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3D hierarchical porous structured carbon nanotube aerogel-supported Sn spheroidal particles: an efficient and selective catalyst for electrochemical reduction of CO₂ to formate†

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A 3D hierarchical porous structured carbon nanotube aerogel-supported Sn spheroidal particles (Sn/CNT-Agls) on carbon cloth (Sn/CNT-Agls/CC) electrode as a selective and efficient cathode for electrochemical reduction of CO₂ to formate is reported. The electrocatalytic activity of Sn/CNT-Agls/CC toward CO₂ reduction is greatly enhanced in comparison with carbon nanotube-supported Sn spheroidal particles (Sn/CNT) on carbon cloth (Sn/CNT/CC) electrodes, which is attributed to the high specific surface area, superior conductivity and excellent 3D hierarchical structure of Sn/CNT-Agls. A maximum faradaic efficiency of 82.7% for formate production has been achieved with high stability at −0.96 V. Strikingly, the selective CO₂ reduction to formate can occur at a low overpotential of 361 mV, and a large current density of 32.9 mA cm^{−2} is obtained on the Sn/CNT-Agls/CC electrode.

The conversion of CO₂ to useful carbon-based fuels is an attractive way to deal with rising CO₂ emission.¹ Recently, the electrochemical reduction of CO₂ for producing value-added fuels in aqueous solutions has attracted much attention due to its high selectivity and energy-efficiency.^{2–5} Among the various products of electrochemical reduction of CO₂, formate is one of the most important products with a high economic value.⁶ Formate is a basic organic chemical raw material, which is widely used in leather, dye, pharmaceutical and rubber industries, and it can also be directly used in fuel cells to generate electricity.^{7–10} Thus, it is very interesting to develop an electrocatalyst that can reduce CO₂ to value-added formate with high electrocatalytic activity.

To date, a great number of metal or metal oxide electrocatalysts have been used in the electrochemical reduction of CO₂ for producing formate.^{11–15} Among these various metal

electrodes, Sn-based electrodes are widely investigated because of their cost-effectiveness and nontoxicity as well as high selectivity to formate.^{16–20} Although Sn electrodes exhibit high faradaic efficiency toward CO₂ reduction, a poor current density and production rate are observed during the process of electrolysis. For example, Zhang *et al.* reported an ultrafine nanostructured Sn catalyst and achieved a high faradaic efficiency of ~93% for producing formate with a current density of ~5.4 mA cm^{−2} at −1.8 V.¹⁹ Lv *et al.* explored the performance of CO₂ reduction to formate on a foil electrode and obtained the highest faradaic efficiency of ~91%, but a current density of only ~2.5 mA cm^{−2} was observed.²¹ Furthermore, the electrocatalytic activity toward CO₂ reduction exhibits a strong dependence on the structure and morphology of the electrocatalysts. As previously reported, the faradaic efficiency for formate production is shown in a wide range from 18% to 93% over different Sn-based electrocatalysts.^{19,22–25} Therefore, developing a new morphological and structured Sn catalyst with a high current density, production rate and selectivity is still challenging and significant.

Carbon nanotube aerogel is a new kind of three-dimensional (3D) porous material with great potential in many fields because of its high specific surface area, good mechanical stability and superior conductivity.^{26,27} Although great progress has been made in carbon nanotube aerogel materials, there are no reports about metals or metal oxides supported on 3D porous carbon nanotube aerogels as electrocatalysts for the electrochemical reduction of CO₂. Such a unique structure of the electrocatalyst is very attractive, as good conductivity and multidimensional mass transfer pathways can be provided.

Herein, a 3D hierarchical porous structured Sn/CNT-Agls electrocatalyst was fabricated *via* a simple three-step process. The biggest difference from previous studies about Sn electrodes is that our study provides a hierarchical porous structured carrier for Sn electrocatalysts. This unique structure of the electrocatalyst leads to a significant increase of current density toward CO₂ reduction and the reasons can be attributed to the following two points. Firstly, the 3D porous structured CNT-Agls

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catalyst carrier can provide better mass transfer pathways for the CO_2 reduction reaction. Therefore, the reactants (CO_2) can be more easily exposed to catalytically active sites (Sn). Secondly, the 3D porous structured CNT-Agls catalyst carrier has excellent conductivity, which can greatly accelerate the electron transfer rate during the reaction. We found that the as-prepared Sn/CNT-Agls/CC electrode exhibited excellent catalytic performance toward CO_2 reduction, including a large current density, a high production rate and selectivity, a good stability and a moderate overpotential. In order to evaluate the effect of the 3D hierarchical porous structure, the electrochemical and catalytic activities of 3D Sn/CNT-Agls and 2D Sn/CNT catalysts were compared.

The 3D structured Sn/CNT-Agls catalyst was fabricated by a three-step process as illustrated in Fig. 1 (see the Experimental section in the ESI† for details). Briefly, a stable hybrid aqueous suspension of CNTs, chitosan (CS) and SnCl_4 was obtained by strong ultrasonic mixing and physical crosslinking (the CS played a role of the physical crosslinking agent in this experiment). Subsequently, the as-prepared hybrid suspension was frozen to ice and then it was freeze-dried to form $\text{Sn}(\text{OH})_x/\text{CNT-Agls}$. Through the physical crosslinking and ice-template self-assembly method, the Sn^{4+} could be uniformly dispersed on the surface of the CNTs and then nucleated and grew on the CNT aerogel-skeleton. Finally, the as-prepared $\text{Sn}(\text{OH})_x/\text{CNT-Agls}$ was converted to Sn/CNT-Agls *via* a simple calcination reduction process under an H_2 atmosphere. The weighing result reveals that the density of the as-prepared Sn/CNT-Agls is only 16.2 mg cm^{-3} .

The morphology and microstructure of the as-prepared Sn/CNT-Agls and Sn/CNT were characterized by SEM, TEM and BET. As shown in Fig. 2a and b, the 3D structured CNT-aerogels with mesopores and macropores were successfully prepared, and the micron-sized spheroidal Sn particles nucleated in the skeleton of the CNT-aerogels. The TEM results (Fig. S3†) show that the Sn particles are not evenly dispersed in the CNT-aerogels, and the average size of the Sn particles is *ca.* $1.65 \mu\text{m}$. But, the hierarchical porous 3D structured material

was not observed in the Sn/CNT composite (Fig. S1a and c†). N_2 adsorption and desorption experiments were performed to investigate the surface area and porosity of the as-prepared samples. A typical type IV isotherm and type H4 hysteresis loop were observed for both samples (Fig. 2c). It is a typical isothermal curve of meso- and macroporous carbon materials. The specific surface area of the Sn/CNT-Agls sample ($71.3 \text{ m}^2 \text{ g}^{-1}$) increased significantly compared with the Sn/CNT sample ($33.7 \text{ m}^2 \text{ g}^{-1}$). Shown in Fig. 3b is the pore size distribution curve of the Sn/CNT-Agls sample, which was obtained by the Barrett-Joyner-Halenda (BJH) method. The pore diameter of Sn/CNT-Agls is mostly mesoporous. The average pore size of Sn/CNT-Agls is *ca.* 26.5 nm , in agreement with the SEM results (Fig. 2a and b). Consequently, it is expected that the 3D hierarchical porous structure will make the mass transfer process easier.

X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were performed to investigate the composition of the catalyst. The XRD result (Fig. S2†) confirmed the formation of metallic state Sn (PDF#86-2264) after calcination reduction under an H_2 atmosphere. Additionally, there is no obvious difference between the diffraction peaks of the Sn/CNT and Sn/CNT-Agls samples. This indicates that the nucleation and growth of Sn particles are not affected by the physical crosslinking and freeze drying processes. The XPS survey spectrum (Fig. S5a†) demonstrates that the elements Sn, O, C and N are present on the surface of the Sn/CNT-Agls, and the high resolution Sn 3d XPS spectrum (Fig. S6†) reveals that a native SnO_x layer exists on the surface of the Sn particles, which is attributed to the exposure to an ambient atmosphere (related discussion in the ESI†). In addition, no significant differences are observed between the Sn/CNT-Agls and Sn/CNT (Fig. S5a and b†).

Cyclic voltammograms (CVs) were obtained to examine the electrochemical activity of Sn/CNT-Agls/CC and Sn/CNT/CC electrodes in 0.5 M KHCO_3 saturated with CO_2 or N_2 (Fig. 3a). The oxidation peaks at *ca.* -0.16 V and 0.14 V correspond to the process in which Sn^0 is oxidized to Sn^{2+} and Sn^{4+} , respectively. The reduction peak at *ca.* 0.26 V is assigned to the process in

Fig. 1 The fabrication process of the 3D Sn/CNT-Agls catalyst. (a) Stable hybrid suspension of CNTs, CS and SnCl_4 . (b) $\text{Sn}(\text{OH})_x/\text{CNT-Agls}$ obtained by physical crosslinking self-assembly and freeze drying. (c) Sn/CNT-Agls obtained after calcination reduction under an H_2 atmosphere.

Fig. 2 Typical SEM images of Sn/CNT-Agls (a and b). Nitrogen adsorption–desorption isotherms of Sn/CNT and Sn/CNT-Agls (c) and the corresponding BJH pore size distribution curve of Sn/CNT-Agls (d).

which Sn^{4+} is reduced to Sn^0 .²⁸ For the Sn/CNT-Agls/CC electrode, the onset reduction potential under N_2 (-0.74 V) is more negative than that under CO_2 (-0.61 V). Moreover, a sharp increase of current density under both N_2 and CO_2 can be observed at more negative potentials, and the current density under N_2 is lower than that under CO_2 . The sharp increase of the current density under N_2 should be caused by the electrolysis of water (H_2 evolution reaction) and that under CO_2 is attributed to both the electrolysis of water and the reduction of CO_2 .²⁹ Obviously, the Sn/CNT-Agls/CC electrode exhibits a higher electrochemical activity than the Sn/CNT/CC electrode under CO_2 . It can be seen that the current density of the Sn/CNT-Agls/CC electrode is three times higher than that of the Sn/CNT/CC electrode, which should be caused by the high

specific surface area, multiple catalytically active sites and excellent conductive network structure of the Sn/CNT-Agls/CC electrode. Together, these results indicate that the Sn/CNT-Agls/CC electrode exhibits excellent electrocatalytic activities toward CO_2 reduction. Furthermore, the control mechanism of electrochemical reaction on the Sn/CNT-Agls/CC electrode was investigated by using the cyclic voltammograms at different sweep rates (Fig. S7†).

Electrochemical impedance spectroscopy (EIS) was performed in CO_2 saturated 0.5 M KHCO_3 electrolyte solution to investigate the kinetic behaviors on the Sn/CNT/CC and Sn/CNT-Agls/CC electrodes. It has been known from the CV results that the onset reduction potential toward CO_2 reduction is around -0.61 V. Consequently, -0.61 V was selected as the

Fig. 3 CVs of Sn/CNT-Agls/CC and Sn/CNT/CC electrodes in 0.5 M KHCO_3 saturated with CO_2 or N_2 at a sweep rate of 50 mV s⁻¹ (a). The Nyquist diagrams and fitting curves of the Sn/CNT/CC and Sn/CNT-Agls/CC electrodes in 0.5 M KHCO_3 and the inset is the fitting equivalent circuit that corresponds to the Nyquist diagrams (b).

test potential of EIS in this experiment. The Nyquist diagrams and the fitting equivalent circuit are shown in Fig. 4b and the fitting values of the electronic components in the equivalent circuit are shown in Table 1. The R_s represents the body impedance of the substrate electrode, the catalyst and the impedance caused by contact with the electrolyte solution, corresponding to the first intersection with the real axis of the Nyquist plots in the high frequency region. Because the same substrate electrode (carbon cloth) and electrolyte solution (0.5 M KHCO_3) are used, the magnitude of the R_s value indicates the change in the body impedance of the as-prepared electrocatalysts. The R_{ct} represents the charge transfer resistance, which indicates the difficulty of kinetic reaction in the electrocatalytic process. It can be seen that the R_s value of the Sn/CNT-Agls/CC electrode is smaller than that of the Sn/CNT/CC electrode. This result demonstrates that the electrical conductivity of the Sn/CNT-Agls/CC electrode improved compared with the Sn/CNT/CC electrode. Furthermore, the R_{ct} value of the Sn/CNT-Agls/CC electrode is smaller compared with the Sn/CNT electrode. This is attributed to the superior conductivity and excellent conductive network structure of the Sn/CNT-Agls. The interfacial electron transfer rate is improved and the difficulty of kinetic reaction is reduced in the process of CO_2 reduction after being crosslinked into the 3D structured Sn/CNT-Agls.

The effect of electrolysis potential on the current density and faradaic efficiency for formate production on the Sn/CNT-Agls/CC electrode was investigated by the controlled potential electrolysis method, and the results are shown in Fig. 4a. In this experiment, no CO and CH_4 were detected and the gas product was only H_2 for the Sn/CNT-Agls/CC and Sn/CNT/CC electrodes. Formate and H_2 together accounted for >99% of the reduction products in the $\text{KHCO}_3/\text{CO}_2$ electrolyte. In addition, no formate was detected for the pure CNTs/CC and CNT-Agls/CC electrodes (Fig. S8†). As previously reported for the Sn electrodes, the current density increases with the electrolysis potential.^{19,21} The faradaic efficiency for producing formate increases from -0.56 to -0.96 V and then decreases at more negative electrolysis potentials. The maximum value (82.7%) is obtained with a current density of 26.7 mA cm^{-2} at a moderate applied potential of -0.96 V. Since the $\text{CO}_2/\text{HCOO}^-$ equilibrium potential is -0.2 V vs. the RHE,³⁰ -0.96 V corresponds to 0.76 V overpotential for HCOO^- production. Additionally, at a low

Table 1 The fitting results of the EIS equivalent circuit

Electrode	R_s	R_{ct}
Sn/CNT	6.5	40.1
Sn/CNT-Agls	5.7	12.6

overpotential of 0.36 V (-0.56 V vs. the RHE), formate can still be detected on the Sn/CNT-Agls/CC electrode with a faradaic efficiency of 20.9%. Strikingly, a large current density of 32.9 mA cm^{-2} (the current density based on the Sn mass loading is 20.6 A g^{-1}) with a relatively high faradaic efficiency at -1.16 V was achieved on the Sn/CNT-Agls/CC electrode, which is the maximum of all reported values of Sn electrodes and even larger than those of most Sn gas diffusion electrodes in aqueous solution (Table S1†). The faradaic efficiency decreases as the electrolysis potential increases further, which is attributed to the enhancement of H_2 evolution, which competes with CO_2 reduction to formate under these conditions.^{31,32} The above results indicate that the appropriate potential for producing formate on the Sn/CNT-Agls/CC electrode could be around -0.96 V and the potential dependence of formate selectivity is consistent with previously reported results.³³ Further experiments were carried out on the Sn/CNT/CC and Sn/CNT-Agls/CC electrodes at -0.96 V to compare their electrocatalytic activities for the electrochemical reduction of CO_2 to formate, and the results are shown in Fig. 4b. The faradaic efficiency of the Sn/CNT-Agls/CC electrode is 1.5-fold higher than that of the Sn/CNT/CC electrode. Moreover, the current density and production rate on the Sn/CNT-Agls/CC electrode are far greater than those on the Sn/CNT/CC electrode. The above results reveal that the electrocatalytic activity of CO_2 reduction on the Sn/CNT-Agls/CC electrode is far superior to that on the Sn/CNT/CC electrode. The excellent electrocatalytic activity on the Sn/CNT-Agls/CC electrode can be attributed to the following three reasons. Firstly, the 3D hierarchical porous structured Sn/CNT-Agls shows a higher specific surface area (Fig. 2c and d) than the Sn/CNT composites. Secondly, a 3D hierarchical porous structure of Sn/CNT-Agls (Fig. 2a–d) makes all the catalytically active sites more easily accessible to the reactants, resulting in a greatly accelerated mass transfer process. Consequently, the difficulty of kinetic reaction toward CO_2

Fig. 4 Variations of the average current density and faradaic efficiency with the electrolysis potential on the Sn/CNT-Agls/CC electrode (a). Comparison of the average current density, Faraday efficiency and production rate of formate on Sn/CNT/CC and Sn/CNT-Agls/CC electrodes at -0.96 V (b).

Fig. 5 Variations of the current density and faradaic efficiency for formate production with the electrolysis time on the Sn/CNT-Agls/CC electrode at -0.96 V (a). Formate partial current density Tafel plots of the Sn/CNT-Agls/CC electrode (b).

reduction had been reduced greatly. Thirdly, the interfacial electron transfer rate had been greatly accelerated (Fig. 3b) due to the good conductivity of the Sn/CNT-Agls (Fig. 3b) and the excellent 3D conductive network structure. Together, it can be concluded that the electrocatalytic activity of Sn/CNT for producing formate is greatly enhanced after being crosslinked into the Sn/CNT-Agls.

To investigate the stability of the Sn/CNT-Agls/CC electrode during the process of CO_2 reduction, a long-term constant potential electrolysis experiment was carried out at an applied electrolysis potential of -0.96 V for 20 000 s (Fig. 5a). The faradaic efficiency for formate production was analyzed every 4000 s in the process of the electrolysis experiment. It can be seen that the Sn/CNT-Agls/CC electrode exhibits excellent stability during the long-term electrolysis experiment. A slight decrease of current density was observed during the long term process of CO_2 reduction and a faradaic efficiency of *ca.* 82% was maintained even after continuous electrolysis for 20 000 s. Furthermore, the morphology of Sn particles did not change significantly during electrolysis (Fig. S2†). Naturally, it is feasible to produce formate continuously with a high stability and faradaic efficiency on the Sn/CNT-Agls/CC electrode.

According to previously reported results, a possible mechanism of electrochemical reduction of CO_2 for producing formate on Sn electrodes is illustrated as the following 5 equations.^{18,19}

In order to determine the chemical rate-determining step (RDS) in the reaction mechanism, the Tafel analysis for the production of formate was performed on the Sn/CNT-Agls/CC electrode and the result is shown in Fig. 5b. A slope of 155 mV dec^{-1} in the low overpotential region is observed on the

Sn/CNT-Agls/CC electrode. The value is close to the slope of 118 mV dec^{-1} (120 mV dec^{-1} was reported by S. Kapusta), which suggests that the RDS was the initial single-electron transfer to hydrated CO_2 to form a surface-adsorbed $\text{CO}_2^{\bullet-}$ intermediate.^{18,34,35} Therefore, a hydrated CO_2 molecule obtains an electron to form a surface adsorbed $\text{CO}_2^{\bullet-}$ intermediate, which is the rate limiting chemical step (eqn (2)) in this experiment.

In summary, a 3D hierarchical porous structured Sn/CNT-Agls electrocatalyst for efficient electrochemical reduction of CO_2 to formate has been fabricated successfully *via* a simple three-step process. Because of the 3D hierarchical porous structure, the high specific surface area and the superior conductive network structure of Sn/CNT-Agls, the as-prepared electrode exhibits excellent electrocatalytic activity toward CO_2 reduction, including a large current density, a high faradaic efficiency and production rate, a good stability and a moderate overpotential. In addition, it will be interesting and meaningful if suitable synthetic conditions can be found to control the size of the Sn particles. Our research has opened up a new way for the preparation of high-performance 3D porous structured catalyst materials toward CO_2 reduction. It can be expected that many other metals/carbon-based 3D materials as efficient electrodes for CO_2 reduction could be prepared *via* this simple method.

Conflicts of interest

There are no conflicts to declare.

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