Supporting Information

Materials and methods

Text S1 Details for detecting hydrogen by Gas Chromatography

The GC conditions were as follows: 1 mL biogas was injected via a syringe, nitrogen was used as the carrier gas, and the temperatures of injector, column (TCD), detector were set as 100℃, 140℃, 100℃ respectively. Nitrogen was purchased from Tianjin Dong Xiang special gas Co., LTD, China. The purity of the BSA was 99.999%.

Text S2 Details for detecting VFAs by Gas Chromatography

Prior to injection, phosphoric acid was added to adjust the sample pH below 3. Phosphoric acid was bought from J & K Chemical Technology, China and the purity was 100%.The GC conditions were showed in the following: the injection volume was1.0 μL, nitrogen was used as the carrier gas, the temperatures of injector and detector (GC-2010, Shimadzu, Japan) were kept at 250℃ and 300℃, the temperature of column maintained at 100℃ for 3 min firstly, from 100℃ to 180℃ at a rate of 20℃/min afterwards, and rose to 210℃ at a rate of 10℃/min finally.

Table S1 Major properties of the concentrated sludge. [a)]

Parameter	Value
pH	6.90 ± 0.01
Total suspended soils (TSS)	18.48 ± 0.15 g/L
Volatile suspended soils (VSS)	10.12 ± 0.09 g/L
Soluble protein	42.35 ± 0.97 mg/L
Soluble carbohydrate	22.83 ± 0.68 mg/L

Notes: a) Results are the averages and their standard deviations of duplicate tests.

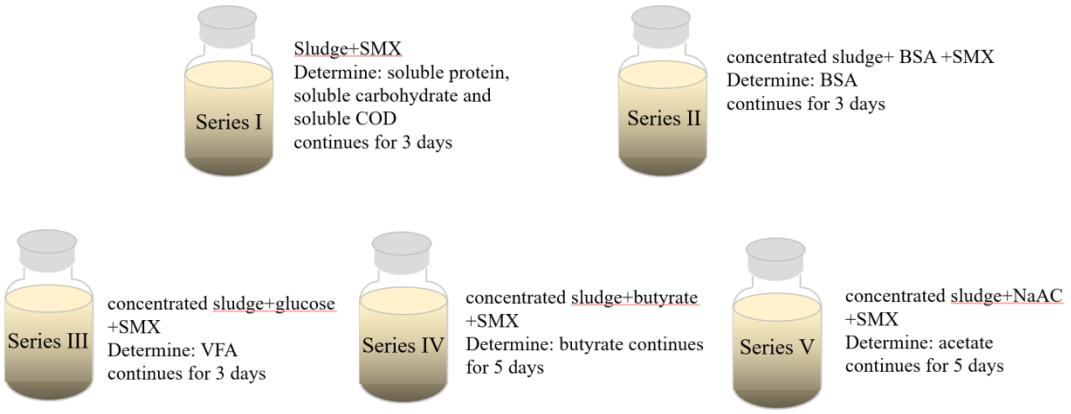

Fig. S1 the experiment process about impact of SMX on each hydrogen production pathway.