Nanocable catalysts MTe (M = Pt, PtCu)@UIO-67 for CO₂ conversion

Huaqian Zhang, Haitao Xu^{*}, Yuanyuan Li, Xinbo Pan and Lishuang Li

ABSTRACT Zr-based metal–organic framework nanocable catalysts comprising MTe (M = Pt, PtCu)@UIO-67 resembling “sugarcoated haws on a stick” were assembled. Ultrathin Te nanowires with diameters of about 8.48 nm served as a sacrificial template for the epitaxial growth of an outer M (Pt or PtCu) to obtain cable cores comprising MTe nanowires with good dispersity, which were then successfully encapsulated in the center of a monodisperse MTe@UIO-67 cable nanostructured catalyst. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and energy dispersive X-ray (EDX) element mapping were used to investigate the morphology, structure and composition of the nanocable catalysts. Six types of catalysts were synthesized, and all of the catalysts demonstrated superior product selectivity to CO for reverse water-gas shift (RWGS) reaction. Especially, the morphology and dispersion of PtCuTe@UIO-67 nanocable catalyst can be maintained to some extent after catalysis at high temperature, and PtTe@UIO-67 catalyzed CO₂ conversion was achieved with 99.86% CO selectivity.

Keywords: metal-organic frameworks, nanowires, nanocable catalyst, reverse water-gas shift reaction

INTRODUCTION

In recent years, unprecedented industrial and economic development has led to excessive emissions of carbon dioxide, which is considered to be a major contributor to global warming and seawater acidification. To mitigate these negative environmental impacts, CO₂ removal from the atmosphere is becoming increasingly urgent [1–4]. Three main strategies have been proposed to prevent the atmospheric CO₂ concentration from increasing: curbing its release, CO₂ storage and CO₂ utilization [5]. CO₂ conversion is an ideal form of CO₂ utilization; it can not

only alleviate CO₂ emission, but also yield value-added products such as methanol [6], methane [7] and other C₂₊ hydrocarbons [8] to supplement or replace chemical feedstocks [9]. The reverse water gas shift (RWGS) reaction is regarded as one of the most preferred routes because its products can be processed further, especially by Fischer–Tropsch synthesis, to produce heavy hydrocarbons [10,11]. Various catalysts such as Pt [12], Fe [13], Pd [14], and Ru [15] have been tested for the RWGS reaction; however, despite unceasing research efforts, the development of high-efficiency catalysts is still underway.

One-dimensional (1D) metal nanowires (NWs) and nanotubes have received much research interest because of their versatility and characteristics such as ultrahigh surface-to-volume ratio, controllable shape, and tunable composition [16–19]. Alloy NWs such as PtRu [20] and PdM (M = Pt, Au) [21] exhibit enhanced catalytic properties compared with their parent metals, mainly due to the electronic interplay between the constituent metals. Many researchers have reported that 1D nanostructure catalysts were attempted for methanol oxidation reaction (MOR) [22,23] and oxygen reduction reaction (ORR) [24,25]; however, to the best of our knowledge, 1D nanostructures have seldom been reported as catalysts for the RWGS reaction.

Metal–organic frameworks (MOFs) are a class of porous infinite-structured materials constructed by metal cations or metal clusters coordinated to organic ligand molecules [26–29], which possess characteristics including modifiable topology [30], excellent chemical and thermal stability [31], and exceptionally high microscopic surface area [32]. These remarkable features endow the MOFs with diverse applications including gas storage [33–35] and separation [36], chemical sensing [37], and catalysis [38,39]. Recently, MOFs were shown to be in-

State Key Laboratory of Chemical Engineering, Membrane Science and Engineering R&D Lab, Chemical Engineering Research Center, East China University of Science and Technology, Shanghai 200237, China

^{*} Corresponding author (email: xuhaitao@ecust.edu.cn)

triguing candidate supports for catalysts integrating single atoms or metal clusters, providing endless possibilities for catalyst design [40]. MOFs anchoring single Ru sites effectively catalyzed chemoselective hydrogenation [41], and MOFs assisted preparation of single-atom Ni catalysts for CO₂ electroreduction [42]. Three-dimensional (3D) MOF@carbon was synthesized for application in Li-S batteries [43], and carbon nanofibers derived from Te@ZIF-8 were developed for high electrocatalytic performance [44]. ZnO NWs encapsulated in ZIF-8 as a nanocomposite (ZnO@ZIF-8) were also studied, which greatly improved the gas sensor selectivity [45].

Here, Te NWs were chosen as templates to fabricate well-defined MTe NWs through the epitaxial growth of Pt or PtCu. UIO-67 served as an applicable host matrix [46,47] with good thermal stability [48], which could protect PtTe or PtCuTe NWs from sintering and aggregating, and thus retain their catalyst activity at high temperature. High surface area and high porosity make UIO-67 adsorb the reactant molecule and transport it to the metal active center, and the pore size effect of UIO-67 could improve the product selectivity, which has been demonstrated by the reported literature [49]. Our synthesis strategy to fabricate MTe@UIO-67 cable catalysts with MTe NWs encapsulated in the core of UIO-67 is shown in Fig. 1. The developed MTe@UIO-67 cable nanostructured catalysts combine the outstanding natures of UIO-67 and MTe NWs, leading to enhanced catalytic efficiency and stability toward RWGS reaction.

EXPERIMENTAL SECTION

Materials

Biphenyl-4,4-dicarboxylic acid (BPDA, 98%) was purchased from Energy Chemical; polyvinylpyrrolidone (PVP, molecular weight (MW) = 58,000, K29-32) and zirconium chloride (ZrCl₄, 98%) were purchased from Shanghai Mclean Biochemical Technology Co., Ltd; PVP (MW = 40,000, K-30) was purchased from Shanghai Yuanye Bio-Technology Co., Ltd. L-ascorbic acid (99.7%) was purchased from Sigma-Aldrich Co.; ammonia solution (NH₃·H₂O, 25%–28%) was purchased from Shanghai Lingfeng Chemical Reagent Co., LTD. Hydrazine hydrate aqueous solution (N₂H₄·H₂O, 85%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Chloroplatinic acid (H₂PtCl₆, 99.95%, Pt≥47%), copper(II) chloride dihydrate (CuCl₂·2H₂O, 99.0%), sodium tellurite (Na₂TeO₃, 99.9%), *N,N*-dimethylformamide (DMF, 99.5%), ethanol (99.7%), acetic acid (≥99.5%) and acetone (≥99.5%) were purchased from Shanghai Titan Scientific Co., Ltd. All the

reagents were used without any further purification.

Characterizations

Scanning electron microscopy (SEM) imaging and energy dispersive X-ray spectroscopy (EDS) were carried out by using a Hitachi S4800 scanning electron microscope at 6.0 kV. Field emission scanning electron microscopy (FESEM) imaging was performed by using a GeminiSEM 500 field emission scanning electron microscope. Transmission electron microscopy (TEM) measurement was performed on a JEM-2100 at 200 kV. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging was carried out on an FEI Tecnai G2 F30 transmission electron microscope operated at 300 kV. Powder X-ray diffraction (PXRD) data were collected and recorded in the 2θ range of 5°–75°. Nitrogen adsorption-desorption measurements were conducted at 77 K on a surface area and pore size analyzer (JK-122F) after the samples were degassed at 120°C for 3 h. The specific surface area and the pore size distribution were calculated by using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The content of Pt and Cu were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). X-ray photoelectron spectroscopy was detected by a Thermo ESCALAB 250Xi. CO₂ adsorption-desorption isotherms were carried out on automatic volumetric adsorption equipment (ASAP20) at 298 K.

Synthesis of UIO-67

BPDA (15 mg) and zirconium chloride (10 mg) were dispersed into 5 mL of DMF, and PVP (100 mg, MW = 58,000) and 200 μL of acetic acid were added into the solution subsequently, each step with sonication for 10 min in order to obtain dispersed solution. Then the above solution was transferred into a 30-mL Teflon-lined autoclave at 120°C for 24 h. The product was recovered by centrifugation (8500 rpm, 5 min), washed several times with DMF and ethanol, and dried at 80°C overnight.

Synthesis of Te NWs

Te NWs were prepared according to previous reports with slight modifications. First, 0.3 g of PVP (MW = 40,000) was dissolved with 11 mL of distilled water under continuous sonication to form a homogeneous solution at room temperature. After that, 0.0553 g of Na₂TeO₃ was added into the previous solution and dissolved. Then, 1 mL of aqueous ammonia (25%–28%, w/w) and 0.5 mL of hydrazine hydrate (85%, w/w) were added to the

Figure 1 Synthetic route to the nanocable catalysts NWs@MOF and subsequent application of the catalysts for the CO₂ RWGS reaction.

mixture with magnetic stirring. The final solution was transferred into the container of Teflon-lined stainless steel autoclave, and maintained at 180°C for 4 h, to obtain the product of Te NWs. The Te NWs were centrifuged with acetone and washed several times with distilled water, and dispersed in 12 mL of water for further use.

Synthesis of MTe (M = Pt, PtCu) NWs

The prepared Te NWs (6 mL) were added into 12 mL of distilled water, followed by the addition of PVP solution (60 mg of PVP in 5 mL of distilled water) under stirring, and the solution was transferred to a water bath (60°C). Then, 400 μL of H_2PtCl_6 (0.1 mol L⁻¹) and 600 μL of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (0.1 mol L⁻¹) were added immediately. About 30 s later, 2 mL of *L*-ascorbic acid (0.1 mol L⁻¹) was injected, and the mixture was stirred at 60°C for 1 h. The product was centrifuged at 11,000 rpm for 10 min, and washed with DMF for several times. Finally, the prepared MTe NWs were dispersed in 2 mL of DMF containing 60 mg of PVP (MW = 58,000) for further use. Furthermore, we changed the amount of Pt and Cu sources added in the precursor solutions to prepare MTe NWs with various compositions, using the volume ratios of H_2PtCl_6 (0.1 mol L⁻¹) and $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (0.1 mol L⁻¹) set as 100:150, 200:300, 400:0, 400:600, 400:1200, 800:1200 (all in μL), respectively.

Synthesis of MTe (M = PtCu, Pt)@UIO-67 nanocable catalysts

In a typical procedure, BPDA (15 mg) and zirconium chloride (10 mg) were dissolved into 4 mL of DMF, fol-

lowed by the addition of PVP (170 mg, MW = 58,000) and 1 mL of the as-prepared MTe NWs. Finally, 100 μL of acetic acid was added into the solution subsequently, each step with sonication for 10 min. Then the solution was transferred into a 30-mL Teflon-lined autoclave at 120°C for 4 h. The product was centrifuged at 10,000 rpm for 8 min, washed twice with DMF and ethanol before being dried under vacuum.

RESULTS AND DISCUSSION

Synthesis and morphology of 1D NWs

MTe NWs were assembled by using ultrathin Te NWs as the sacrificial templates. Te samples with deep blue color in aqueous solution (Fig. S1) were prepared under hydrothermal conditions [50]. TEM images (Fig. S2, Fig. 2a) of the prepared samples reveal uniformly monodispersed Te NWs with diameters of about 8.48 nm and lengths of tens of nanometer (marked with red circles) to a few microns. As shown in Fig. 2, metal (Pt, PtCu) NPs were deposited on Te NWs to obtain monodispersed MTe NWs, during which the Te NWs acted as both the template and reductant, and *L*-ascorbic acid was employed as an assisting reductant. PVP was used as a guiding agent and polymer-functionalized stabilizer [51], which not only controls the shape of the MTe NWs, but also improves their dispersion and protects the NPs from oxidation. Six MTe NW samples with varying metal contents were prepared under otherwise identical conditions using H_2PtCl_6 and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, by changing the volume ratio (in μL) of H_2PtCl_6 (0.1 mol L⁻¹) and $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (0.1 mol L⁻¹): 100:150 for $\text{Pt}_{81}\text{Cu}_{12}\text{Te}_7$, 200:300 for

Figure 2 TEM (a–e, g, h) and FESEM (f, i) images. (a) Te NWs, (b) UiO-67, (c) Te@UiO-67 (d) $\text{Pt}_{99}\text{Te}_1$ NWs, (e, f) $\text{Pt}_{99}\text{Te}_1$ @UiO-67, (g) $\text{Pt}_{81}\text{Cu}_{18}\text{Te}_1$ NWs, (h, i) $\text{Pt}_{81}\text{Cu}_{18}\text{Te}_1$ @UiO-67.

$\text{Pt}_{81}\text{Cu}_{16}\text{Te}_3$, 400:0 for $\text{Pt}_{99}\text{Te}_1$, 400:600 for $\text{Pt}_{81}\text{Cu}_{18}\text{Te}_1$, 400:1200 for $\text{Pt}_{64}\text{Cu}_{35}\text{Te}_1$, and 800:1200 for $\text{Pt}_{78}\text{Cu}_{21}\text{Te}_1$, respectively. The samples of MTe NWs are denoted based on the actual atomic ratio determined by ICP-OES (Table S1), and the EDS results (Fig. S3) are also consistent with the ICP-OES data, where the content of Te is very little in MTe NWs because it is employed as the sacrificial templates to be consumed. The actual atomic ratio of Pt to Cu is higher than that of the theoretical molar proportion, due to that the reduction potential of $\text{PtCl}_6^{2-}/\text{Pt}$ (+0.75 V *versus* normal hydrogen electrode (NHE)) is higher than that of Cu^{2+}/Cu (+0.153 V *versus* NHE) [52–54]. The structure and morphology of MTe NWs were initially characterized by TEM as shown in Fig. S4, obviously indicating that these six types MTe NWs can be synthesized by using the sacrificial template method with a length of several tens of nanometer or longer with high yield, and the diameter increases from about 8 to 14 nm with increasing metal content. As indicated in the inset images in Fig. 2, the MTe metal NW surface is different from that of Te NWs due to the deposition of metal nanoparticles. EDX elemental mapping images (Fig. 3d–i) demonstrate that Pt and Cu are distributed uniformly through whole PtCuTe NWs, illustrating that PtCuTe NWs are composed of Pt, Cu and Te. Fig. S5b shows the XRD patterns of MTe NWs. There is

no diffraction peak of Te, due to that Te NWs have been effectively consumed as the sacrificial templates. The vertical lines show the standard XRD peak locations of Pt and Cu, where the 2θ peaks of Pt (111), Pt (200) and Pt (220) are at 39.76° , 46.24° and 67.45° (PDF # 04-0802), and the 2θ peaks of Cu (111), Cu (200) and Cu (220) are at 43.29° , 50.43° and 74.13° (PDF # 04-0836), respectively. The diffraction peaks in the XRD pattern of PtCuTe NWs are located between the peaks of pure Pt and Cu; compared with pure Pt, the XRD diffraction peaks have a positive shift, and a negative shift compared with pure Cu peaks, confirming the formation of PtCu alloy. From further comparison of $\text{Pt}_{99}\text{Te}_1$, $\text{Pt}_{81}\text{Cu}_{18}\text{Te}_1$ and $\text{Pt}_{64}\text{Cu}_{35}\text{Te}_1$, the shift of diffraction angles is observed when the molar ratio between Pt and Cu is changed. These results are also consistent with previous reports [52,53,55]. And from Fig. S6, the 0.22 nm lattice spacing corresponds to PtCu (111) plane, and the SAED pattern also reveals that the formation of polycrystalline PtCu [24,53,56] with an ordered intermetallic structure. The introduction of Cu to modify PtTe NWs, forming PtCuTe NWs, is expected to enhance their catalytic performance.

Fabrication and characterization of NWs@MOF nanocable catalysts

UiO-67 was prepared following a procedure in literature

Figure 3 HAADF-STEM images of PtCuTe@UIO-67. (a) STEM image, (b) HAADF-STEM image, (d–i) EDX elemental mapping image, (c) select region for line-scan EDX, (j–n) corresponding line-scan EDX spectra.

[57]. Typically, BPDA (15 mg), ZrCl_4 (10 mg), PVP (100 mg), and acetic acid (200 μL) were added to DMF (5 mL) and maintained at 120°C for 24 h, resulting in octahedral nanocrystals of UIO-67 of ~ 272 nm (Fig. S7). The MTe@UIO-67 composites were prepared following a similar procedure. MTe NWs were dispersed in DMF, and then introduced to an MOF precursor solution for self-assembly. The obtained products were nanocable catalysts resembling “sugarcoated haws on a stick” (Fig. 2). MTe@UIO-67 is about 50–60 nm in diameter, which is much smaller than pure UIO-67 (~ 272 nm). But the length of MTe@UIO-67 nanocomposite is only tens of nanometer, which is much shorter than MTe NWs, probably owing to the large size of original UIO-67 nanocrystals, making the MTe NWs prone to be partly broken in the assembly process of nanocomposite. So the final products MTe@UIO-67 are only tens of nanometer long. Some reported literature also illustrated the similar phenomenon [44].

Acetic acid acted as a modulator in the above process, and the amount of acetic acid (Fig. S8) was the key factor influencing the MTe@UIO-67 morphology. In the absence of acetic acid, MTe NWs encapsulated by UIO-67 were not observed; instead, tiny disordered nanocrystals of UIO-67 formed, which could be due to a higher nucleation rate and more nucleation centers. The

MTe@UIO-67 morphology was uniform when acetic acid was present in a certain amount (100 μL). Further increasing the acetic acid content led to product aggregation and irregular morphologies. This was the reason why the cable MTe@UIO-67 did not form when only MTe NWs were added to the original system (200 μL of acetic acid) with UIO-67 nanocrystals. These observations can be explained by the acetic acid modulator competing for coordination with Zr^{4+} to control the nucleation rate [58,59]. MTe@UIO-67 with a perfect morphology can be prepared by optimizing the acetic acid amount. PVP, a nonionic and amphiphilic polymer, was also vital for nanomaterial morphology regulation and prevention of particle aggregation [60,61]. Without PVP, no product (Fig. S9) was obtained and NWs were severely aggregated. Upon addition of PVP, the morphologies of UIO-67-encapsulated MTe nanostructures were significantly improved. Further increase in PVP content (100 mg) led to higher yields of the product MTe@UIO-67. When 200 mg of PVP was used, the MTe@UIO-67 nanostructures were monodispersed and uniform. All the above observations illustrate that PVP significantly influences the formation of MTe@UIO-67, due to that PVP can not only act as a stabilizer (steric hindrance effect) to improve the dispersion of NWs, but also assist controlling the shape and size of MOF as capping agent, by adhering to the surface

of NWs to boost the MOF nucleation and growth. Based on these studies, we conclude that the optimized condition for the assembly of cable MTe@UIO-67 is 100 μL of acetic acid and 200 mg of PVP. The results also prove that this strategy is suitable for the preparation of a series of MTe NWs for incorporation into MTe@MOF catalysts (Fig. S10), which are denoted as $\text{Pt}_{81}\text{Cu}_{12}\text{Te}_7\text{@UIO-67}$, $\text{Pt}_{81}\text{Cu}_{16}\text{Te}_3\text{@UIO-67}$, $\text{Pt}_{99}\text{Te}_1\text{@UIO-67}$, $\text{Pt}_{81}\text{Cu}_{18}\text{Te}_1\text{@UIO-67}$, $\text{Pt}_{64}\text{Cu}_{35}\text{Te}_1\text{@UIO-67}$, and $\text{Pt}_{78}\text{Cu}_{21}\text{Te}_1\text{@UIO-67}$. It is worth noting that, the theoretical atomic ratio (Pt:Cu) in the assembly process of the catalysts $\text{Pt}_{81}\text{Cu}_{12}\text{Te}_7\text{@UIO-67}$, $\text{Pt}_{81}\text{Cu}_{16}\text{Te}_3\text{@UIO-67}$, $\text{Pt}_{81}\text{Cu}_{18}\text{Te}_1\text{@UIO-67}$ and $\text{Pt}_{78}\text{Cu}_{21}\text{Te}_1\text{@UIO-67}$ are all same (1:1.5), but their theoretical metal contents are different; the theoretical addition amount of Pt in the assembly process of the catalysts $\text{Pt}_{99}\text{Te}_1\text{@UIO-67}$, $\text{Pt}_{81}\text{Cu}_{18}\text{Te}_1\text{@UIO-67}$ and $\text{Pt}_{64}\text{Cu}_{35}\text{Te}_1\text{@UIO-67}$ are all same, but the theoretical atomic ratio of Pt to Cu are different (Table S1). Te@UIO-67 cannot be obtained by this approach (Fig. 2, Fig. S11), showing that the metal (Pt or PtCu) improves the Te surface properties.

Fig. S5a shows the PXRD patterns of the samples, which match well with the simulated patterns of pure UIO-67, confirming that NWs encapsulated in UIO-67 do not disrupt the crystal structure of UIO-67. But the characteristic peaks of metal cannot be observed ob-

viously except $\text{Pt}_{78}\text{Cu}_{21}\text{Te}_1\text{@UIO-67}$ due to the lower metal content and too small sizes of the metal nanoparticles (about 2–3 nm) (Fig. S12). The HAADF-STEM image in Fig. 3 also indicates that the prepared PtCuTe@UIO-67 has a cable core-shell skeleton comprising an NW core encapsulated in a series of UIO-67 shells. The corresponding elemental mapping images reveal the spatial distributions of the constituent elements, confirming that ultrathin PtCuTe NWs are in the central region and surrounded by C, O, and Zr-containing compounds consistent with the UIO-67. The BET specific surface area of $\text{Pt}_{99}\text{Te}_1\text{@UIO-67}$ (Fig. S13) is $483\text{ m}^2\text{ g}^{-1}$, which is lower than that of pure UIO-67 ($1503\text{ m}^2\text{ g}^{-1}$), and the average pore sizes of the samples are 4.31 nm for $\text{Pt}_{99}\text{Te}_1\text{@UIO-67}$ and 2.37 nm for UIO-67, the difference being attributed to the introduction of NWs during the growth process of the MOF. As shown in Fig. S14, the maximum CO_2 uptake is $19.6\text{ cm}^3\text{ g}^{-1}$ for $\text{Pt}_{99}\text{Te}_1\text{@UIO-67}$, and $18.9\text{ cm}^3\text{ g}^{-1}$ for $\text{Pt}_{64}\text{Cu}_{35}\text{Te}_1\text{@UIO-67}$, both of which are lower than that of UIO-67 ($27.1\text{ cm}^3\text{ g}^{-1}$), due to the introduction of MTe NWs.

Catalytic performance

The catalytic process is described in Supplementary information (Scheme S1). The effectiveness of nanocable catalysts PtTe@UIO-67 and PtCuTe@UIO-67 in the

Figure 4 Catalysis results for the RWGS reaction. CO_2 conversion and CO selectivity of the catalysts at 400°C , 2 MPa, $\text{H}_2:\text{CO}_2 = 3:1$, and $24,000\text{ mL h}^{-1}\text{ g}^{-1}$ space velocity (left abscissa; orange, red, and black columns). CO_2 conversion and CO selectivity under different reaction conditions for a $\text{Pt}_{99}\text{Te}_1\text{@UIO-67}$ catalyst at $24,000\text{ mL h}^{-1}\text{ g}^{-1}$ space velocity (right abscissa): 2 MPa, $\text{H}_2:\text{CO}_2 = 3:1$ (green columns); 400°C , $\text{H}_2:\text{CO}_2 = 3:1$ (blue columns); 400°C , 2 MPa (deep red columns).

RWGS reaction is shown in Fig. 4. At 400°C, UIO-67 has no effect on CO₂ conversion, and 2.69% CO₂ conversion of Pt₆₄Cu₃₅Te₁ NWs is less than that of Pt₆₄Cu₃₅Te₁@UIO-67 (22.06%). It is well accepted in the reported literature that oxygen vacancies play an important role in the RWGS reaction [62–64]. UIO-67 is a Zr-based oxide component in our experiment, which not only provides oxygen vacancies but also prevents the nanoparticles from sintering to some extent at high temperature. So, bare catalysts without UIO-67 have poor catalytic performance. Only 4.24% CO₂ conversion is obtained for Te@UIO-67. With increasing alloy loading (Table S1), CO₂ conversion significantly increases: 7.73% for Pt₈₁Cu₁₂Te₇@UIO-67, 14.81% for Pt₈₁Cu₁₆Te₃@UIO-67, 21.79% for Pt₈₁Cu₁₈Te₁@UIO-67, and 21.57% for Pt₇₈Cu₂₁Te₁@UIO-67, and CO selectivity is all above 90% for the four types of catalysts with metal content increasing under the condition of gas volume ratio of H₂:CO₂ = 3:1, 2 MPa pressure and 24,000 mL h^{−1} g^{−1} space velocity. Further increasing the metal content has no influence on the catalytic effects, and compared with Pt₈₁Cu₁₈Te₁@UIO-67, no enhancement in CO₂ conversion is observed for Pt₇₈Cu₂₁Te₁@UIO-67. This may be because too much metal loading makes excess metal nanoparticles liable to aggregation, which abates the active sites on the catalyst and thus cannot improve the catalytic performance. Furthermore, the conversion of CO₂ changes negligibly for Pt₉₉Te₁@UIO-67, Pt₈₁Cu₁₈Te₁@UIO-67 and Pt₆₄Cu₃₅Te₁@UIO-67, when the Cu content is increased, but the CO selectivity slightly decreases from 99.86% to 93.04%. Importantly, TEM images of the MTe@UIO-67 sample after 40 h of catalysis at 400°C (Fig. S15) clearly show that Pt₉₉Te₁@UIO-67 catalysts are sintered seriously; however, Pt₆₄Cu₃₅Te₁@UIO-67 also aggregates to some extent, but it still could be observed with some products which maintain dispersed well. The stability of Pt₆₄Cu₃₅Te₁@UIO-67 exhibits an improvement to some extent (Fig. S16). The reason may be that the incorporation of Cu generates an electronic effect, as shown in the Pt 4f spectrum (Fig. S17). The binding energy of Pt 4f for the PtCuTe NWs shifts negatively by about 0.3 eV compared with that of PtTe NWs, primarily due to the difference between electronegativities of Pt (2.28) and Cu (1.9), which makes the electron transfer from Cu atoms to the Pt atoms, leading to the change of Pt electronic structure [52,56,65–68]. Therefore, PtCuTe NWs combine with UIO-67 more favorably than PtTe NWs. Another possible reason is that the introduction of Cu may improve the CO tolerance of the catalyst [52].

For the nanocable catalyst Pt₉₉Te₁@UIO-67, the CO₂

conversion was only 4.73% at 350°C, and reached 21.84% at 400°C, and CO selectivity increased from 88.36% to 99.86%, which was due to the high chemical stability of CO₂. RWGS (CO₂ + H₂ = CO + H₂O, $\Delta H_{298.15\text{ K}} = +41.2\text{ kJ mol}^{-1}$) is an endothermic reaction, while the side reaction (CO₂ + 4H₂ = CH₄ + 2H₂O, $\Delta H_{298.15\text{ K}} = -165.0\text{ kJ mol}^{-1}$) is exothermic, and therefore high temperature is in favour of CO₂ conversion, improving the CO selectivity. As for their pressure dependence, CO₂ conversion was 13.63% at 1 MPa, 21.84% at 2 MPa, and 22.53% at 3 MPa. With increasing pressure, more active molecules will be produced, resulting in more interactions with metal active sites, thus boosting the rate of CO₂ hydrogenation. However, high pressure favors CO₂ methanation, and CO selectivity is decreased to 91.11% at 3 MPa. When the feed gas volume ratio $R(V_{\text{H}_2}:V_{\text{CO}_2}) = 1:1$, CO₂ conversion is only 15.44%, and with higher ratios, the CO₂ conversion continues to increase as follows: 21.84% at $R = 3$ and 23.40% at $R = 5$. Table S2 compared our results with literature results. The stability of the catalytic performance was also investigated. CO₂ conversion (Fig. S18) slightly decreases but is still approximately at the 20% level, and CO selectivity remains essentially unchanged after 40 h catalysis. The reason may be that NWs are encapsulated in the UIO-67, which could prevent NWs from aggregation to some extent (Fig. S19), and furthermore, UIO-67 converts into ZrO₂ at high temperature (Fig. S20), which also well supports the RWGS reaction. So the stability of Pt₉₉Te₁@UIO-67 can be maintained although its structure has been changed. PXRD patterns of the sample after catalysis prove the framework of UIO-67 has converted into ZrO₂. It was reported that C–C bond started cleavage between the phenyl ring and the carboxylic acid group at high temperature, and benzene was detected as fragment by TG-MS experiment [48,69], indicating that its ligands converted into benzene.

Two models have been proposed to elucidate the CO₂ hydrogenation to form CO in the RWGS reaction: the so-called redox mechanism and the formate decomposition mechanism. In the redox mechanism, CO₂ oxidizes the metal catalyst to generate CO, and then H₂ acts as a reducing agent to reduce the oxidized metal (MOx) back to its original state: CO₂ + Mⁿ⁺ → CO + MOx, MOx + H₂ → Mⁿ⁺ + H₂O [70]. In the formate decomposition mechanism, CO is formed *via* the decomposition of formate intermediate species during CO₂ hydrogenation [71]. UIO-67 in MTe@UIO-67 exhibits microporous features, which are not beneficial to the transport of formic acid molecules but are beneficial to the transport of linear CO

molecules, and formate intermediate species are more likely to produce other products in addition to CO [72,73]. These facts are contrary to our results of outstanding CO selectivity; therefore, the redox mechanism can interpret the CO₂ reduction to CO in our study. CO₂ molecules were adsorbed to the surface of catalyst support UIO-67 and then diffused to the metal active sites (Pt/PtCu nanoparticles). Finally, CO₂ molecules were dissociated and CO was produced: CO₂ + Pt/PtCu → Pt/PtCuOx + CO, Pt/PtCuOx + H₂ → H₂O + Pt/PtCu. In this process, H₂ only indirectly participated in CO formation.

CONCLUSIONS

In summary, we successfully fabricated nanocable catalysts MTe@UIO-67 resembling “sugarcoated haws on a stick”, comprising MTe NW cable cores in the center of monodispersed MTe@UIO-67 cables. The morphology and dispersion of PtCuTe@UIO-67 as catalysts can be maintained to some extent at high temperature; however, PtTe@UIO-67 aggregated and was sintered seriously. This phenomenon maybe due to the incorporation of Cu which improved the interaction between the PtCuTe NW cores and UIO-67 shells. The prepared catalysts showed excellent CO selectivity in the RWGS reaction and therefore offer a promising new strategy for the fabrication of efficient cable catalysts for CO₂ hydroconversion.

Received 24 October 2019; accepted 21 January 2020;
published online 3 March 2020

- Aminu MD, Nabavi SA, Rochelle CA, *et al.* A review of developments in carbon dioxide storage. *Appl Energy*, 2017, 208: 1389–1419
- Rahman FA, Aziz MMA, Saidur R, *et al.* Pollution to solution: Capture and sequestration of carbon dioxide (CO₂) and its utilization as a renewable energy source for a sustainable future. *Renew Sustain Energy Rev*, 2017, 71: 112–126
- Li B, Duan Y, Luebke D, *et al.* Advances in CO₂ capture technology: A patent review. *Appl Energy*, 2013, 102: 1439–1447
- Jiang X, Guan D. The global CO₂ emissions growth after international crisis and the role of international trade. *Energy Policy*, 2017, 109: 734–746
- Saeidi S, Amin NAS, Rahimpour MR. Hydrogenation of CO₂ to value-added products—A review and potential future developments. *J CO₂ Utilization*, 2014, 5: 66–81
- Goeppert A, Czaun M, Jones JP, *et al.* Recycling of carbon dioxide to methanol and derived products—closing the loop. *Chem Soc Rev*, 2014, 43: 7995–8048
- Aziz MAA, Jalil AA, Triwahyono S, *et al.* Highly active Ni-promoted mesostructured silica nanoparticles for CO₂ methanation. *Appl Catal B-Environ*, 2014, 147: 359–368
- Guo L, Sun J, Ge Q, *et al.* Recent advances in direct catalytic hydrogenation of carbon dioxide to valuable C₂₊ hydrocarbons. *J Mater Chem A*, 2018, 6: 23244–23262
- Hu B, Guild C, Suib SL. Thermal, electrochemical, and photochemical conversion of CO₂ to fuels and value-added products. *J CO₂ Utilization*, 2013, 1: 18–27
- Melaet G, Ralston WT, Li CS, *et al.* Evidence of highly active cobalt oxide catalyst for the Fischer–Tropsch synthesis and CO₂ hydrogenation. *J Am Chem Soc*, 2014, 136: 2260–2263
- Khodakov AY, Chu W, Fongarland P. Advances in the development of novel cobalt Fischer–Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels. *Chem Rev*, 2007, 107: 1692–1744
- Goguet A, Meunier FC, Tibiletti D, *et al.* Spectrokinetic investigation of reverse water-gas-shift reaction intermediates over a Pt/CeO₂ catalyst. *J Phys Chem B*, 2004, 108: 20240–20246
- Kim DH, Han SW, Yoon HS, *et al.* Reverse water gas shift reaction catalyzed by Fe nanoparticles with high catalytic activity and stability. *J Industrial Eng Chem*, 2015, 23: 67–71
- Dagle RA, Platon A, Palo DR, *et al.* PdZnAl catalysts for the reactions of water-gas-shift, methanol steam reforming, and reverse-water-gas-shift. *Appl Catal A-General*, 2008, 342: 63–68
- Tsuchiya K, Huang JD, Tominaga K. Reverse water-gas shift reaction catalyzed by mononuclear Ru complexes. *ACS Catal*, 2013, 3: 2865–2868
- Xia BY, Wu HB, Li N, *et al.* One-pot synthesis of Pt-Co alloy nanowire assemblies with tunable composition and enhanced electrocatalytic properties. *Angew Chem Int Ed*, 2015, 54: 3797–3801
- Hong W, Wang J, Wang E. Dendritic Au/Pt and Au/PtCu nanowires with enhanced electrocatalytic activity for methanol electrooxidation. *Small*, 2014, 10: 3262–3265
- Hong W, Shang C, Wang J, *et al.* Bimetallic PdPt nanowire networks with enhanced electrocatalytic activity for ethylene glycol and glycerol oxidation. *Energy Environ Sci*, 2015, 8: 2910–2915
- Sai Siddhardha RS, Kumar MA, Lakshminarayanan V, *et al.* Anti-fouling response of gold–carbon nanotubes composite for enhanced ethanol electrooxidation. *J Power Sources*, 2014, 271: 305–311
- Zhao GY, Xu CL, Guo DJ, *et al.* Template preparation of Pt–Ru and Pt nanowire array electrodes on a Ti/Si substrate for methanol electro-oxidation. *J Power Sources*, 2006, 162: 492–496
- Zhu C, Guo S, Dong S. PdM (M = Pt, Au) bimetallic alloy nanowires with enhanced electrocatalytic activity for electro-oxidation of small molecules. *Adv Mater*, 2012, 24: 2326–2331
- Qi Y, Bian T, Choi SI, *et al.* Kinetically controlled synthesis of Pt–Cu alloy concave nanocubes with high-index facets for methanol electro-oxidation. *Chem Commun*, 2014, 50: 560–562
- Fu X, Zhao Z, Wan C, *et al.* Ultrathin wavy Rh nanowires as highly effective electrocatalysts for methanol oxidation reaction with ultrahigh ECSA. *Nano Res*, 2019, 12: 211–215
- Chen B, Cheng D, Zhu J. Synthesis of PtCu nanowires in non-aqueous solvent with enhanced activity and stability for oxygen reduction reaction. *J Power Sources*, 2014, 267: 380–387
- Yu M, Wang Z, Hou C, *et al.* Nitrogen-doped Co₃O₄ mesoporous nanowire arrays as an additive-free air-cathode for flexible solid-state zinc-air batteries. *Adv Mater*, 2017, 29: 1602868
- Bai Y, Dou Y, Xie LH, *et al.* Zr-based metal–organic frameworks: design, synthesis, structure, and applications. *Chem Soc Rev*, 2016, 45: 2327–2367
- Lustig WP, Mukherjee S, Rudd ND, *et al.* Metal–organic frameworks: functional luminescent and photonic materials for sensing

- applications. *Chem Soc Rev*, 2017, 46: 3242–3285
- 28 Li JR, Sculley J, Zhou HC. Metal–organic frameworks for separations. *Chem Rev*, 2012, 112: 869–932
- 29 Huang YB, Liang J, Wang XS, *et al.* Multifunctional metal–organic framework catalysts: synergistic catalysis and tandem reactions. *Chem Soc Rev*, 2017, 46: 126–157
- 30 Zhu Y, Ciston J, Zheng B, *et al.* Unravelling surface and interfacial structures of a metal–organic framework by transmission electron microscopy. *Nat Mater*, 2017, 16: 532–536
- 31 Furukawa H, Cordova KE, O’Keeffe M, *et al.* The chemistry and applications of metal–organic frameworks. *Science*, 2013, 341: 1230444
- 32 Rowsell JLC, Yaghi OM. Metal–organic frameworks: a new class of porous materials. *Microporous Mesoporous Mater*, 2004, 73: 3–14
- 33 Liu J, Strachan DM, Thallapally PK. Enhanced noble gas adsorption in Ag@MOF-74Ni. *Chem Commun*, 2014, 50: 466–468
- 34 Wang X, Xie L, Huang KW, *et al.* A rationally designed amino-borane complex in a metal organic framework: a novel reusable hydrogen storage and size-selective reduction material. *Chem Commun*, 2015, 51: 7610–7613
- 35 Adhikari AK, Lin KS. Improving CO₂ adsorption capacities and CO₂/N₂ separation efficiencies of MOF-74(Ni, Co) by doping palladium-containing activated carbon. *Chem Eng J*, 2016, 284: 1348–1360
- 36 Zhu H, Yang X, Cranston ED, *et al.* Flexible and porous nanocellulose aerogels with high loadings of metal–organic-framework particles for separations applications. *Adv Mater*, 2016, 28: 7652–7657
- 37 Kreno LE, Leong K, Farha OK, *et al.* Metal–organic framework materials as chemical sensors. *Chem Rev*, 2012, 112: 1105–1125
- 38 Lee JY, Farha OK, Roberts J, *et al.* Metal–organic framework materials as catalysts. *Chem Soc Rev*, 2009, 38: 1450–1459
- 39 Mondloch JE, Katz MJ, Isley III WC, *et al.* Destruction of chemical warfare agents using metal–organic frameworks. *Nat Mater*, 2015, 14: 512–516
- 40 Zhou HC, Long JR, Yaghi OM. Introduction to metal–organic frameworks. *Chem Rev*, 2012, 112: 673–674
- 41 Wang X, Chen W, Zhang L, *et al.* Uncoordinated amine groups of metal–organic frameworks to anchor single Ru sites as chemoselective catalysts toward the hydrogenation of quinoline. *J Am Chem Soc*, 2017, 139: 9419–9422
- 42 Zhao C, Dai X, Yao T, *et al.* Ionic exchange of metal–organic frameworks to access single nickel sites for efficient electroreduction of CO₂. *J Am Chem Soc*, 2017, 139: 8078–8081
- 43 Zhang H, Zhao W, Zou M, *et al.* 3D, mutually embedded MOF@carbon nanotube hybrid networks for high-performance lithium-sulfur batteries. *Adv Energy Mater*, 2019, 9: 1805764
- 44 Zhang W, Wu ZY, Jiang HL, *et al.* Nanowire-directed templating synthesis of metal–organic framework nanofibers and their derived porous doped carbon nanofibers for enhanced electrocatalysis. *J Am Chem Soc*, 2014, 136: 14385–14388
- 45 Drobek M, Kim JH, Bechelany M, *et al.* MOF-based membrane encapsulated ZnO nanowires for enhanced gas sensor selectivity. *ACS Appl Mater Interfaces*, 2016, 8: 8323–8328
- 46 Zang X, Zhang X, Chang Q, *et al.* Metal-organic framework UiO-67-coated fiber for the solid-phase microextraction of nitrobenzene compounds from water. *J Sep Sci*, 2016, 39: 2770–2776
- 47 Hester P, Xu S, Liang W, *et al.* On thermal stability and catalytic reactivity of Zr-based metal–organic framework (UiO-67) encapsulated Pt catalysts. *J Catal*, 2016, 340: 85–94
- 48 Cavka JH, Jakobsen S, Olsbye U, *et al.* A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. *J Am Chem Soc*, 2008, 130: 13850–13851
- 49 Na K, Choi KM, Yaghi OM, *et al.* Metal nanocrystals embedded in single nanocrystals of MOFs give unusual selectivity as heterogeneous catalysts. *Nano Lett*, 2014, 14: 5979–5983
- 50 Qian HS, Yu SH, Gong JY, *et al.* High-quality luminescent tellurium nanowires of several nanometers in diameter and high aspect ratio synthesized by a poly(vinyl pyrrolidone)-assisted hydrothermal process. *Langmuir*, 2006, 22: 3830–3835
- 51 Huang Z, Zhou H, Chen Z, *et al.* Facile synthesis of porous Pt botryoidal nanowires and their electrochemical properties. *Electrochim Acta*, 2014, 147: 643–649
- 52 Hong W, Wang J, Wang E. Facile synthesis of PtCu nanowires with enhanced electrocatalytic activity. *Nano Res*, 2015, 8: 2308–2316
- 53 Cao X, Wang N, Jia S, *et al.* Detection of glucose based on bimetallic PtCu nanochains modified electrodes. *Anal Chem*, 2013, 85: 5040–5046
- 54 Mintsouli I, Georgieva J, Armanov S, *et al.* Pt–Cu electrocatalysts for methanol oxidation prepared by partial galvanic replacement of Cu/carbon powder precursors. *Appl Catal B-Environ*, 2013, 136–137: 160–167
- 55 Fu S, Zhu C, Shi Q, *et al.* PtCu bimetallic alloy nanotubes with porous surface for oxygen reduction reaction. *RSC Adv*, 2016, 6: 69233–69238
- 56 Su L, Shrestha S, Zhang Z, *et al.* Platinum–copper nanotube electrocatalyst with enhanced activity and durability for oxygen reduction reactions. *J Mater Chem A*, 2013, 1: 12293–12301
- 57 Xu H, Li Y, Luo X, *et al.* Monodispersed gold nanoparticles supported on a zirconium-based porous metal–organic framework and their high catalytic ability for the reverse water–gas shift reaction. *Chem Commun*, 2017, 53: 7953–7956
- 58 Zhao Y, Zhang Q, Li Y, *et al.* Large-scale synthesis of monodisperse UiO-66 crystals with tunable sizes and missing linker defects via acid/base Co-modulation. *ACS Appl Mater Interfaces*, 2017, 9: 15079–15085
- 59 Masoomi MY, Beheshti S, Morsali A. Shape control of Zn(II) metal–organic frameworks by modulation synthesis and their morphology-dependent catalytic performance. *Cryst Growth Des*, 2015, 15: 2533–2538
- 60 Cai X, Lin J, Pang M. Facile synthesis of highly uniform Fe-MIL-88B particles. *Cryst Growth Des*, 2016, 16: 3565–3568
- 61 Lu G, Li S, Guo Z, *et al.* Imparting functionality to a metal–organic framework material by controlled nanoparticle encapsulation. *Nat Chem*, 2012, 4: 310–316
- 62 Keturakis CJ, Zhu M, Gibson EK, *et al.* Dynamics of CrO₃–Fe₂O₃ catalysts during the high-temperature water-gas shift reaction: molecular structures and reactivity. *ACS Catal*, 2016, 6: 4786–4798
- 63 Cheng Z, Sherman BJ, Lo CS. Carbon dioxide activation and dissociation on ceria (110): A density functional theory study. *J Chem Phys*, 2013, 138: 014702
- 64 Daza YA, Kuhn JN. CO₂ conversion by reverse water gas shift catalysis: comparison of catalysts, mechanisms and their consequences for CO₂ conversion to liquid fuels. *RSC Adv*, 2016, 6: 49675–49691
- 65 Du C, Chen M, Wang W, *et al.* Platinum-based intermetallic nanotubes with a core–shell structure as highly active and durable catalysts for fuel cell applications. *J Power Sources*, 2013, 240: 630–635

- 66 Jiang Y, Jia Y, Zhang J, *et al.* Underpotential deposition-induced synthesis of composition-tunable Pt-Cu nanocrystals and their catalytic properties. *Chem Eur J*, 2013, 19: 3119–3124
- 67 Xu D, Liu Z, Yang H, *et al.* Solution-based evolution and enhanced methanol oxidation activity of monodisperse platinum-copper nanocubes. *Angew Chem Int Ed*, 2009, 48: 4217–4221
- 68 Yu X, Wang D, Peng Q, *et al.* Pt-M (M=Cu, Co, Ni, Fe) nanocrystals: from small nanoparticles to wormlike nanowires by oriented attachment. *Chem Eur J*, 2013, 19: 233–239
- 69 Gutterød ES, Øien-Ødegaard S, Bossers K, *et al.* CO₂ hydrogenation over Pt-containing UiO-67 Zr-MOFs—the base case. *Ind Eng Chem Res*, 2017, 56: 13206–13218
- 70 Zhao X, Xu H, Wang XX, *et al.* Monodisperse metal-organic framework nanospheres with encapsulated core-shell nanoparticles Pt/Au@Pd@{Co₂(oba)₄(3-bpdh)₂}·4H₂O for the highly selective conversion of CO₂ to CO. *ACS Appl Mater Interfaces*, 2018, 10: 15096–15103
- 71 Chen CS, Wu JH, Lai TW. Carbon dioxide hydrogenation on Cu nanoparticles. *J Phys Chem C*, 2010, 114: 15021–15028
- 72 Han Y, Xu H, Su Y, *et al.* Noble metal (Pt, Au@Pd) nanoparticles supported on metal organic framework (MOF-74) nanoshuttles as high-selectivity CO₂ conversion catalysts. *J Catal*, 2019, 370: 70–78
- 73 Andersson MP, Abild-Pedersen F, Remediakis IN, *et al.* Structure sensitivity of the methanation reaction: H₂-induced CO dissociation on nickel surfaces. *J Catal*, 2008, 255: 6–19

Acknowledgements We gratefully acknowledge the financial support from the National Natural Science Foundation of China (21371058).

Author contributions Zhang H performed the experiments, analyzed the data and wrote the draft of manuscript under the guidance of Xu H; Li Y, Pan X and Li L provided some suggestions.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Huaqian Zhang is a master candidate at East China University of Science and Technology (ECUST). Her current research interest focuses on the synthesis of functional nanomaterials and CO₂ conversion.

Haitao Xu obtained his Master and PhD degrees from the University of Science and Technology of China (USTC) in 1999 and 2002, respectively. After a postdoctoral fellowship at Tsinghua University, he became an associate professor at Tongji University in 2005. He studied in Kyushu University as a JSPS fellow in 2007. He moved to ECUST in 2009. His research focuses on multi-function materials, metal-organic frameworks, nanocatalyst, adsorption/separation, and CO₂ conversion.

纳米电缆状催化剂MTe (M=Pt, PtCu)@UIO-67的组装及其催化二氧化碳转化

张华倩, 许海涛*, 李媛媛, 潘新波, 李立双

摘要 本文以锆系金属有机骨架为载体合成了具有“糖葫芦”结构形貌的纳米电缆状催化剂 MTe (M = Pt, PtCu)@UIO-67. 首先以直径大约为8.48 nm的超细Te纳米线作为牺牲模板, 用于外延生长外部的金属粒子(Pt或PtCu), 得到具有良好分散性的电缆芯形状的MTe纳米线, 然后成功地封装在单分散的MTe@UIO-67电缆状纳米结构催化剂的中心. 采用透射电子显微镜、扫描电子显微镜、粉末X射线衍射和能谱等方法对纳米电缆催化剂的形貌结构和组成进行了表征. 本文合成的六种催化剂均表现出良好的CO产物选择性, 在高温催化后, PtCuTe@UIO-67催化剂的形貌和分散性能得到一定程度的保持, 而PtTe@UIO-67催化CO₂转化成CO的选择性可以达到99.86%.