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Efficient Electrochemical Reduction of CO₂ to HCOOH over Sub-2 nm SnO₂ Quantum Wires with Exposed Grain Boundaries

Subiao Liu, Jing Xiao, Xue Feng Lu, Jiong Wang, Xin Wang, and Xiong Wen (David) Lou*

[*] Dr. S. Liu, Dr. X. F. Lu, Dr. J. Wang, Prof. X. Wang, Prof. X. W. Lou

School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore, 637459, (Singapore)

Email: xwlou@ntu.edu.sg; Webpage: <http://www.ntu.edu.sg/home/xwlou/>

J. Xiao

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 1H7, Canada.

Abstract

Electrochemical reduction of CO₂ to high-value products holds the potential to mitigate the environmental problems originated from CO₂ emission. Although grain boundaries (GBs) have been tailored to tune the binding energies of reaction intermediates and consequently accelerate the CO₂ reduction reaction (CO₂RR), it still remains challenging to exclusively clarify the correlation between GBs and the enhanced reactivity in nanostructured materials with small dimension (e.g., below 10 nm). Herein, sub-2 nm SnO₂ quantum wires (QWs) composed of individual quantum dots (QDs) and numerous GBs on the surface were synthesized, and examined for CO₂RR toward HCOOH formation. In contrast to SnO₂ nanoparticles (NPs) with a larger electrochemically active surface area (ECSA), the ultrathin SnO₂ QWs with exposed GBs show enhanced current density (j), significantly improved Faradaic efficiency (FE) of over 80% for HCOOH and ~90% for C1 products as well as energy efficiency (EE) of over 50% in a wide potential window, among which maximum values of FE (87.3%) and EE (52.7%) are achieved. The collective contributions of GBs, lowered work function and increased CO₂ adsorption capacity highlight the superiority of the ultrathin SnO₂ QWs as an electrocatalyst for CO₂RR toward HCOOH formation.

Keywords: CO₂ electroreduction; formic acid; C1 products; grain boundary; SnO₂.

The excessive depletion of fossil fuels worldwide has resulted in the unprecedented levels of atmospheric CO₂, which inevitably aggravates the global climate and is currently a serious environmental concern.^[1-2] To struggle against the greenhouse effect, research efforts have been extensively concentrated on the development of technologies for both reducing CO₂ emission and enabling CO₂ utilization. Commendably, advances have been achieved with varying degrees of success to produce valuable fuels by employing CO₂ as a carbon source to date.^[3-6] Among them, electrochemical CO₂ reduction reaction (CO₂RR) has been recognized as one of the most attractive and environmentally friendly approaches for reducing CO₂ emissions, especially when integrated with the utilization of renewable energies.^[7-8] Importantly, it provides a strategy to solve the storage issue associated with renewable but intermittent energy generation through the synthesis of carbon-neutral fuels. However, the inertness of CO₂ molecules and the complicated multi-electron transfer steps^[7] over most electrocatalysts during CO₂RR usually result in large thermodynamic energy barrier [i.e., high overpotential (η)], sluggish kinetics [i.e., low current density (j)] and broad distribution of target products [i.e., low Faraday efficiency (FE)]. Consequently, the more kinetically favorable reduction of protons to H₂ (i.e., hydrogen evolution reaction (HER)) always outcompetes CO₂RR, particularly in aqueous media,^[9] which further erodes the reaction selectivity. Therefore, it is imperative to develop highly active and selective electrocatalysts for efficient conversion of CO₂ into high-value fuels.

Of all energy-dense fuels, the liquid product, i.e., HCOOH, produced via CO₂RR holds particular potential as an attractive hydrogen-storage media because of its portability, stability and remarkably high volumetric capacity.^[10] In addition, HCOOH has emerged as an alternative feedstock for direct fuel cells.^[11] Although numerous materials, including nanostructured metals (e.g., Au^[12-13] and Ag^[14-15]), oxides (e.g., CuO^[8]/Cu₂O^[16] and ZnO^[17]) and chalcogenides (WSe₂^[18]/MoSe₂^[19] and Ag₂S^[20]), have previously been used to promote CO₂RR with enhanced performance toward various desired fuels,

Sn-based materials are potentially more selective for HCOOH formation through tuning the particle size, morphology and composition.^[21-24] Besides, computational studies have suggested that the broken local spatial symmetry adjacent to grain boundary (GB) can alter the binding energies of reaction intermediates, and consequently accelerate CO₂RR toward CO formation.^[25-26] Kanan's group has studied the GB effect for CO₂RR toward CO formation on flat, polycrystalline Au wires (i.e., diameter of 500 μ m) with large grain size of $\sim$ 200 μ m.^[26] However, it still remains very challenging to explicitly clarify the correlation between GBs and the enhanced reactivity in nanostructured materials with small dimension (e.g., below 10 nm). To achieve this goal, one ideal model electrocatalyst would be ultrathin one-dimensional (1D) nanostructures composed of individual ultrafine nanoparticles (NPs) with GBs exposed completely on the surface. Furthermore, 1D nanostructures have attracted extensive interests in energy storage and conversion fields because of their intriguing properties, e.g., facilitated electrical transport, shortened ion diffusion length and enlarged electrolyte-electrode contact area.^[27] To this end, ultrathin sub-2 nm 1D SnO₂ quantum wires (QWs) composed of individual quantum dots (QDs) with GBs exposed on the surface were synthesized, and evaluated as an electrocatalyst for CO₂RR toward HCOOH formation. Our results reveal that the ultrathin SnO₂ QWs deliver comparably higher j , and remarkably higher FE of HCOOH in a wide potential window as compared to the ultrafine SnO₂ NPs without exposed GBs.

The sub-2 nm SnO₂ QWs were synthesized through a modified hydrothermal method (see Supporting Information for details), and the schematic illustration on the morphology evolution from SnO₂ QDs to ultrathin QWs with time is displayed in **Figure 1a**. Specifically, ultrafine SnO₂ QDs are initially formed upon the initiation of reaction, followed by the gradual growth and interconnection of individual QDs and finally the formation of twisted QWs. X-ray diffraction (XRD) peaks of the as-prepared sub-2 nm SnO₂ QWs after completely removing oleic acid (OA) and oleylamine (OAm)

match well with the standard pattern (PDF #41-1445) of a tetragonal structure (P42/mnm), demonstrating the successful preparation of the crystallized SnO₂ QWs without impurities (Figures S1 and S2). The low- (Figure S3) and high-resolution (Figure 1b and c) transmission electron microscopy (TEM) images of the SnO₂ QWs show uniform morphology with an average diameter of ~1.7 nm (Figure 1c, Figure S4), which guarantees the substantial amount of active sites for CO₂RR. Further inspection of the QWs (Figure 1d, Figure S5) clearly verifies that the QWs are composed of individual SnO₂ QDs. The insets are images of the selected square areas in Figure 1d after being processed using fast Fourier transformation (FFT) filter, which clearly show that SnO₂ dots attach tightly with junctions (i.e., GBs) being exposed on the surface (see marked lines). Moreover, three main modes of junctions for the GB formation are observed over various SnO₂ QWs. More specifically, the interconnected SnO₂ QDs in the insets of Figure 1d originate from different planes with a certain angle (Mode I), which inevitably causes lattice distortion and induces strain on the GBs. Nevertheless, Figure 1e presents the joints of twin QDs (Mode II), where SnO₂ QDs share an interface with the same plane, together with the attachments of individual QDs (Mode III), where separate SnO₂ QDs orient precisely in series to form a rod-like single QW. All modes of GBs in the ultrathin SnO₂ QWs are thus expected to remarkably enhance the electrocatalytic activity for CO₂RR, with an emphasis on the selectivity. The crystal lattice analysis (Figure 1g) of the selected square region in Figure 1f, coupled with the corresponding selected-area electron diffraction (SAED) pattern along the zone axis of $[11\bar{3}]$ (Figure 1h), was also investigated. The periodic lattice spacing of 0.34 nm is closely aligned with the value determined by XRD result for the (110) plane of tetragonal SnO₂.

The CO₂RR catalytic activity of the ultrathin SnO₂ QWs, with bare glassy carbon electrode (GCE) as the reference, was electrochemically examined in CO₂-saturated 0.1 M KHCO₃ within a custom-built cell separated by a Nafion-117 membrane. The cathodic polarization curves of all materials were

recorded in a sweeping potential window between 0 and -1.256 V at a scan rate of 20 mV s^{-1} ; all potentials are with reference to the reversible hydrogen electrode (RHE). To persuasively clarify the enhanced catalytic activity of the ultrathin SnO_2 QWs for CO_2RR , identical measurements were also carried out for SnO_2 NPs with an average size of 5.5 nm (Figure S6) for comparison. As observed from the linear sweep voltammetry (LSV) curves in **Figure 2a**, the SnO_2 NPs reach a j value of -16.2 mA cm^{-2} at the potential of -1.256 V in the CO_2 -saturated media, whereas the ultrathin SnO_2 QWs deliver a comparably higher j value of -18.1 mA cm^{-2} , which also outperforms most of the benchmarking materials.^[22, 24]

To rule out the surface area effect due to the different morphologies of QW and NP, the electrochemically active surface area (ECSA) of both materials was determined (Figure 2b, and Figure S7, see Supporting Information for details). The ultrathin SnO_2 QWs possess a smaller ECSA ($C_{\text{dl}} = 5.7\text{ mF cm}^{-2}$) than SnO_2 NPs ($C_{\text{dl}} = 7.1\text{ mF cm}^{-2}$) perhaps due to the interconnections of SnO_2 QDs. That implies that the ~ 1.4 -fold higher specific catalytic activity of SnO_2 QWs should originate from the presence of intrinsically more active sites associated with the exposed GBs on the surface. This evidently proves the GB-enhanced effect on materials with extremely small dimension. Nonetheless, the enhanced electrocatalytic activity derived from LSV results cannot confirm the selective promotion of CO_2RR over the ultrathin SnO_2 QWs, since HER and CO_2RR often simultaneously occur in aqueous media. To discriminate the preferred occurrence of CO_2RR rather than HER, the products were further characterized after electrolyzing at various potentials (Figure S8), among which the liquid and gaseous products were quantitatively measured using high-performance liquid chromatography (HPLC) and online gas chromatography (GC), respectively. The results indicate that HCOOH is the only liquid product, together with minor gaseous products (i.e., CO and H_2), throughout the entire potential window. Currently, a consensus has been reached that higher selectivity toward HCOOH against CO is

limited to a quite narrow potential range in KHCO_3 , as demonstrated by previous studies that only one peak FE of ~80% can be achieved over different Sn-based nanostructures.^[22-24] However, the ultrathin SnO_2 QWs are extremely selective for HCOOH formation (FE of ~80%) under a wide potential window ranging from -0.856 to -1.256 V (Figure 2c), and reach a maximum FE value of 87.3% at -1.156 V (i.e., -0.82 V with iR compensation, see Figure S9 and S10), which is comparably higher than most of the state-of-the-art materials (see Table S1). For comparison, the FE toward HCOOH formation over SnO_2 NPs was also analyzed, and the results are shown in Figure 2d. Apparently, the SnO_2 NPs achieve lower FE of HCOOH throughout the entire potential range, where a remarkably lower maximum value of 61.4% is reached as compared to 87.3% on the ultrathin SnO_2 QWs.

We further synthesized SnO_2 QDs with a similar average size of ~1.9 nm as a comparison to persuasively exclude the size effect (Figure S11). Indeed, the j of SnO_2 QDs is slightly higher than that of SnO_2 NPs due to the size effect, but is still comparably lower than that of SnO_2 QWs (Figure S12a). In addition, the FEs of SnO_2 QDs are quite close to those of SnO_2 NPs, and are remarkably lower than those of SnO_2 QWs throughout the entire potential window (Figure S12b). Clearly, the enhanced j of SnO_2 QDs can be attributed to the size effect due to the smaller particle size of SnO_2 QDs than that of SnO_2 NPs. However, the slightly increased FEs of SnO_2 QDs (i.e., 1.9 nm) suggest that the different sizes of QDs (i.e., 1.9 nm) and NPs (i.e., 5.5 nm) show limited effect on the selectivity. These evidences further confirm that the enhanced catalytic activity of SnO_2 QWs should originate from the presence of intrinsically more active sites associated with the exposed GBs on the surface rather than the size effect. Despite the fact that the paralleled CO pathway strongly competes with or even deactivates the desired HCOOH generation, the easy separation of gaseous CO and liquid HCOOH makes the formation of C1 products (i.e., HCOOH and CO) also attractive during CO_2RR . Remarkably, under a potential window ranging from -0.756 to -1.256 V, the total FE for C1 products on the

ultrathin SnO₂ QWs is approaching nearly 90%, whereas the FE for H₂ is effectively suppressed within 10% (Figure 2c), indicative of high selectivity of the ultrathin SnO₂ QWs for CO₂RR over the competitive HER.

To clearly show the exclusive catalytic activities of both catalysts toward HCOOH formation during CO₂RR, the HCOOH partial current densities [$j_{(\text{HCOOH})}$] of the ultrathin SnO₂ QWs and SnO₂ NPs were determined on the basis of steady-state j and HCOOH FE at various potentials, as shown in **Figure 3a**. It is found that, at the potential of -1.156 V, the ultrathin SnO₂ QWs deliver a $j_{(\text{HCOOH})}$ of ~ 13.7 mA cm⁻², around 4.6 mA cm⁻² higher than SnO₂ NPs (~ 9.1 mA cm⁻²). More importantly, the ultrathin SnO₂ QWs need an η of only 630 mV to acquire a $j_{(\text{HCOOH})}$ of ~ 4.0 mA cm⁻², whereas the required η on SnO₂ NPs positively shifts by approximately 100 mV (Figure 3b). To achieve an equivalent HCOOH FE of 60%, the SnO₂ NPs require a remarkably higher η of 847 mV compared to η of 504 mV for ultrathin SnO₂ QWs. The large $j_{(\text{HCOOH})}$ and η differences of the ultrathin SnO₂ QWs with GBs exposed on the surface and SnO₂ NPs suggest the GB-driven electrocatalytic activity for CO₂-to-HCOOH. As a direct evaluation of the conversion efficiency of electrical energy to target product at various potentials, the energy efficiency (EE) of the ultrathin SnO₂ QWs and SnO₂ NPs was also determined (see Supporting Information for details). The relatively lower η and the comparably higher FE of SnO₂ QWs contribute to EE of over 50% in a wide potential range (Figure 3c). Moreover, the maximum EE of 52.7% is also comparable with that of the most efficient materials for the formation of HCOOH (see Table S2). In addition, the stability of the ultrathin SnO₂ QWs was also evaluated at a fixed potential of -0.956 V over an extended period. The j slightly increases due to the accumulated HCOO⁻ in the aqueous media and the gradual activation of carbon black in the catalyst ink, but roughly fluctuates at ~ 9.9 mA cm⁻² over 25,000 s (Figure 3d). Moreover, the FEs of HCOOH show negligible changes during the stability test (Figure S13). In addition, no apparent changes are

observed in composition and morphology (Figure S14), implying the good stability of the ultrathin SnO₂ QWs.

ECSA-corrected Tafel plots were shown in **Figure 4a** based on the $j_{(HCOOH)}$ at various η to gain further kinetic insights for CO₂RR in aqueous media. In contrast with the Tafel slope of 155.2 mV dec⁻¹ for SnO₂ NPs, a smaller Tafel slope of 149.5 mV dec⁻¹ is acquired over the ultrathin SnO₂ QWs^[28] which is an indication of faster surface-area-independent kinetics toward the formation of the adsorbed intermediate (i.e., CO₂⁻). The kinetic analysis further supports the fact that the exposed GBs on the ultrathin 1D SnO₂ QWs can tailor the binding energies of reaction intermediates, and consequently lead to the enhanced CO₂RR performance. Besides, investigations on how the ultrathin SnO₂ QWs affect the surface electronic states and electronic property caused by the surface terminated GBs were also carried out. The surface electronic states of the ultrathin SnO₂ QWs and SnO₂ NPs were first studied by X-ray photoelectron spectroscopy (XPS), as exhibited in Figure 4b (see also Figure S15). The peaks located at 495.5 and 487.2 eV in the Sn3d XPS spectra of the ultrathin SnO₂ QWs and SnO₂ NPs match well with the characteristic peaks assigned to Sn 3d_{3/2} and Sn 3d_{5/2} ionization states,^[22] which clearly confirms the formation of Sn(IV)O₂. Moreover, negligible shifts are observed on the spectra of the ultrathin SnO₂ QWs as compared to those of SnO₂ NPs, an indication of ignorable effect of the exposed GBs on the binding energies of Sn 3d. The work functions of the ultrathin SnO₂ QWs and SnO₂ NPs were measured by ultraviolet photoelectron spectroscopy (UPS). It has been widely accepted that the work function strongly correlates with the catalytic activity as measured by j . It is apparently observed in Figure 4c that the ultrathin SnO₂ QWs possess a lower work function (4.91 eV) than SnO₂ NPs (5.26 eV) (Figure S16), revealing the faster electron transfer properties of the former which consequently results in the promoted CO₂RR catalytic activity. The relatively low solubility of CO₂ in aqueous media, coupled with the CO₂(aq)/HCO₃⁻/CO₃²⁻ equilibrium, causes a mass transfer

constraint during CO₂RR that limits the j to about 10 mA cm⁻² under typical conditions.^[29-30] Volumetric CO₂ adsorption-desorption isotherms were thus measured to explore the CO₂ adsorption capacity over the ultrathin SnO₂ QWs and SnO₂ NPs (Figure 4d and Figure S17). The results reveal that the ultrathin SnO₂ QWs with exposed GBs can absorb more CO₂ than SnO₂ NPs. Therefore, the enhanced performance of the ultrathin SnO₂ QWs for CO₂RR might be attributed to the collective factors of existence of GBs on surface, lowered work function and increased CO₂ adsorption capacity.

In summary, we have successfully synthesized ultrathin sub-2 nm SnO₂ QWs composed of separate QDs with grain boundaries (GBs) on surface, and explored their GB-engineered electrocatalytic performance for electrochemical reduction of CO₂ to HCOOH. Remarkably, the ultrathin SnO₂ QWs with exposed GBs show significantly higher current density as compared to SnO₂ NPs. For instance, a current density of ~13.7 mA cm⁻² is reached at the potential of -1.156 V, around 4.6 mA cm⁻² higher than that of SnO₂ NPs (i.e., ~9.1 mA cm⁻²). Moreover, the ultrathin SnO₂ QWs show significantly improved Faradaic efficiency of over 80% for HCOOH and ~90% for C1 products as well as energy efficiency of over 50% in a wide potential window. These findings can significantly advance the current understanding on the correlation between grain boundary and the enhanced electrocatalytic activity for CO₂RR in nanostructured materials with extremely short dimensions.

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Figures and Captions

Figure 1. a) Schematic illustration of the formation of ultrathin sub-2 nm SnO_2 QWs; b) Low-resolution TEM image and c) statistics of diameters of ultrathin SnO_2 QWs; d) high-resolution STEM image of ultrathin SnO_2 QWs, the insets indicate the grain boundaries in the QWs (Mode I); e) high-resolution STEM image of ultrathin SnO_2 QWs showing twin-crystal (Mode II) and single attachments (Mode III); f) high-resolution STEM image and g) the enlarged square area in (f) showing the crystal lattice; h) the corresponding SAED pattern.

Figure 2. a) Cathodic LSV results of the ultrathin SnO₂ QWs and SnO₂ NPs in 0.1 M CO₂-saturated KHCO₃; b) charging j differences (Δj) plotted against scan rates; c) FE of all products over the ultrathin SnO₂ QWs and d) FE of HCOOH over the ultrathin SnO₂ QWs and SnO₂ NPs.

Figure 3. a) $j_{(HCOOH)}$ of the ultrathin SnO₂ QWs and SnO₂ NPs, $j_{(HCOOH)}$ is the partial current density of forming HCOOH; b) η at FE of ~60% and 4.0 mA cm⁻² over the ultrathin SnO₂ QWs and SnO₂ NPs; c) EE and d) long-term stability tests of the ultrathin SnO₂ QWs and SnO₂ NPs.

Figure 4. a) ECSA-corrected Tafel plots for HCOOH production; b) XPS results of Sn 3d, c) UPS plots, and d) CO₂ adsorption isotherms of the ultrathin SnO₂ QWs and SnO₂ NPs.

For Table of Content Entry

Ultrathin sub-2 nm SnO₂ quantum wires (QWs) composed of individual quantum dots with grain boundaries (GBs) being terminated on the surface were synthesized, and examined for CO₂ electrochemical reduction toward HCOOH formation. The ultrathin SnO₂ QWs deliver higher current densities, and remarkably higher Faraday efficiencies of HCOOH in a wide potential window as compared to SnO₂ nanoparticles without exposed GBs.