Testing a Silver Nanowire Catalyst for the Selective CO$_2$ Reduction in a Gas Diffusion Electrode Half-cell Setup Enabling High Mass Transport Conditions

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Abstract: In this work, we discuss the application of a gas diffusion electrode (GDE) setup for benchmarking electrocatalysts for the reductive conversion of CO$_2$ (CO$_2$RR: CO$_2$ reduction reaction). Applying a silver nanowire (Ag-NW) based catalyst, it is demonstrated that in the GDE setup conditions can be reached, which are relevant for the industrial conversion of CO$_2$ to CO. This reaction is part of the so-called 'Rheticus' process that uses the CO for the subsequent production of butanol and hexanol based on a fermentation approach. In contrast to conventional half-cell measurements using a liquid electrolyte, in the GDE setup CO$_2$RR current densities comparable to technical cells (>100 mA cm^{-2}) are reached without suffering from mass transport limitations of the CO$_2$ reactant gas. The results are of particular importance for designing CO$_2$RR catalysts exhibiting high faradaic efficiencies towards CO at technological reaction rates.

Keywords: CO$_2$ reduction · Gas diffusion electrode · Silver nanowire catalyst

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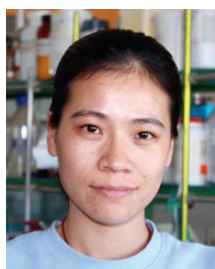
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1. Introduction

The mitigation of the increase of the greenhouse gas CO_2 in our atmosphere is one of the major societal challenges we are currently facing. The large-scale conversion of CO_2 captured from the atmosphere, into high-value products is considered a technologically feasible approach to address this goal. If combined with renewables (hydro, wind, and solar) that provide 'clean' electric power, the electrochemical CO_2 reduction (CO_2RR: CO_2 reduction reaction) is particularly interesting and significant R&D efforts are addressed to develop selective electrocatalysts.[1] A prime example of such a CO_2RR process is the so-called 'Rheticus' process which combines an electrochemical conversion of CO_2 into CO, an essential reactant for the subsequent production of butanol and hexanol based on a fermentation approach.[2] Thus the CO_2RR might become not only sustainable but also economically feasible.

In the search for cheap, abundant and selective electrocatalysts for the CO_2RR many academic studies apply so-called H-type electrochemical cells with liquid electrolyte. The cells are designed as electrochemical half-cells containing the working electrode (WE) and the reference electrode (RE) in one compartment, and the counter electrode (CE) in another one. These two compartments are separated by a membrane to avoid product crossover,[3] (Fig. 1). The reactant (CO_2 gas) is physically dissolved into the liquid electrolyte where it reaches the active catalyst *via* convection and diffusion. The advantage of such a setup is its straightforward use in screening different electrode materials under defined conditions. However, the product formation can easily be affected by mass transport limitations due to the low gas solubility in the electrolyte, which is limited to about 35 mM, as well as relative slow gas diffusion in liquids. Therefore, in liquid electrolytes the limited availability of CO_2 reactant influences the overall reaction rate as well as the product selectivity. While the CO_2 concentration at the catalyst surface is limited, water, (or protons depending on the electrolyte pH) the reactant to form H_2 gas, is readily available. As a consequence, in more applied studies often electrochemical reactors with a two (or three) electrode setup are used.[4] Such setups are technologically relevant as they allow realistic reaction rates. However, the different factors that determine such rates are often complex and

Fig. 1. Schematic drawings of a) typical measurement configuration using an H-type cell in a three-electrode configuration; the CO_2 reactant is dissolved in the liquid electrolyte b) measurement configuration using the GDE setup; the CO_2 reactant is led to the catalyst layer through the GDL and does not need to pass through liquid electrolyte; at the same time a three-electrode configuration is maintained.
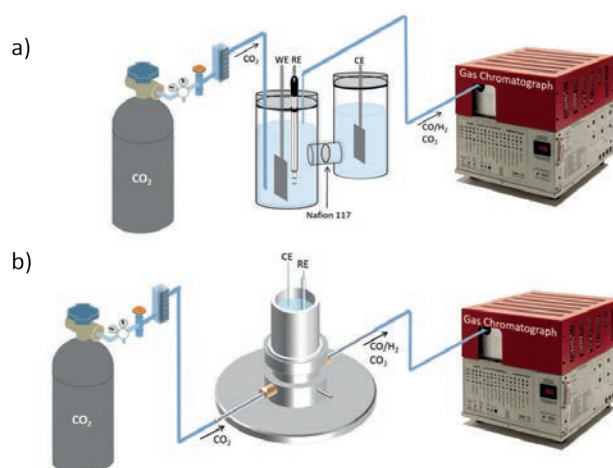
difficult to distinguish. Furthermore, cathode (CO_2RR) and anode processes (oxygen evolution reaction; OER) might influence each other and often no information of the individual electrode potentials is obtained.[5]

In the present work, we demonstrate an 'intermediate' setup that bridges measurements in H-type cells and electrochemical reactors, *i.e.* a gas diffusion electrode (GDE) setup with a three-electrode configuration. The GDE setup has originally been developed to benchmark oxygen reduction reaction (ORR) electrocatalysts under realistic mass transport conditions.[6] Similar to a real fuel cell, in the GDE setup the gaseous reactant is guided to the catalyst layer through a gas diffusion layer (GDL) avoiding mass transport limitations typically experienced when working with liquid electrolyte. The catalyst layer is not in contact with any liquid electrolyte, but instead a membrane electrolyte separates the working electrode (catalyst layer) compartment from an electrochemical cell housing the liquid electrolyte, the CE and the RE. Thus a realistic condition for the WE environment is combined with the advantages offered by a three electrode setup.[6] To investigate CO_2RR catalysts the setup has been slightly adapted, as described below. Applying a silver nanowire (Ag-NW) based catalyst that has been previously tested in an H-type cell,[7] it is demonstrated that high currents (reaction rates) can be reached without mass transport limitation of the CO_2 reactant.

2. Experimental

2.1 *Synthesis of Silver Nanowires (Ag-NWs)*

Ag-NWs were synthesized according to a modified protocol introduced by Liu *et. al.*[7] 125 mg of polyvinylpyrrolidone (M = 1,300,000 g/mol, Acros Organic) were dissolved in 20 mL of ethylene glycol (Sigma-Aldrich, 99.8%) and heated to 160 °C for 1 h in an oil bath. The solution was thoroughly agitated (320 rpm). Subsequently, 250 µL of 50 mM sodium bromide (Alfa Aesar, 99.0%) was added to the previous solution. After 15 min, 7.5 mL of 100 mM silver nitrate (Alfa Aesar, 99%) was dropwise injected within 65 min. After the complete addition of the $AgNO_3$ solution, the reaction bath was kept at 160 °C for 35 min, followed by immersion in an ice-water bath. The formed Ag-NWs were washed 3 times with acetone (Honeywell) followed by centrifugation. Finally, the Ag-NWs were thoroughly washed (3 times) with H_2O.

2.2 *Preparation of the Ag-NWs Ink*

For the preparation of the carbon-supported Ag-NW ink, 5 mg of the Ag NWs and 0.9 mg of carbon black (Vulcan XC 72R, Cabot) were separately dispersed in 10 mL of isopropanol (VLSI Selectipur, BASF) by 1 h sonication. Both suspensions were intermixed, sonicated for 1 h and dried using a Rotavapor. Thus, the obtained carbon-supported Ag-NWs were re-dispersed in 1 mL of isopropanol containing 50 µL of Nafion (5 wt.%, 15–20% water, Sigma-Aldrich). This suspension was subjected to sonication for 1 h yielding a homogeneous catalyst ink (85% Ag-NW and 15% C black).

2.3 *Electrochemical Reduction of CO_2 (CO_2RR) Using Ag-NWs as Electrocatalyst*

Gas diffusion electrodes were prepared using Sigracet 39 BC carbon paper as the GDL substrate. The Sigracet 39 BC carbon paper is covered by a microporous layer (MPL) treated with 5% of PTFE (Fuel Cell Store). The carbon paper was cut into circular pieces (2 cm in diameter) and subsequently placed onto a nylon membrane filter (pore size 0.22 µm, Fischerbrand) on top of the funnel of a vacuum filtrating system. This assembly was then covered with a paper mask bearing a central hole of 3 mm in diameter. Subsequently, 40 µL of the as-prepared carbon-supported Ag-NW ink was drop-cast on the carbon paper, thus resulting in a GDE exposed geometric surface area of 7.07×10^{-2} cm². The ob-

tained GDEs were dried at ambient conditions for at least 30 min. The employed flow-cell was assembled by placing the prepared GDE on the lower cell body, and a Sustainion X37-50 RT alkaline membrane (Dioxide materials) on top of it. 10 mL of 2 M KOH (solution pH: 14.3, ≥85%, Merck) were used as supporting electrolyte placed above the membrane. The Ag-NW catalyst had no direct contact with the supporting electrolyte. A Ag/AgCl electrode (3 M KCl, Metrohm, double junction design) and Pt wire served as reference and counter electrode, respectively. Both ECi-200 (Nordic electrochemistry) and Autolab PGSTAT128 N (Metrohm) potentiostats were used to perform the CO_2RR electrolysis experiments.

During electrolysis, a humidified CO_2 stream (16 ml min⁻¹, 99.999% Carbagas, Switzerland) was continuously fed through the channels of the stainless-steel cell body adjacent to the prepared GDEs. Potentiostatic CO_2 electrolysis experiments were carried out for 1 h at selected applied electrode potentials. To avoid a possible influence of catalyst layer degradation on the product distribution, a newly prepared GDE was used for each CO_2 electrolysis experiment. Analysis of the gaseous products was carried out every 10 min by online gas chromatography (GC) triggered by the potentiostat.

The continuous flow of humidified CO_2 was used to transport the gaseous products from the GDE flow-cell to the sample loop of the gas chromatograph (Model 8610C, SRI Instruments) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) coupled to a methanizer to detect hydrogen and carbon monoxide, respectively. To avoid damage the column of the GC, the outlet gas of the CO_2RR was passed by a drying tube to remove the excess of water (Cole-Parmer Drierite, Fisher Scientific) before reaching the sample loop of the GC. Eqn (1) was used to determine the faradaic efficiency (FE) for a given gaseous product *i*:

$$FE_i = \frac{I_i}{I_{total}} = \frac{c_i \cdot v \cdot F \cdot z}{10^6 \cdot V_m \cdot I_{total}} \qquad (1)$$

where I_i represents the partial current for the conversion of CO_2 into product *i*, c_i its concentration in ppm measured by online GC using an independent calibration standard gas (Carbagas, Switzerland), v the gas flow rate (measured by a universal flowmeter 7,000 GC by Ellutia), F represents Faraday's constant, z the number of electrons involved in the formation of the particular product, V_m the molar volume and I_{total} the total current at the time of the measurement.

Electrochemical impedance spectroscopy measurement was conducted to determine the solution resistance between RE and WE (iR drop).

The electrolyte was analyzed after the electrolysis (*post reaction*) to quantify the formate content by means of ion exchange chromatography (Metrohm Ltd., Switzerland). This chromatograph was coupled to a L-7100 pump, a separation and an ion exclusion column (Metrosep A Supp 7-250, columns) and a conductivity detector.

For comparison, the performance of the catalyst was also tested in a conventional half-cell configuration using a custom-built gas-tight H-type glass cell with a proton exchange membrane (Nafion 117, Sigma Aldrich) separating the catholyte and the anolyte. The working electrode consisted of a rectangular piece (0.8 cm × 3 cm) of a carbon paper prepared in a similar way as the electrodes for the GDE measurements. The back side and the edges of the electrode were masked with Teflon tape thus leading to a geometric surface area of 0.2 cm⁻². A single junction Ag/AgCl (saturated KCl, Pine Research) and a Pt foil (0.25 cm × 0.8 cm) were used as reference and counter electrode, respectively. Prior to the CO_2 electrolysis, the cathodic and anodic compartments

were both filled with 30 mL of 0.5 M $KHCO_3$ (ACS grade, Sigma-Aldrich) electrolyte solution and saturated with CO_2 for 30 min, achieving a final pH value of 7.2. The CO_2 flow was kept constant throughout the potentiostatic CO_2 electrolysis and enabled the transport of gaseous products from the headspace of the catholyte to the sample loop of the GC. The CO_2 electrolysis experiments in the half-cell configuration were performed in an analogous way as the ones carried out in the GDE set up. The analysis of gaseous products was carried out in intervals of 20 min. The total electrolysis time per applied potential was 1 hour

The catalyst layers were characterized before and after CO_2 electroreduction by means of scanning electron microscopy (Zeiss Gemini 450 SEM equipped with an Inlens SE detector). An accelerating voltage of 1.5 kV was applied at a working distance of 2–3 mm.

3. Results and Discussion

Potentiostatic CO_2 electroreduction experiments on carbon-supported Ag-NWs (85 wt.% Ag-NWs and 15 wt.% of C black) were carried out in the GDE setup to investigate their activity and selectivity as a function of the applied electrolysis potential. Fig. 2 displays the resulting potential-dependent product distribution in terms of faradaic efficiencies (FEs, panel a) and partial current densities (PCDs, panel b). CO and H_2 were the only gaseous products detected by GC analysis. As a third product formate could be detected and quantified *post reaction* in the (liquid) electrolyte compartment of the cell (see Fig. 1) by means of ionic exchange chromatography. Note that in our experiments, the FE of formate is substantially higher than the typically reported values on polycrystalline Ag electrocatalysts (commonly ~ 8% at -1.4 V vs RHE).[8]

The FE vs E plot (Fig. 2a) can be subdivided into three characteristic sections. Hydrogen is the predominant electrolysis product in the first potential regime (> –1.55 V vs Ag/AgCl) with FE_{H2} values never dropping below to 40%, while FE_{CO} does not exceed 35%. In the second characteristic potential section ranging from –1.55 to –1.9 V vs Ag/AgCl FE_{H2} starts to decrease and the CO efficiency passes a maximum of about 70% at –1.75 V vs Ag/AgCl. From Fig. 2a it becomes evident that the FE values for CO and H_2 are strongly anti-correlated to each other, similar to what is known from polycrystalline Ag catalysts tested in a liquid electrolysis environment.[8c] Formate appears as a by-product of the CO_2 electrolysis at applied potentials of < –1.6 V vs Ag/AgCl and reaches a maximum of about 25% at –1.9 V vs Ag/AgCl. In the third characteristic section of the FE vs E plot, at E < –1.9 V

vs Ag/AgCl, the parasitic HER becomes the dominant electrolysis process on the expense of the CO_2RR.

The corresponding potential-dependent PCDs for CO, H_2 and formate production are displayed in Fig. 2b. It is seen that by using gas diffusion electrodes, CO_2RR current densities can be achieved which are ~1 order of magnitude higher than the ones typically observed in classical half-cell electrolysis measurements carried out in unstirred aqueous electrolytes.[9] In the present case, a PCD_{CO} of ~130 mA cm^{-2} (normalized to the geometric surface area) at FE_{CO} = 70% was determined at a potential of ~ –1.78 V vs Ag/AgCl. Pre-screening experiments on the same catalyst, carried out in classical H-type half-cell arrangements, resulted in a higher selectivity of the Ag-NWs reaching CO faradaic efficiencies of >95% (Fig. 3), those results are comparable to the previously reported results by Liu *et. al.* However, the PCD for CO production was substantially higher in this present study. Liu *et. al.* reported a maximum PCD for CO of –3 mAcm^{-2} at ~ –1.2 V vs RHE[7] whereas in our pre-screening experiments a maximum PCD of ~16 mA cm^{-2} was achieved at a potential of –1.73 V vs Ag/AgCl.

As discussed above, the significantly lower CO_2RR current densities in the conventional H-type cells using aqueous electrolyte environment as compared to the GDE setup can be explained by transport limitations. In the liquid electrolyte the CO_2 solubility is limited and diffusion significantly inhibited as compared to the gas phase. A direct comparison of the overpotentials in both setups is less straightforward. The thermodynamic CO_2 reduction potentials are pH and product dependent. At pH 7 the reduction potential of CO_2 to CO with respect to NHE (recall that at pH 7 and 1 atm of H_2, the H_2/H^+ couple is –0.420 V) is:[10]

$$CO_2 \text{ (g)} + 2\,H^+ + 2\,e^- \rightarrow CO \text{ (g)} + H_2O, \; E°_{redox} = -0.520\text{ V}$$

Thus in both setups significant overpotentials are observed. To refer to the pH-independent RHE scale one needs to establish the pH of the reaction environment. In the conventional H-type cell this is straightforward and all measured electrode potentials can be easily plotted on an RHE scale. In the GDE setup the pH at the RE might be different from the one the catalyst experiences. Thus a referral to RHE with regard of the pH in the liquid electrolyte enclosing the RE might lead to misleading shifts in the reduction potentials.

It should be further noted that it is expected that both the partial CO_2RR current densities and the corresponding faradaic efficiencies observed for the Ag-NW catalyst in the GDE setup can be further improved. In the GDE setup the overall GDE performance
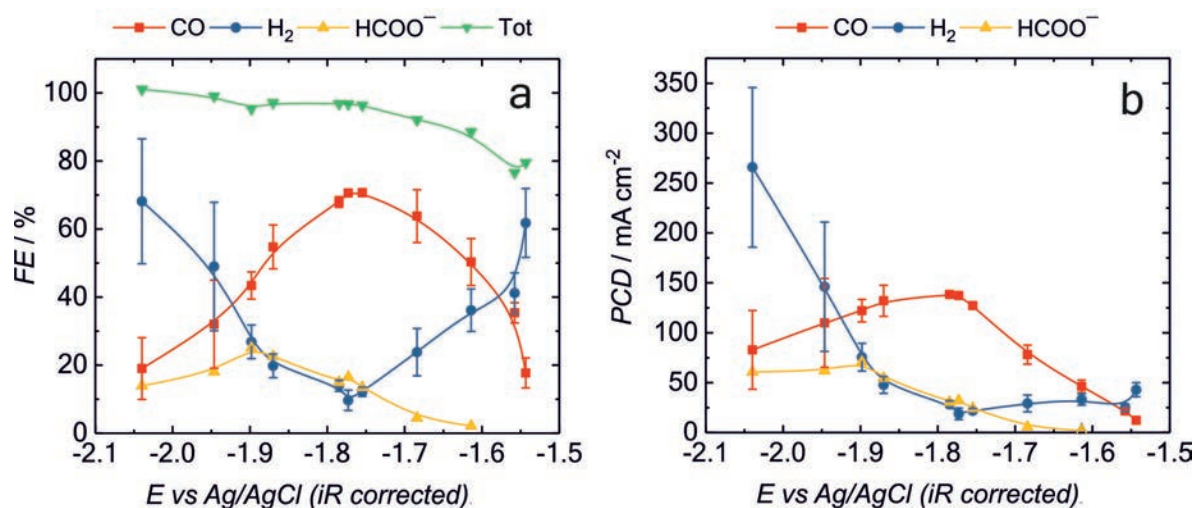

Fig. 2. a) Product distribution of the CO_2RR carried out in the new GDE cell set-up over Ag-NW based electrocatalysts (85% wt.% Ag NW and 15% wt.% of C) at different applied potentials (2 M KOH electrolyte); each value for FE_{CO} and FE_{H2} is the average from six measurements taken every 10 min for in total 1 h of electrolysis; the error bars indicate the standard deviation; b) corresponding partial current densities (PCDs).
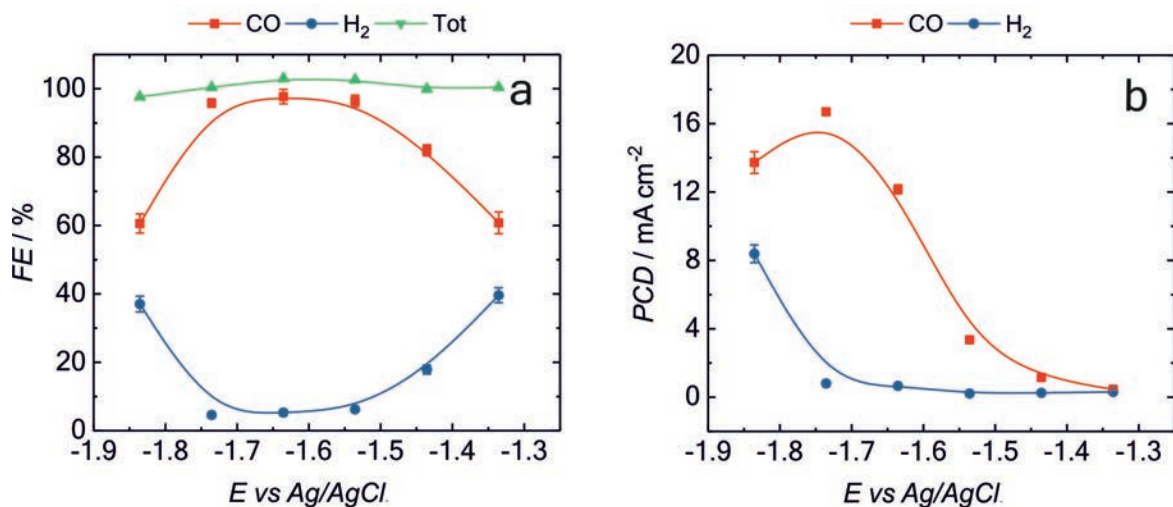
Fig. 3. a) Product distribution of the CO_2RR carried out in an H-type cell over Ag-NW based electrocatalysts (85% wt.% Ag NW and 15% wt.% C) at different applied potentials (0.5 M $KHCO_3$ electrolyte); b) corresponding partial current densities (PCDs).

depends not only on the intrinsic electrocatalytic properties of the Ag-NWs but also on their particular mass loading, their spatial distribution inside the GDE, the local pH as well as the pore distribution. For example, in initial tests of the GDE setup with the same Ag-NW catalyst, a Nafion membrane and/or acidic electrolyte in the upper compartment were used. This led to a significant increase in hydrogen production (FE_{H_2}) and almost no CO could be detected (not shown). We addressed this behavior to the acidic pH of Nafion and a simple exchange of the membrane and electrolyte in the CE and RE compartment led to a drastic improvement in CO formation.

Not only are the activity and selectivity of importance for the evaluation of the overall catalyst performance but also its stability. Particularly the higher current densities at higher applied overpotentials might lead to an undesired detachment of the active NWs from the carbon support or might cause other structural degradation processes. Therefore, in an effort to shed light into this issue, identical location (IL) scanning electron microscopy was applied to the Ag-NWs catalyst before (Fig. 4a,b) and after (Fig. 4c,d) the CO_2 electrolysis. The carbon-supported Ag-NW/C catalyst was stressed for 133 min at –0.83 V vs RHE (total charge density

2,453C cm^{-2}). Clearly, there are no severe morphological changes visible in the IL-SEM inspection by comparing the catalyst morphology at the same location before and after CO_2 electrolysis, suggesting that the Ag-NW/C catalyst exhibits superior structural stability, at least under the given experimental conditions.

4. Conclusions

Herein we present a study of a Ag-NW catalyst for the selective CO_2RR to CO. The catalyst performance has been tested in a GDE setup allowing high CO_2 reactant mass transport as well as in a classic H-type cell using liquid electrolyte. In the GDE setup current densities sufficient for technological applications (>100 mA cm^{-2}) are reached with FE_{CO} up to 70%, depending on the applied electrode potential. Comparison to the same catalyst in liquid electrolyte environment suggests that the FE towards CO can be further improved by optimizing the catalyst layer with respect to mass loading, spatial distribution, pore distribution, local pH, *etc*. Our results highlight that for technical applications, catalyst testing in H-type cells and aqueous electrolyte environment is not sufficient, and GDE setups such as the one presented in this work can bridge basic and applied catalyst development.
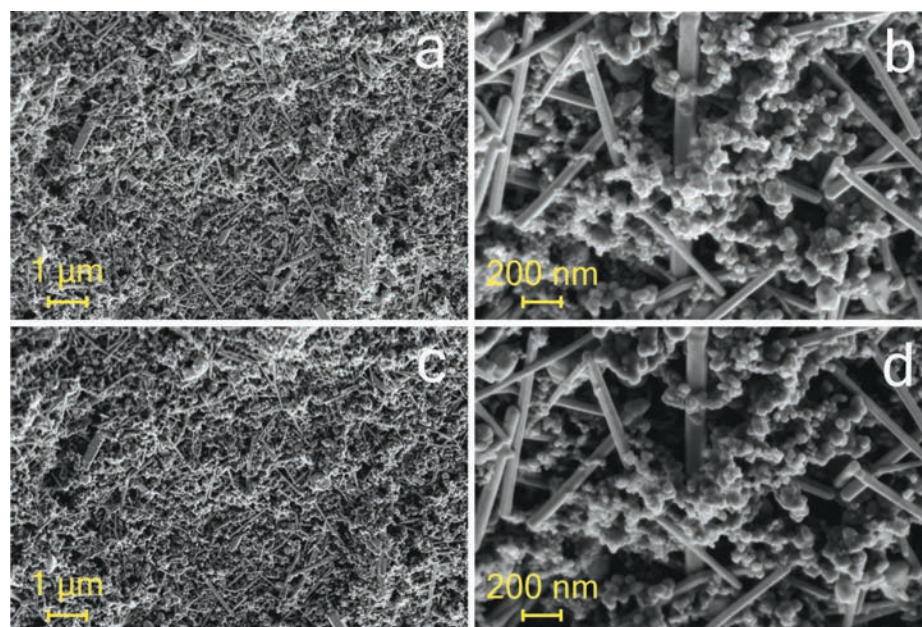

Fig. 4. Identical location (IL) analysis of the Ag NW before (a,b) and after (c,d) performing the CO_2 electrolysis at –0.83 V vs RHE for 133 min (total charge density applied = 2,453C cm^{-2}).

Notes

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