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Base-free hydrogen generation from formaldehyde and water catalyzed by copper nanoparticles embedded on carbon sheets

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Catalytic dehydrogenation from formaldehyde and water provides a promising pathway to produce the renewable and clean energy resource of hydrogen. Copper-based heterogeneous catalysts show promises to catalytically generate hydrogen from formaldehyde. However, those catalysts incompletely dehydrogenate formaldehyde into formic acid and hydrogen in the presence of base, leading to only partial utilization of carrier. Herein, we report a simple and facile synthesis of uniform Cu nanoparticles embedded on carbon sheets (Cu@CS), which enable hydrogen generation through the complete dehydrogenation between formaldehyde and water in the absence of any additives under mild reaction conditions. The exceptional performance is linked to the unique embedded structure of catalysts by confining Cu nanoparticles within carbon sheets as well as the strong interaction between Cu and supports.

1. Introduction

The decrease in fossil fuel supply and severe fossil fuel-related environmental problems have stimulated the ever-growing and intensive efforts to seek for the renewable and clean energy resources. As a clean energy resource with a high energy density of 142 MJ kg⁻¹, hydrogen is a promising alternative of the fossil fuels.1 Unfortunately, its gaseous and explosive physicochemical properties make the transport and handling of hydrogen difficult, which might restrict its wide utilizations.² Various solid or liquid chemicals have been investigated as hydrogen storage materials for both mobile and stationary applications.^{3,4} Currently, the most promising materials are the hydrides with high hydrogen weight densities, such as ammonia borane and it's derivatives,⁵⁻¹⁰ hydrous hydrazine,¹¹ formic acid,¹²⁻¹⁸ and methanol.¹⁹⁻²⁶ Ammonia borane is a stable solid with a high theoretical gravimetric hydrogen capacity of 19.4 wt%.5,7 However, the release of hydrogen from ammonia borane entails the problem with accompany of large scale solid wastes.⁶ Although formic acid as liquid hydrogen carrier can release hydrogen at room temperature catalyzed by various homogeneous or heterogeneous catalysts,¹⁴⁻¹⁸ its relative low hydrogen content (4.4 wt%) limits its practical applications. Thus, small organic molecules with high hydrogen contents, such as methanol with a hydrogen capacity of 12.5 wt% and formaldehyde with a hydrogen capacity of 6.7 wt%, would be better choices as liquid hydrogen carriers.

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Advances have now been made in the developments of various catalytic systems for the low-temperature hydrogen generation from methanol or formaldehyde.¹⁹⁻³⁶ Compared with the endothermic process for hydrogen generation from methanol and water, the exothermic process from formaldehyde and water should provide a stronger driving force for H₂ production.²⁹ Most of the successful systems are catalyzed by homogeneous noble metal complexes (e.g. Rh, Ru, Ir).^{19,23,24,26,31} Generally, the sophisticated ligands, strong base and/or other additives are required to promote the efficient hydrogen generation under mild conditions. Among them, the complete dehydrogenation between water and formaldehyde with the release of H₂ and CO₂ can further improve the effective hydrogen content from 6.7 wt% of formaldehyde to 8.4 wt% of formaldehyde and water. Noble metal Ru and Ir complexes have been reported to deliver high catalytic performance for dehydrogenation between formaldehyde and water.27,28,30

Nevertheless, the separation and recycle of those expensive catalysts from the homogeneous hydrogen generation system are difficult and costly. Moreover, some of those homogeneous noble metal catalysts might be sensitive to air and decompose under oxidative conditions.¹⁹ Also, their catalytic activities are highly dependent on the basicity of reaction solution and/or assisted by other additives, leading to the harsh reaction environments and additional cost for the reactors with high resistance to the basic corrosion. Therefore, the developments of the heterogeneous catalysts based on earth-abundant metals (e.g. Fe, Co, Ni, Cu) with copious supply are important to realize sustainable hydrogen generation from formaldehyde and water. Among various transition metals, heterogeneous copper nanocatalysts delivered the capability for efficient catalytic dehydrogenation.^{25,37-43} The Cu-based nanoparticles anchored on supports have been reported to catalyze formaldehyde into hydrogen and formic acid under room temperature with basic additives.³⁷⁻³⁹ The incomplete

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dehydrogenation of formaldehyde leads to the significantly decreased hydrogen content of 4.2*wt%* compared with the theoretical value of 8.4 *wt%*. Also, the formed formates might corrode the metal catalysts, leading to their poor catalytic stability.³⁷ In addition, the Cannizzaro reaction of formaldehyde could happen under the high concentration of base, lowering the effective hydrogen storage content.³⁸ In this case, it is of great significance to realize the complete dehydrogenation from formaldehyde and water, which is catalyzed by non-noble metal heterogeneous catalysts in the absence of base and other additives under the mild conditions.

Herein, we report a base-free hydrogen generation through the completed dehydrogenation from formaldehyde and water catalyzed by Cu nanoparticles embedded on carbon sheets (Cu@CS). The Cu@CS catalysts were synthesized by a facile and cost-effective pyrolysis of the solid mixture of Cu²⁺ and chitosan under argon (Ar) atmosphere. Experimental results showed that one molecule of formaldehyde and one molecule of water were completely transformed into two molecules of H₂ and one molecule of CO₂. The hydrogen generation rate reached 1.15 mol mol_{Cu}⁻¹ h⁻¹ at 120 °C and remained catalytic activity for at least 50 h. Control experiments, kinetic and X-ray photoelectron spectroscopy (XPS) analysis exhibited that the unique embedded structures of Cu@CS catalysts not only stabilized the Cu nanoparticles during the hydrogen generation reaction but also promoted their catalytic activity.

2. Experimental

2.1 Sample preparation and characterization

Materials: All chemicals were purchased from commercial suppliers and used as provided: $Cu(NO_3)_2 \cdot 3H_2O$ (Energy Chemical, 99%), Chitosan (TCI, 200-600mPa.s, 0.5% Acetic Acid at 20 °C), Acetic acid (Sigma-Aldrich, 99.7%), Formaldehyde (Alfa Aesar, 37 *wt*% in aq. soln., ACS, 36.5-38.0%, stab. with 10-15% methanol Liquid), D₂O (Energy Chemical, 99.9% D, for NMR), sodium hydroxide (Sigma-Aldrich, \geq 97%).

Synthesis of Cu@CS catalysts. Briefly, Cu(NO₃)₂·3H₂O (473 mg) and chitosan (500 mg) were dissolved in 80 mL of 1.25 *wt%* acetic acid solution and adequately mixed under stirring to obtain the blue Cu-chitosan solution at 80 °C. After dried at 100 °C overnight, the obtained Cu-chitosan precursor was pyrolyzed at 600 °C for 2 h with heating rate of 1 °C min⁻¹ under Ar atmosphere.

Synthesis of carbon particles (C). In the absence of copper salts, 500 mg of chitosan dissolved in 80 mL of 1.25 *wt*% acetic acid solution under stirring to obtain the transparent solution at 80 °C. After dried at 100 °C overnight, the obtained precursor was pyrolyzed at 600 °C for 2 h with heating rate of 1 °C min⁻¹ under Ar atmosphere.

Chemical etching of Cu nanoparticles of Cu@CS. Typically, 200 mg of Cu@CS was dispersed in a round-bottom flask contained 20 mL of 1 M HNO₃ with reflux condensation at 80 °C for 20 h. And then, the obtained carbon sheets were washed with deionized water for several times until the solution pH at 7. Synthesis of Cu/C catalysts. Cu nanoparticles supported on C

with 10 *wt%* metal loading were prepared through a wet impregnation method. Briefly, 200 mg^D of 10.1510 ports were dispersed in a 15 mL of ethanol solution with 0.3125 mmol Cu(NO₃)₂·3H₂O. Then, the ethanol solution was evaporated at 40 °C after continuous stirring for several hours at room temperature, and the obtained solid catalysts were dried overnight at 60 °C. Finally, the catalysts were treated with 5 *vol*% H₂/Ar at 300 °C for 2 h with a ramping rate of 1 °C min⁻¹.

Characterization. The structure and composition of the samples were monitored by powder X-ray diffraction (XRD, Cu Ka Shimadzu XRD-6000), Transmission electron radiation, microscopy (TEM, Hitachi HT-7700) with an accelerating voltage of 120 kV and high-resolution TEM (FEI Tecnai G2 F20 S-TWIN) with an accelerating voltage of 200 kV were performed to analyze the microstructures of Cu@CS catalysts. The yield of hydrogen was analyzed by gas-chromatography (Techcomp GC 7900). The X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB Xi+) was measured Fisher with monochromatic Al K α line. The mass spectrum was obtained on a Pfeiffer Vacuum instrument with model GSD 320 O2. The Cu content of Cu-based catalysts were identified by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 350D ICP-MS). The Brunauer-Emmett-Teller (BET) specific surface areas of catalysts are measured from the nitrogen adsorption-desorption isotherms at 77 K (Quadrasorb si-3).

2.2. Catalytic activity test.

In general reaction conditions, 5 mg of Cu@CS catalysts were added to 4.3 mL of solution with various concentration of formaldehyde in a 30 mL sealed glass bottle. After bubbled with argon for 30 min, the hydrogen generation between formaldehyde and water were proceeded at certain temperatures (100, 110, 120, and 130 °C) with reflux condensation. For other catalysts, 20 mg of carbon sheets, carbon particles (C) and Cu/C catalysts were used. For quantifying the generated hydrogen, 100 μ L of gases was taken out from the vessel and tested by GC at intervals. The hydrogen generation rates were normalized based on each exposed Cu atoms to avoid the affection of morphology, specific surface area and the size of Cu nanoparticles.

3. Results and discussion

Synthetic schematic of the Cu@CS catalysts was illustrated in Figure 1a. Typically, Cu(NO₃)₂·3H₂O and chitosan were dissolved in 1.25 *wt%* acetic acid aqueous solution and mixed under the vigorous stirring to obtain the blue Cu-chitosan solution. After drying at 100 °C overnight, the obtained Cu-chitosan precursors were pyrolyzed under Ar atmosphere. The powder X-ray diffraction (XRD) patterns of as-synthesized Cu@CS exhibited three diffraction peaks at 43.3, 50.5 and 74.2°, which corresponded to the characteristic diffraction peaks of (111), (200) and (220) lattice planes of the cubic phase metallic Cu (PDF No. 65-9026), respectively (Figure 1b). Transmission electron microscopy (TEM) image of the Cu@CS catalysts

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HCHO + H2O HCHO + H2O + Cu@C 600 °C 0.016 - Cu@CS Ar je 0.012 ,0. 00.00 H 0.6 0.00 0.000

Figure 2 Catalytic hydrogen production from formaldehyde and water. (a) Plots of hydrogen production vs reaction time under various conditions. Reaction conditions: 5 or 0 mg of the Cu@CS catalysts, 4.3 mL of aqueous HCHO solution (0 M/0.70 M) and 120 °C. Ar. (b) Hydrogen release rates in aqueous HCHO solution with various concentrations. Reaction conditions: 5 mg of the Cu@CS catalysts, 4.3 mL of aqueous HCHO solutions with various concentrations and 120 °C, Ar. (c) Hydrogen production rates under various reaction temperatures. Reaction conditions: 5 mg of the Cu@CS catalysts, 4.3 mL of aqueous HCHO solution (0.70 M) and various temperatures, Ar.

0.70 1.18 C(HCHO) (M)

catalysts (Figure S4a[†]). As a parallel, the carbon particles were also synthesized through the direct pyrolysis of chitosan without Cu²⁺ ions by the identical synthetic procedure of the Cu@CS catalysts (Figure S4b[†]). Both of the carbon sheets and carbon particles delivered bare catalytic activity for the hydrogen generation from formaldehyde and water under the same conditions (Figure S5a[†] and Figure S5b[†]). Meanwhile, the Cu@CS catalysts also catalyzed the hydrogen generation under air atmosphere. As shown in Figure S6a[†], the H₂ production was increased for initial 6 h reaction and then tend to balance under the same reaction conditions. The disappeared catalytic activity of Cu@CS during the hydrogen generation in the air atmosphere can be attributed to the partial oxidized surface of Cu to Cu_2O obtained from the XRD pattern (Figure S6b⁺). Therefore, these control experiments suggested that the metallic Cu nanoparticles in the Cu@CS catalysts served as the catalytic active components for the catalytic hydrogen generation from the formaldehyde and water system.

The effects of the dosage of catalysts, concentrations of formaldehyde and reaction temperatures were also investigated. Although the hydrogen production could be increased with the increase of catalyst dosage, the rates were decreased from 1.15 mol mol_{Cu} -1 h-1 to 1.02 mol mol_{Cu} -1 h-1 and then to 0.65 mol mol_{cu}⁻¹ h⁻¹ for the 5 mg, 10 mg and 20 mg catalysts, respectively, as shown in Figure S7[†]. Thus, the 5 mg of Cu@CS was selected as the optimized catalyst dosage for the hydrogen generation. With the increase of the concentrations of formaldehyde, the hydrogen generation rates initially increased and then decreased, as shown in Figure 2b and Figure S8[†]. The highest hydrogen generation rate of 1.15 mol mol_{Cu}⁻¹ h⁻¹ could be yielded with the concentration of formaldehyde of 0.7 M. Meanwhile, with the increase of the reaction temperatures from 100 °C, to 110 °C, 120 °C and then 130 °C, the hydrogen release rates increased from 0.55 mol mol_{cu}⁻¹ h⁻¹, to 0.88 mol mol_{Cu} ⁻¹ h⁻¹, 1.15 mol mol_{Cu} ⁻¹ h⁻¹ and then 1.67 mol mol_{Cu}⁻¹ h⁻¹, respectively (Figure 2c and Figure S9[†]). In addition, the hydrogen production could be occurred even at 30 °C by the Cu@CS catalysts in the presence of base (Figure S10[†]).

To understand hydrogen generation through such a dehydrogenation process of the aqueous formaldehyde solution, the generated gases were analyzed by GC to monitor their compositions and yields. Generally, the hydrogen release from formaldehyde and water involves three steps: (1) the

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Figure 1 Synthesis and characterization of catalysts (a) Schematic illustration of synthesis of the Cu@CS catalysts. (b) XRD pattern, (c) TEM image and (d) HRTEM image of the Cu@CS catalysts.

showed that Cu nanoparticles with an average size of 14.6 ± 4.0 nm were uniformly embedded within carbon sheets (Figure 1c and Figure S1a[†]). As shown in Figure 1d, the measured lattice fringe spacing of 1.806 Å could be well ascribed to the (200) crystal face of metallic Cu, consistent with the XRD measurements. Also, the Cu nanoparticles were surrounded by amorphous carbon sheets, observed from the high resolution TEM image. The actual Cu content in the Cu@CS catalysts was 52.8 wt%, determined by ICP-MS measurements. Meanwhile, the specific surface area of Cu@CS could be measured as 107.7 m² g⁻¹ with average pore size of 1.13 nm from the Brunauer-Emmett-Teller (BET) analysis (Figure S2[†]).

The Cu@CS catalysts were used to catalyze the hydrogen generation through dehydrogenation from formaldehyde and water. In general reaction conditions, 5 mg of the Cu@CS catalysts were added into 4.3 mL of aqueous formaldehyde solution with various concentrations in air-tight glass bottles (30 After degassed with Ar for 30 min, the hydrogen mL). generation reactions were proceeded at 120 °C. In the presence of only catalysts, formaldehyde and water, the Cu@CS catalysts gave a linearly increased hydrogen production with a rate of 1.15 mol mol_{Cu}^{-1} h⁻¹ (Figure 2a). On the contrary, there was no hydrogen generation in the absence of the Cu@CS catalysts under the same reaction conditions, indicating their catalytic capability for dehydrogenation between formaldehyde and water. Also, there was no hydrogen produced from the hot water with or without the Cu@CS catalysts, suggesting formaldehyde indeed involved in hydrogen production. The possible influence of small amount methanol in formaldehyde solution can be excluded by the no hydrogen generation from methanol solution with the Cu@CS catalysts under the same reaction conditions (Figure S3[†]). Importantly, no base and any other additives were required for this catalytic hydrogen production system.

In order to understand the role of Cu and carbon for hydrogen generation, the copper nanoparticles of the Cu@CS catalysts were removed by nitric acid (1 M) at 80 °C. The etched catalysts left the carbon sheets with many bowl-like pits, also confirming embedded structural features of the Cu@CS the

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formation of methanediol in the aqueous formaldehyde solution; (2) the conversion of methanediol into formic acid with the release of one hydrogen molecule; and (3) subsequent decomposition of formic acid with the release of one more hydrogen molecule and one CO₂ molecule.²⁷ Thus, the complete dehydrogenation between formaldehyde and water should give two molecules of H₂ and one molecule of CO₂. For the Cu@CS catalyzed reaction, both H_2 and $CO_2\ could$ be released from the initial period (Figure 3a). However, the molar ratio of H₂: CO₂ was 4.27:1 much larger than the theoretical value of 2:1. The phenomenon can be attributed to the dehydrogenation of methanediol to formic acid³⁶ and the dissolution of CO₂ in formaldehyde and water at the initial stage of the hydrogen generation. Afterwards, the molar ratios of H₂:CO₂ could be fluctuated around 2:1, indicating the complete dehydrogenation between formaldehyde and water.

Based on the above analysis, water should be involved in the hydrogen generation to realize the complete dehydrogenation. Detailed analysis of the dehydrogenation process exhibited that one H atom of generated H_2 molecule derived from H_2O molecule. To confirm the origin of H₂, D₂O was used to replace H₂O for the hydrogen generation. As shown in Figure 3c and Figure 3d, the hydrogen generation rate of 0.29 mol mol_{cu}⁻¹ h⁻¹ in D_2O , 3.97 times lower than the rate in H_2O , indicated that water played a crucial role in the dehydrogenation process. Meanwhile, the gaseous products were analyzed by mass spectrometry (MS). As shown in Figure 3e and Figure 3f, CO₂ molecules were detected in the gaseous phase products for both H₂O and D₂O as the reactants, suggesting their similar catalytic pathways. By comparing the hydrogen generation from H_2O and formaldehyde, the MS signal of m/z 3 for hydrogen generated from D₂O and formaldehyde was observed and assigned to HD, revealing H₂ generation with one H atom from water and another H atom from formaldehyde. While, the observation of the m/z 4.0 peak of D_2 can be attributed to the exchange of H and D between formaldehyde and D_2O . Therefore, the analysis on the gaseous phase products by MS provided the direct evidences for both water and formaldehyde as the source of hydrogen molecule and hydrogen generation dehydrogenation between through the water and formaldehyde.

The embedded structure of Cu nanoparticles on the carbon sheets in the Cu@CS catalysts is also expected to provide a strong interaction between metal and supports, which improves both the catalytic activity and structural stability of catalysts during the reaction. In this case, the catalytic performances of Cu nanoparticles with average size of 26.7 ± 6.6 nm supported on the surface of carbon particles (Cu/C. TEM images, size distribution and XRD pattern were shown in Figure S11[†], Figure S12a[†] and Figure S13[†], respectively), and the Cu content was 9.57 wt% according to the ICP-MS results. The Cu/C samples were also tested as reference catalysts under the identical reaction conditions. Figure 4a exhibited the catalytic performance of the Cu@CS and Cu/C catalysts for the hydrogen generation from formaldehyde and water system. Obviously, the initial hydrogen generation rate of 0.61 mol mol_{Cu} -1 h-1 for the Cu/C catalysts was 1.9 times lower than the rate of the



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Figure 3 Catalytic pathway for hydrogen production from formaldehyde and water by the Cu@CS catalysts. (a) Plot of the mole of the generated H_2 and CO_2 vs reaction time. (b) Plot of the molar ratio of the generated H_2 and CO_2 as a function of reaction time. Isotope-labelling experiments of D_2O and H_2O : (c) H_2 production at 120 °C with H_2O or D_2O . (d) H_2 generation rates in H_2O and D_2O during 5 h reaction. Mass spectrogram of the gases generated form formaldehyde (e) H_2O and (f) D_2O system. Reaction conditions: 5 mg of the Cu@CS catalysts, 4.3 mL of aqueous HCHO solution (0.70 M), and 120 °C, Ar.

Cu@CS catalysts (1.15 mol $mol_{Cu}^{-1} h^{-1}$) (Figure S14[†]). More importantly, the hydrogen generation catalyzed by the Cu/C catalysts tended to be deactivated after 180 min reaction, while the hydrogen generation of the Cu@CS catalysts was linear increased steadily.

To understand their different catalytic performance, the catalysts were examined by XPS. Both of the Cu@CS and Cu/C catalysts exhibited the metallic Cu from the XPS analysis of Cu 2p peaks (Figure 4b and Figure S15†). However, the 932.1 eV binding energy of Cu 2p_{3/2} peak for the Cu@CS catalysts was higher than that of the Cu/C catalysts at 931.3 eV, indicating the more electrons transition from Cu nanoparticles to carbon sheet in the Cu@CS catalysts. The Cu 2p_{1/2} peaks also exhibited the similar tendency. In this case, the surface $Cu^{\delta+}$ fraction of the Cu@CS catalysts was higher than that of the Cu/C catalysts, due to the stronger electronic metal-support interaction (EMSI) in the Cu@CS catalysts with lager contact area between embedded Cu nanoparticles and carbon sheets. Therefore, Cu nanoparticles in the Cu@CS catalysts exhibited the lower electronic density. Previous reports have proved that the slightly positively charged Cu species in Cu nanoparticles are more efficient for the dehydrogenation between formaldehyde Published on 07 January 2019. Downloaded on 1/21/2019 1:19:33 AM

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and water.²⁵ Therefore, it is easy to understand the higher catalytic activity of the Cu@CS catalysts for hydrogen



Figure 4 Catalytic stability. (a) Hydrogen production of the Cu@CS and Cu/C catalysts. Reaction conditions: Cu@CS (5 mg) or Cu/C (20 mg), HCHO (0.70 M, 4.3 mL), and 120 °C, Ar. (b) Cu 2p XPS spectra of the Cu/C and Cu@CS catalysts. (c) Catalytic stability of hydrogen release in the Cu@CS-HCHO-H₂O system (Insert image was TEM image of the used Cu@CS catalysts). **Reaction conditions:** Cu@CS (5 mg), 4.3 mL of aqueous HCHO solution (0.70 M), and 120 °C, Ar.

production through the dehydrogenation between formaldehyde and water.

In addition, the embedded structure of the Cu@CS catalysts also benefit for their catalytic stability. To expose the catalytic stability of Cu@CS catalysts for the hydrogen generation from formaldehyde and H₂O system, the long-term durability experiments were performed by using 5 mg of Cu@CS catalysts in 4.3 mL of HCHO solution with a concentration of 0.7 M at 120 °C under Ar atmosphere. As shown in Figure 4c, hydrogen could continuously generate with average rate of 0.73 mol mol_{Cu}⁻¹ h⁻¹ for at least 50 h. Both of the unchanged morphology (Insert, Figure 4c and Figure S1b[†]) and phase (Figure S13[†]) of the used Cu@CS catalysts indicated their structural robustness and subsequent catalytic stability for the hydrogen generation from formaldehyde and water system. In contrast, the very poor catalytic stability of the Cu/C catalysts was observed, in which the hydrogen generation rate obviously decreased from the initial stage and then lost their catalytic activity after 12 h $\,$ (Figure S16a[†]). TEM image of the used Cu/C catalysts suggested the severe agglomeration of small Cu nanoparticles into large nanoparticles during the hydrogen generation process (Figure S16b[†] and Figure S12b[†]). The increased size of Cu nanoparticles led to very low activity for hydrogen generation. In contrast, the embedded Cu nanoparticles of the Cu@CS catalysts were effectively and strongly confined within the carbon matrix, suppressing the aggregation of Cu nanoparticles during the hydrogen generation and preserving their catalytic activity over a long period subsequently.

4. Conclusions

In conclusion, the Cu@CS catalysts with unique embedded structures have been developed as heterogeneous catalysts for the complete dehydrogenation of formaldehyde and water into H₂ and CO₂ with a final molar ratio of 2:1 in the absence of base media and any other additives under mild conditions. The catalysts were synthesized through a facile and cost-effective pyrolysis of Cu²⁺ and chitosan mixture. The unique embedded structure of Cu@CS can stabilize Cu nanoparticles compared with the supported catalysts, which avoids the agglomeration of Cu nanoparticles during the reaction. The embedded structure also guarantees the strong electronic interaction between Cu nanoparticles and carbon supports, which can modulate the electronic structure of the active copper and enhance their hydrogen generation activity. The exciting demonstration of Cu@CS catalysts provides the high possibility for practical applications of hydrogen generation from formaldehyde solution.

Conflicts of interest

There are no conflicts to declare.

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