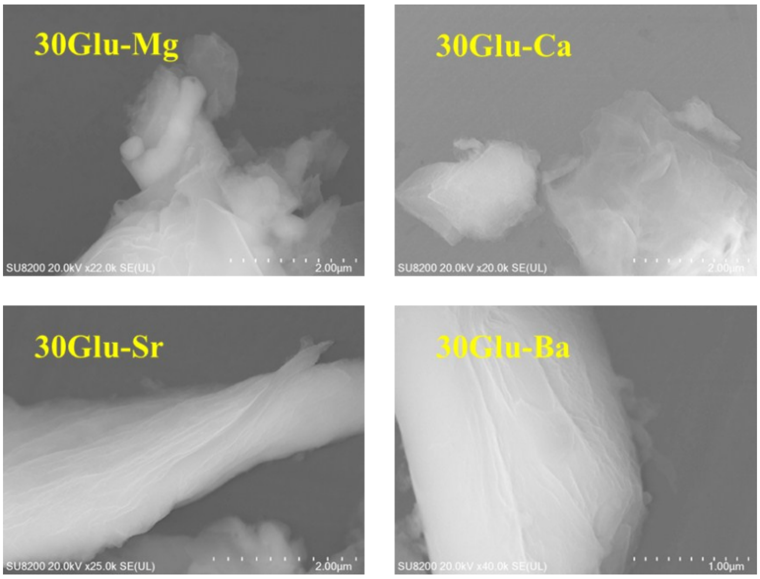
Supplementary Figure 4. XRD patterns of 30Glu-Me (Me=Mg, Sr, Ba) samples after annealed at 1,000 °C. All samples show the existence of alkaline earth metal borate and h-BCN.



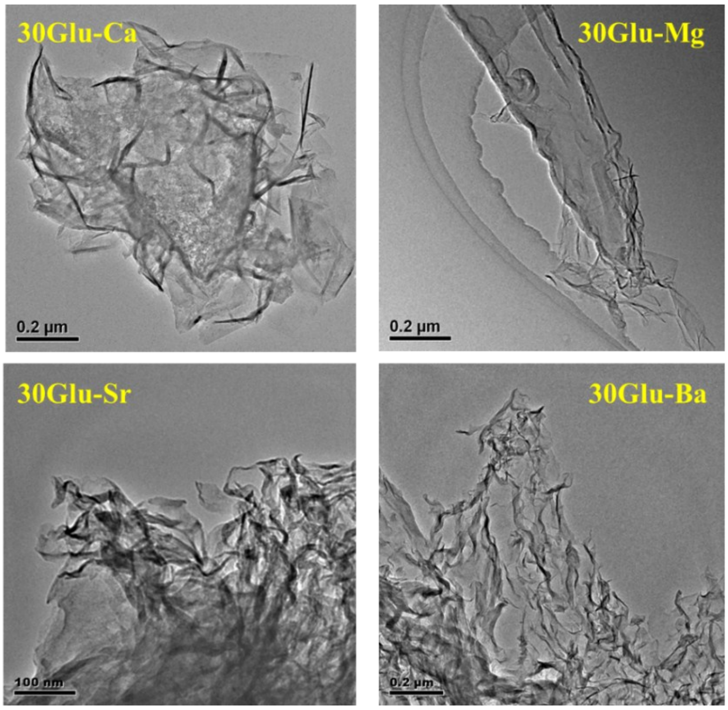
Supplementary Figure 5. TGA analysis result of 30Glu-Ca sample.



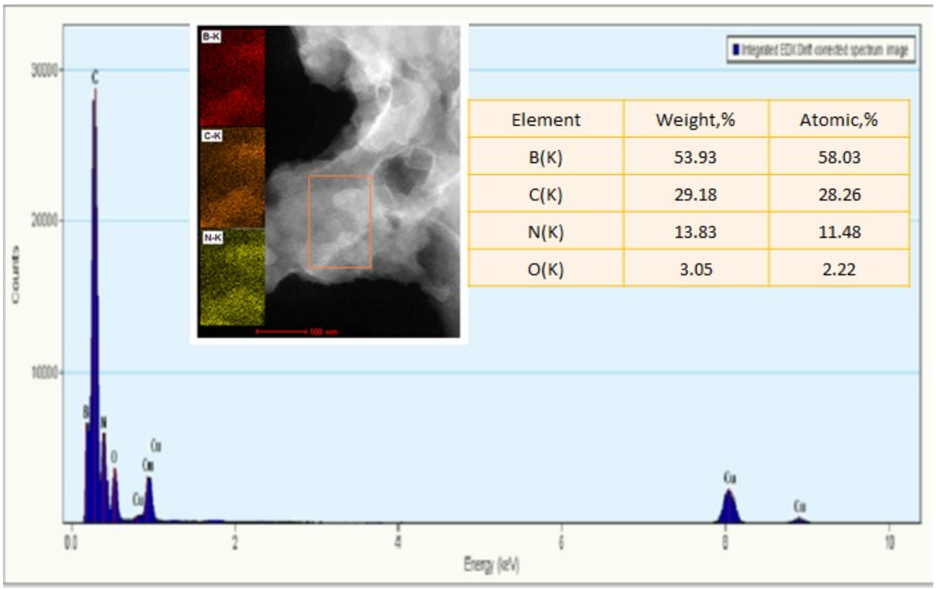
Supplementary Figure 6. XPS high-resolved spectra of 30Glu-Ca sample.



Supplementary Figure 7. SEM images of 30Glu-Me (Me = Mg, Ca, Sr, Ba) samples. All samples show the flake-stacked morphology

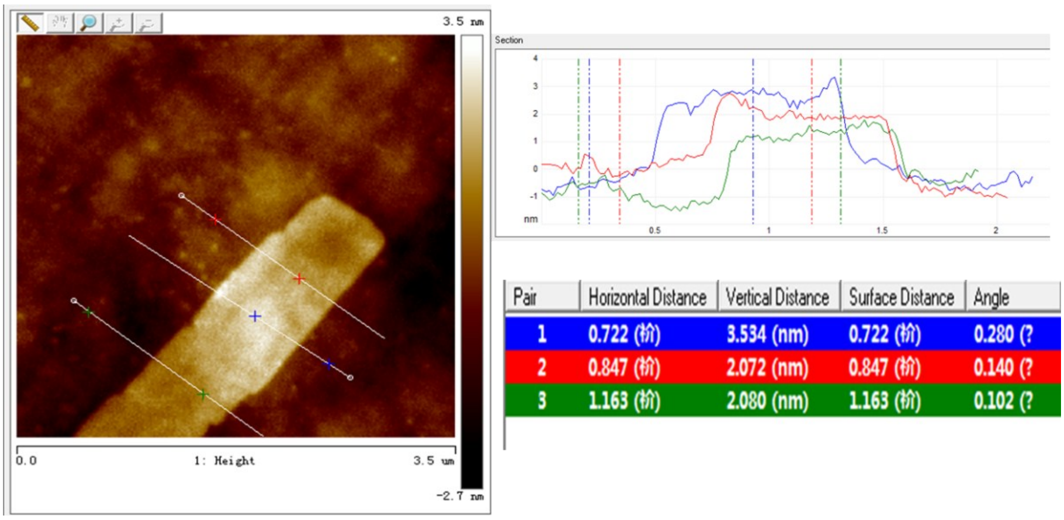


Supplementary Figure 8. TEM images of 30Glu-Me (Me = Mg, Ca, Sr, Ba) samples.



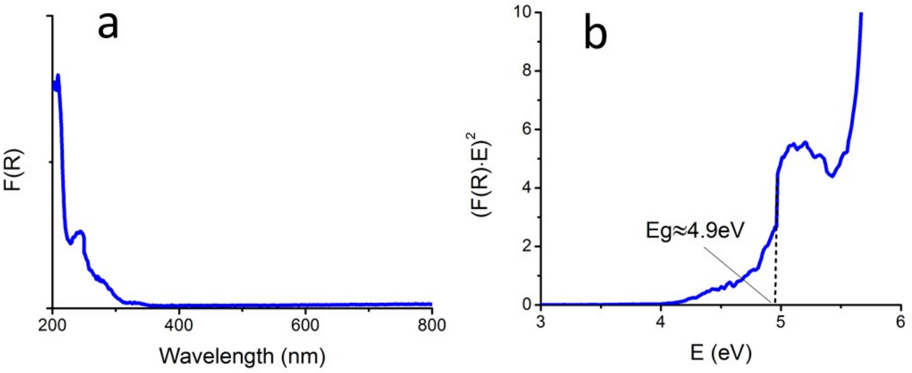
Element	Weight,%	Atomic,%
B(K)	53.93	58.03
C(K)	29.18	28.26
N(K)	13.83	11.48
O(K)	3.05	2.22

Supplementary Figure 9. The elemental mapping images of B, C and N of the enlargement of selected-area in the picture.

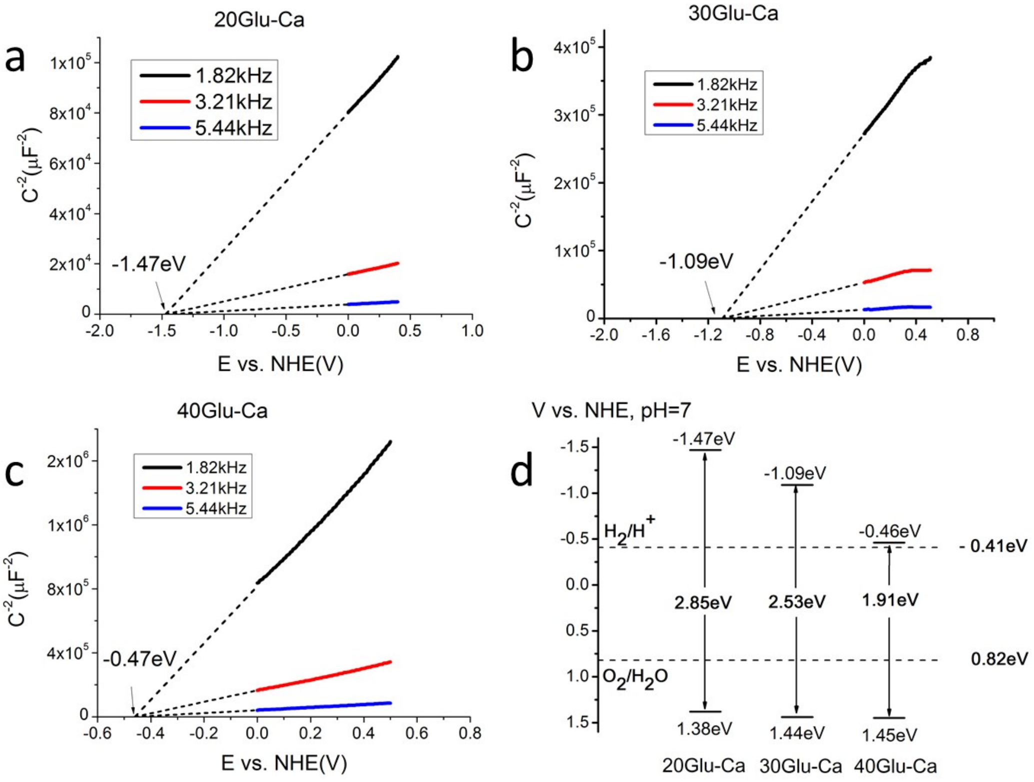


Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle
1	0.722 (柃)	3.534 (nm)	0.722 (柃)	0.280 (?
2	0.847 (柃)	2.072 (nm)	0.847 (柃)	0.140 (?
3	1.163 (柃)	2.080 (nm)	1.163 (柃)	0.102 (?

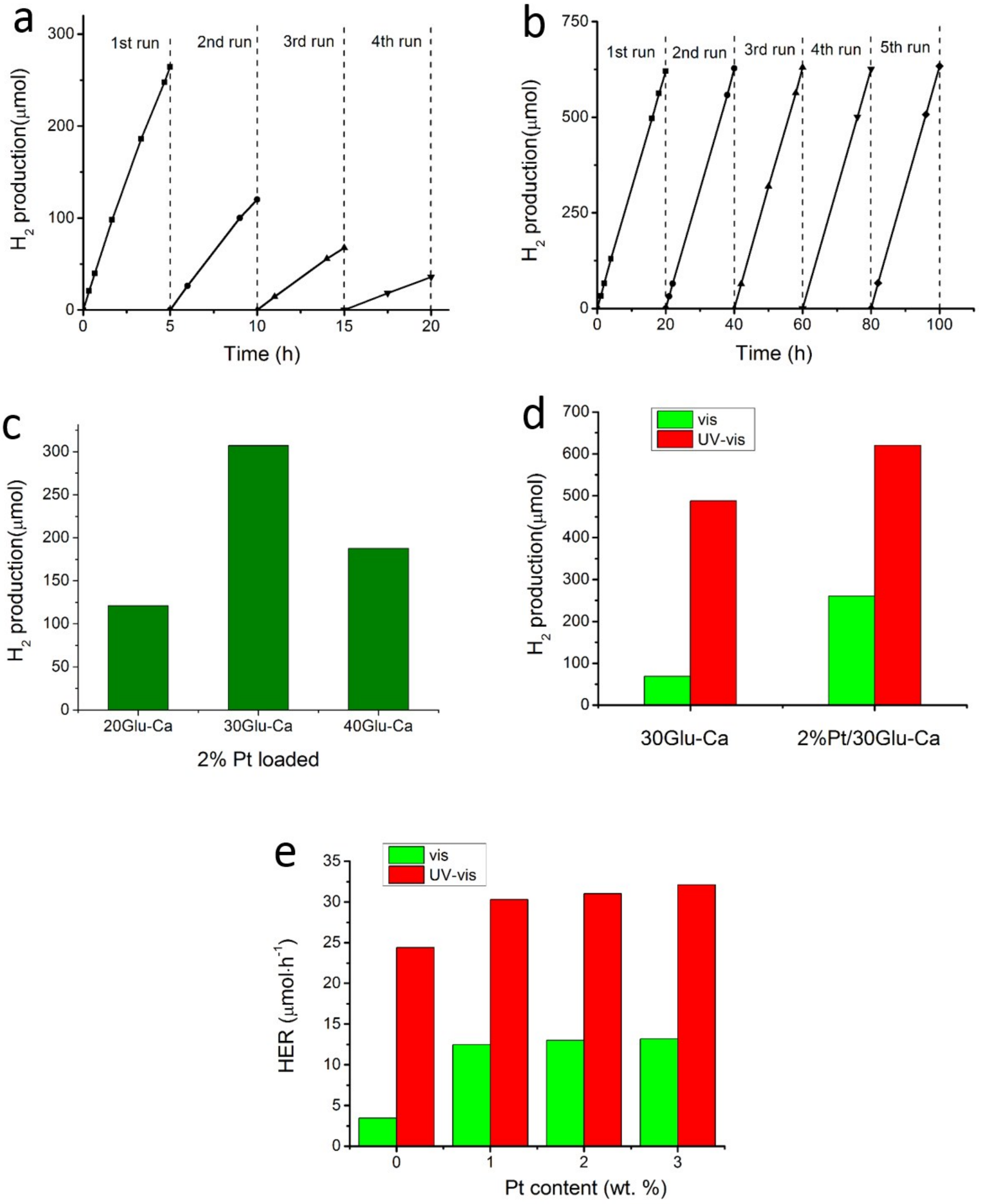
Supplementary Figure 10. AFM analysis of 30Glu-Ca sample. its thickness was determined to be 2~4 nm, which corresponds to the thickness of ~10 stacked layers.



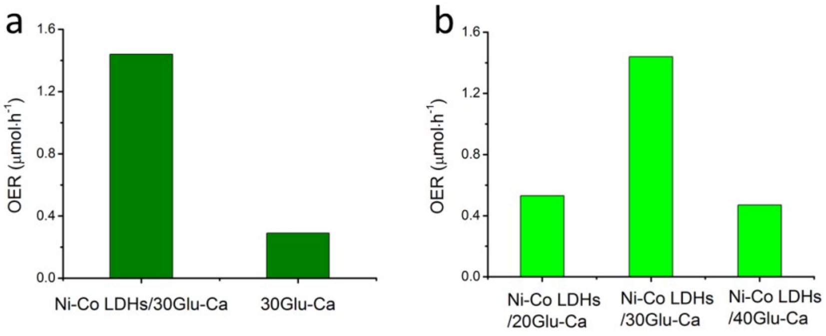
Supplementary Figure 11. UV-vis spectra and band gap energy of the prepared h-BN sample



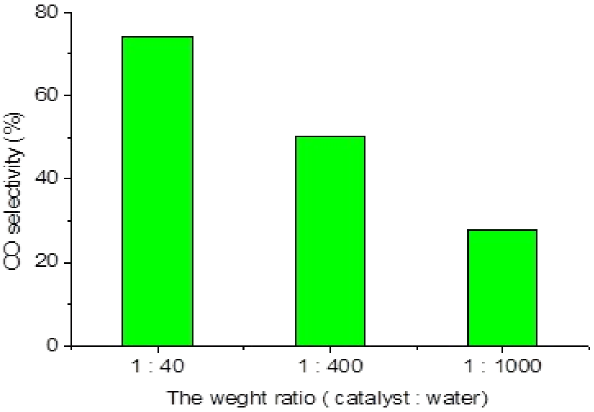
Supplementary Figure 12. The determination of the conduction band minimum (CBM) of xGlu-Ca (x=20, 30, 40) samplex by Mott-Schottky method (a, b, c) and the determined band structure of xGlu-Ca samples with respect to Normal hydrogen electrode (NHE), together with the reduction and oxidation potential of H_2O (d).



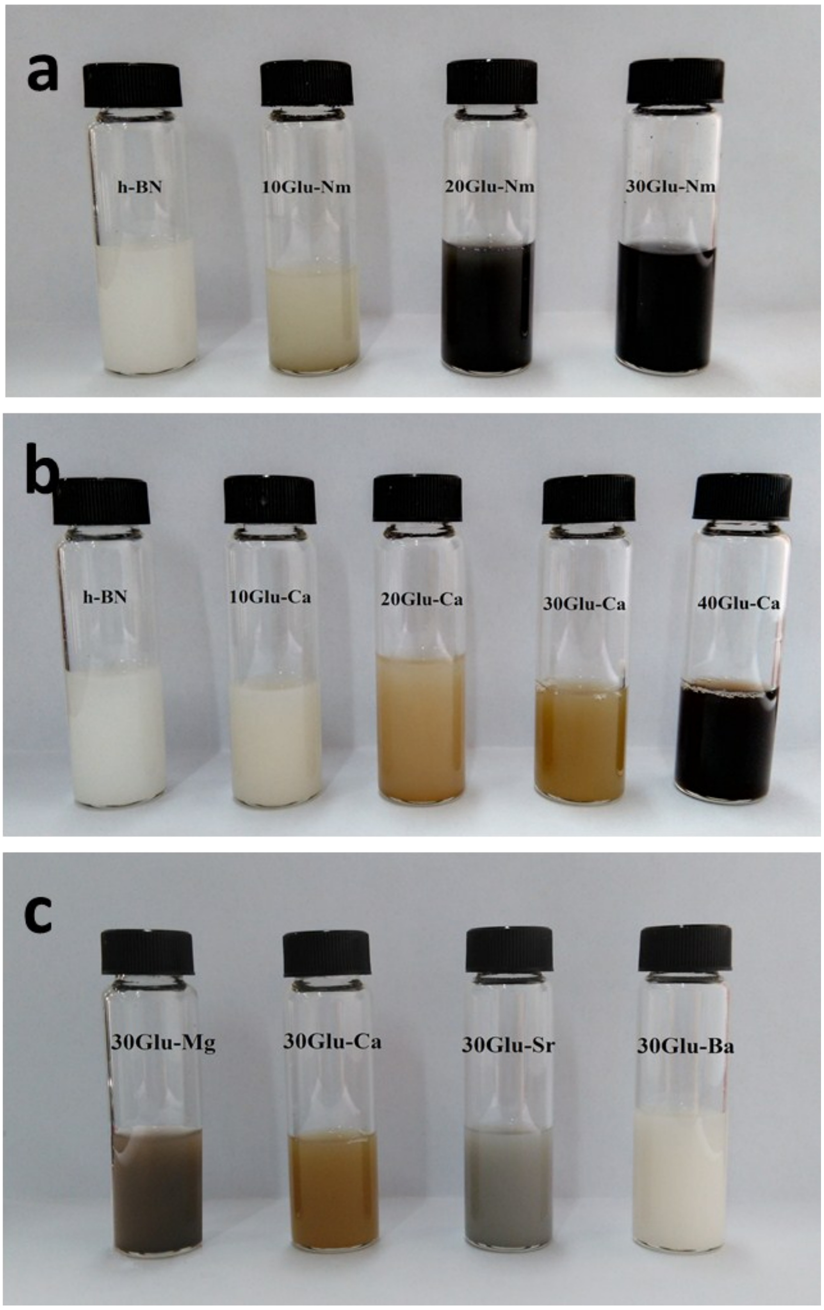
Supplementary Figure 13. H_2 productions under different conditions. a) The H_2 evolution of pure 30Glu-Ca sample for 20 hrs under ultraviolet light b) The stable H_2 evolution of 2% Pt/30Glu-Ca sample for 100 hrs under ultraviolet light c) H_2 productions with 2% Pt/xGlu-Ca samples for 20 hrs under visible light. d) The comparison of H_2 productions of 30Glu-Ca sample under different conditions. e) H_2 production rates according to the content of loaded Pt.



Supplementary Figure 14. Oxygen evolution rate (OER) a) with pure 30Glu-Ca sample and Ni-Co LDHs/30Glu-Ca sample. b) with Ni-Co LDHs/xGlu-Ca (x=20, 30 and 40) samples.



Supplementary Figure 15. CO selectivity according to the wt. ratio of water to catalyst



Supplementary Figure 16. Photographs of xGlu-Me samples suspensions. a) xGlu-Nm (No metal), b) xGu-Ca samples, c) 30Glu-Me (Me=Mg, Ca, Sr and Ba)