Copper doped TiO_2 for H_2 Production in Ethanol/Water photoreforming

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Abstract: In our work, low copper loading materials shows highly photoreformaing activity which can be 4 times higher than pure titanium dioxide. On nitrogen absorption and desorption measurement the result of specific surface area (S_{BET}) up to 155 m^2/g which is better than commercial P25 and many of references. The hydrogen production represents a well correlation with S_{BET}. XRD image presents a well crystallized anatase titanium characteristic peaks. The evolution of H_2 without significant decrease after 20 hours irradiation.

Keywords: Copper, Hydrogen Production, Ethanol Photoreforming.

1. Introduction

Increasing the attention of renewable energy is for sustainable development of our environment and economy. Recently, hydrogen production from oxygenated compounds shows a great alternative to conventional water splitting which higher hydrogen conversion ability and less complex reaction pathway. It attributed to the oxygenated compounds representing as a sacrificial agent to cause a longer lifetime of electron-hole.

In many of references, copper has been reported that an appropriate amount of loading can be performance a higher catalytic capability, include red-shift effect in nanoscale. Both copper oxides are abundant natural p-type semiconductors, their bandgap are suitable for photosplitting water to produce hydrogen.

The sample were synthesised by a novel and rapid method: Aerosol-Assisted Self Assembly Process (AASA) to synthesis. AASA is a large-scale continuous production route. It is a variable way for metal doping. Materials preparation is modified from Stucky and his coworker previous study. It's firstly introduced aerosol-assisted self-assembly process combine with spray method, this strategy shows a facile pathway for metals doping and scalable route for producing high surface area mesostructure materials.

2. Experimental

In this contest, Cu-doped TiO_2 mesosphere were prepared from a sol-gel solution, the solution homogeneously aged tetrabutyl titanate (TBOT), acetic acid, ethanol, hydrochloride acid and copper nitrate at room temperature for 4h as a precusor.

During the spray process, volumetric flow rate was set at 2 L (STP) min^{-1} in the air by a compressor as a driving force. The assembly starts when the precusor solution into a 2 L (15 cm diameter) homemade atomizer with 1 m silica tube furnace, temperatures maintain at 400℃. The resultant was collected on 200 nm Cellulose Acetate Membranes filter assisted by a back-end vacuum pump. All the sample was calcined with 1.5 g of resultant powder at 400℃for 5 hours in atmosphere (ramp rate 2℃min^{-1}) every batch.

For estimated the materials photocatalytic characterization, using a Solar Simulator with a 150W Xe lamp filtered with a 300 nm of Atmospheric Edge Filter, 500 mg catalyst were suspended in 80 mL of water/ethanol solution (rate is 1:1 by volume) purge with Ar an hour befor irradiation. The output gaseous products were real time measured by HP 7890 GC-TCD couple with HP 5975C Mass in Ar.

3. Results and discussion

The material photocatalytic ability evaluation results on fig. 1(a) CuTS hydrogen production rate, the hydrogen production rate is related to copper loading amount. On fig. 1(b) Different pretreatment hydrogen

generation, the pretreatment can provied a better hydrogen generation ability, especially with hydrogen. The better assessment on below table 1.

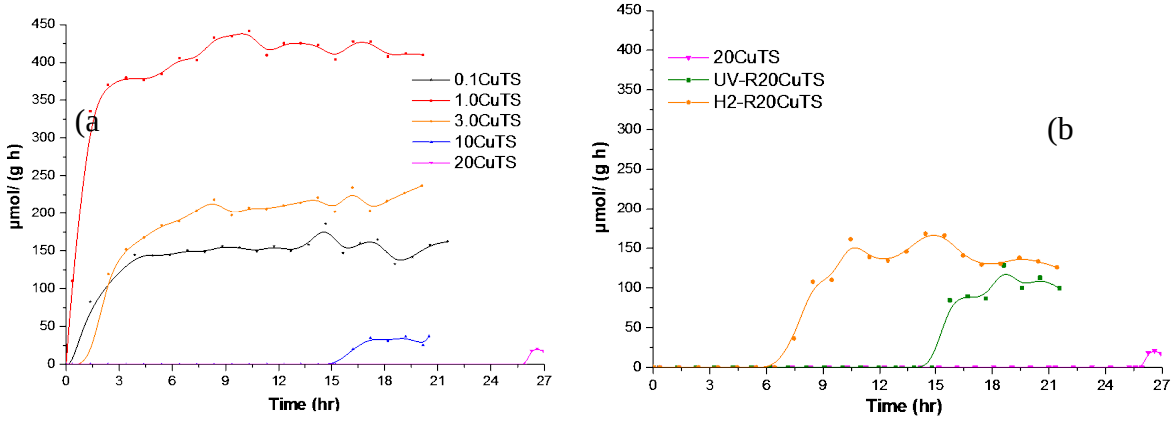

Figure 1. CuTS. hydrogen generation with different copper loading and pretreatment

Table 1. The material S_{BET} and hydrogen production rate correlation

Photocatalys	S_{BET}[a] (m^2 g^{-1})	Pore size[b] (nm)	Hydrogen Production (μmol g^{-1} h^{-1}) [e]	Morphology Contribution (μmol $h^{-1}m^{-2}$)[f]
TS	96	7.2	92.7	0.97
0.1CuTS	128	6.7	156.9	1.23
1.0CuTS	155	6.8	412	2.66
3.0CuTS	146	8.0	317	2.17
10CuTS	80	11.8	30.4	0.38
20CuTS	101	8.2/12.9	17.9	0.18

4. Conclusions

The result of CuTS photoreforming highly stable ability of ethanol photoreforming for H_2 production after 20 hours irradiation, for optimal copper loading conditionis is 1.0 wt.%, the photoreforming ability can be up to 412μmol/g/h.

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