

Enhanced stability and activity of Cu-BTC by trace Ru³⁺ substitution in water photolysis for hydrogen evolution

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Preparation of Bi-BTC

0.236 g Bi (NO₃)₃·5H₂O (0.49 mmol) and 0.193 g H₃BTC (0.92 mmol) were completely dissolved in a mixture of DMF/MeOH (5 mL, 1:3), the homogeneous solution was then transferred into a 25 mL Teflon-lined autoclave and maintained at 120 °C for 45 h. The obtained products were washed by DMF, methanol and then dried in vacuum at 60 °C.

Preparation of Ce-BTC

2.17 g Ce (NO₃)₃·6H₂O (10 mmol) and 0.63 g H₃BTC (3 mmol) were completely dissolved in 50 mL DMF, the homogeneous solution was then transferred into a 100 mL Teflon-lined autoclave and maintained at 130 °C for 24 h. The obtained products

were washed by DMF, ethanol and then dried in vacuum at 80 °C.

Preparation of Co-BTC, Zn-BTC

The preparation process of the two catalysts was similar, taking Zn-BTC as an example. First, 1.681 g H₃BTC (8 mmol) and 3.570 g Zn (NO₃)₂·6H₂O (12 mmol) were dispersed in a mixture of 200 mL ethanol and water (v/v=1:1), the obtained mixture was stirred till completely dissolved. Then 0.960 g NaOH (24 mmol) was added and kept continuous stirring for more than 30 min to precipitate out the products. The obtained products were washed by deionized water, ethanol and then dried in vacuum at 80 °C.

Preparation of Ru-MOF and H₂O/Ru-MOF

0.311 g RuCl₃ (1.5 mmol) and 0.210 g H₃BTC (1 mmol) were completely dissolved into a mixture of 16 mL H₂O and 0.3 mL glacial acetic acid, then the mixture was transferred into a 25 mL Teflon-lined autoclave and maintained at 160 °C for 72 h. The obtained products were washed by deionized water and then dried in vacuum at 80 °C. The preparation of H₂O/Ru-MOF was similar to that of H₂O/Cu-BTC.

Electrochemical measurements

Electrochemical workstation (CHI660E) was used for photoelectrochemical measurement.

Cyclic voltammetry (CV): Working electrode: 3 mg sample was dispersed in a mixture of 250 uL EtOH and 250 uL H₂O, then 10 uL Nafion was added as binder. After ultrasonic treatment of the mixed solution for 30 minutes, 100 uL mixed solution was added to the polished glassy carbon electrode and dried at room temperature. CV test conditions: platinum plate (counter electrode), saturated calomel electrode

(reference electrode), working electrode, electrolyte (0.2 M Na₂SO₄ (pH=7) solution).

CV test was carried out in the range of - 0.4 ~ 1.6 V at the scanning speed of 100 mV.s⁻¹.

Photocurrent response, Mott-Schottky (M-S), AC impedance (EIS): Working

electrode: 3 mg sample was dispersed in a mixture of 250 uL EtOH and 250 uL H₂O,

then 10 uL Nafion was added as binder. After ultrasonic treatment for 30 minutes, 100

uL mixed solution was added to the conductive glass and dried at room temperature.

Test conditions: The electrode system was the same as CV. A 300 W xenon lamp

(FX300) was used as the light source. The photocurrent response of the sample was

tested at a bias voltage of - 0.6 V and a chopping period of 10 s. At the same time, the

EIS of the sample was tested at a constant voltage of 0.6 V. Mott-Schottky was

measured in the open circuit voltage range of ± 1 V.

Different Ru substituting amounts on photocatalytic H₂ evolution activity

Ru/Cu-BTC with different Ru amounts doping (the mass ratios of Ru to Cu-BTC

were 1%, 3% and 5%) was carried out in our previous work, and we found that the

order of the photocatalytic H₂ evolution activity was: 1% > 3% > 5% (Fig. S8).

However, although the H₂ evolution activity of the sample (the substitution amount was

1%) was outstanding, the continuous use of the sample in water also caused structural

damage. When the substitution amount was 3% (used in the original manuscript), the

stability and H₂ evolution activity could be taken into account. Moreover, although the

H₂ evolution activity of Ru-MOF was better than that of Cu-BTC, the activity of trace

Ru-substituted MOF Ru/Cu-BTC (3%) was better than that of Ru-MOF (Figure 5), that

is, it was not that the more the substitution, the higher the activity.

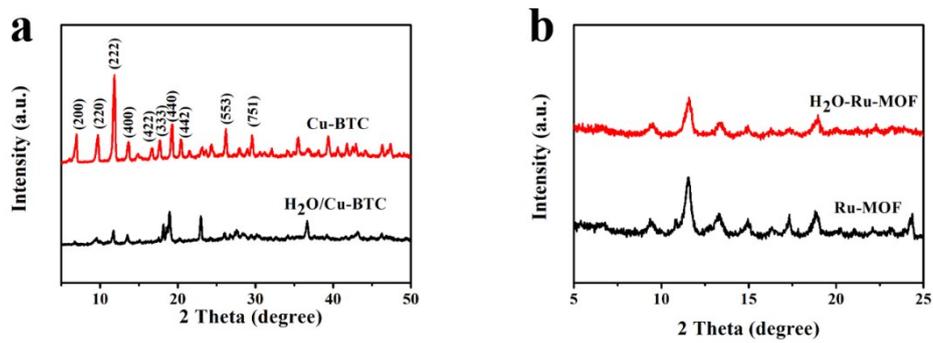


Fig. S1. XRD patterns of (a) Cu-BTC, H₂O/Cu-BTC (b) Ru-MOF and H₂O/Ru-MOF.

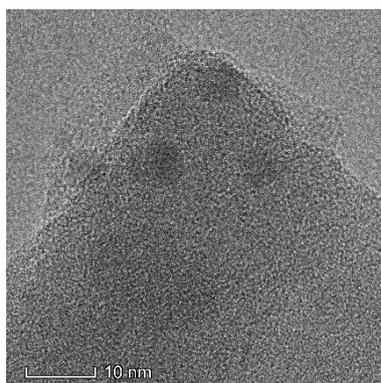


Fig. S2. HR-TEM image of Ru/Cu-BTC.



Fig. S3. The supernatant after adding ammonia monohydrate, H₂O/Cu-BTC (left) and Ru/Cu-BTC (right).

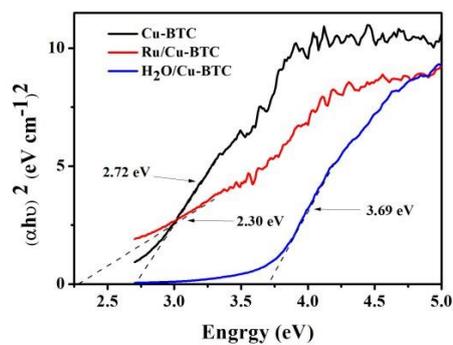


Fig. S4. Band gap energies of Cu-BTC and Ru/Cu-BTC.

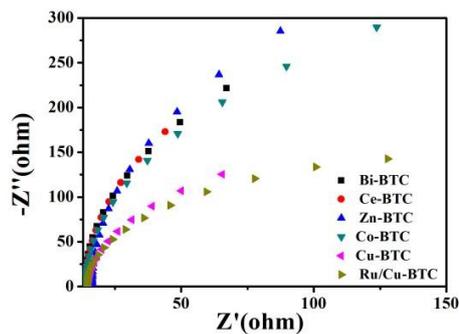


Fig. S5. The enlarged diagram of the curve at the high frequency region in Fig 5b.

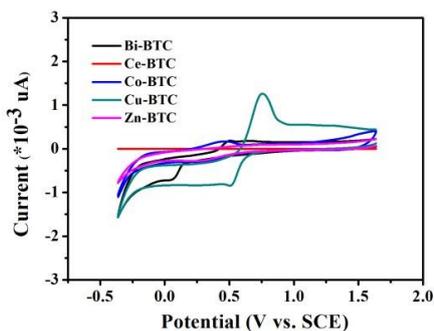


Fig. S6. CV curves of Bi-BTC, Ce-BTC, Co-BTC, Cu-BTC and Zn-BTC.

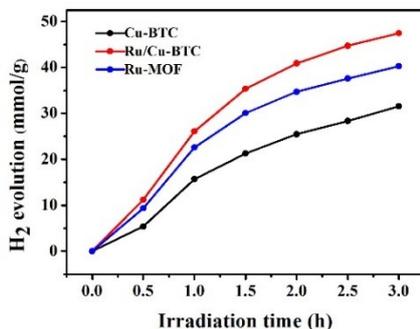


Fig. S7. Effect of Cu-BTC, Ru/Cu-BTC and Ru-MOF on photocatalytic H₂ evolution activity under visible light.

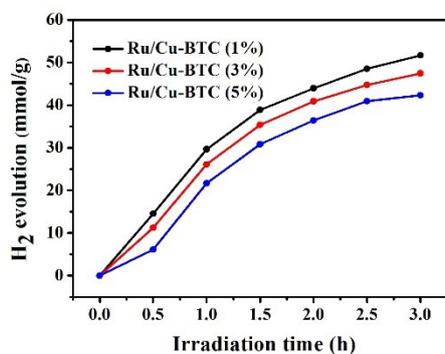


Fig. S8. Effect of different Ru substituting amounts on photocatalytic H₂ evolution activity under visible light.