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Dealloying assisted high-yield growth of surfactant-free <110> highly active Cu-doped CeO₂ nanowires for low-temperature CO oxidation†

Tianyi Kou,^{a,b} Conghui Si,^a John Pinto,^c Chunyan Ma^d and Zhonghua Zhang ^{*a}

CeO₂ is widely used as a commercial CO oxidation catalyst, but it suffers from high-temperature (>200 °C) complete conversion. Despite enormous efforts made to promote its low-temperature activity by interfacing CuO and CeO₂, it is still a long-standing challenge to balance the desired catalytic activity with high-yield preparation. Creating intimate synergistic interfaces between Cu and Ce species and exploring surfactant-free large-scale methods are both critical and challenging. To address these concerns, we synthesized highly active Cu doped CeO₂ nanowires for low-temperature CO oxidation, relying on intentionally maneuvering precursor alloy compositions and a high-yield dealloying method. The favorable one-dimensional doping structure inherited from the nanowire bundles of the as-dealloyed precursors, clean surfaces and intimate synergistic effects between Cu and Ce contribute to excellent CO oxidation performances, with 5% room-temperature conversion triggered at 35 °C and 100% conversion at 100 °C. 96% of O₂ selectivity at 88 °C in CO preferential oxidation was also obtained. The long-term durability for 24 hours at 100% CO conversion without any decay confirms the robust characteristics of the catalysts. Moreover, this work offers some insights into the reasonable design of alloy precursors to realize property-oriented alloys to nanowires batch transformation for the study of industrial catalysts.

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1. Introduction

Carbon monoxide (CO) is a well-confirmed highly toxic gas that can easily combine with hemoglobin in the human body, leading to asphyxiation at a lethal concentration of about 650 ppm.¹ In addition, CO, as a by-product, is also proved to deactivate the Pt catalyst in a polymer electrolyte membrane fuel cell (PEMFC), restricting the electrochemical activity of Pt in the oxidation of H₂ and the reduction of O₂ within the operating temperature range from 80 to 200 °C.² Eliminating CO from emission sources such as an automobile exhaust system or PEMFC has thus become an important goal for the sake of reducing hazardous pollution and retaining the high efficiency

of energy conversion devices. Low-temperature CO catalytic oxidation is believed to be an effective strategy to handle the challenge whilst minimizing the thermal energy input. Traditionally, noble metals such as Pt, Pd and Rh supported on oxides are applied in the three-way automobile exhaust catalyst system to deal with CO oxidation.¹ However, the ultra-low abundance of the as-mentioned noble metals greatly increases the costs and largely restricts their wide application. Looking for highly efficient inexpensive transition metal oxides has become significant in efforts to replace noble metal catalysts. Among those metal oxides catalysts, special attention has been paid to CeO₂, which has a relatively high oxygen storage capacity (OSC) and a redox cycle of Ce⁴⁺/Ce³⁺.³ The intrinsic attributes of CeO₂ are believed to offer an oxidant (lattice oxygen) to CO and to create active oxygen vacancies to facilitate the adsorption of oxygen-containing species.³ Depending on this unique feature, CeO₂ has been extensively explored, but the temperature for complete CO conversion is still much higher than 200 °C.^{4,5} Interfacing CuO and CeO₂ has been found to be an effective method in enhancing CO oxidation activity by introducing additional oxygen vacancies through the incorporation of low-valence Cu and accelerating the double redox cycles of Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺.⁶ For example, CuO–CeO₂ nanoparticles synthesized by Luo *et al.*

^aKey Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), School of Materials Science and Engineering, Shandong University, Jingshi Road 17923, Jinan, 250061, P.R. China.
E-mail: zh_zhang@sdu.edu.cn

^bDepartment of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064, USA

^cDepartment of Physics, University of California, Santa Cruz, California 95064, USA

^dResearch Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P.R. China

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through a cetyltrimethyl ammonium bromide (CTAB) assisted template method showed that complete CO conversion can be realized between around 100 °C and 200 °C, depending on the concentration of Cu in the composites, and they are much more active than CuO and CeO₂ catalysts separately.⁴

Albeit enormous efforts have been made to boost the catalytic activity of Cu-involved CeO₂ catalysts, to apply these catalysts for wide practical use still requires the urgent issues of balancing decent activity and low-cost batch preparation to be addressed. For instance, surfactants or stabilizing agents are usually applied for the large-scale synthesis of CeO₂ based catalysts, but the involvement of a surfactant can form an additional barrier between the catalysts and reactants, resulting in impaired performances and is therefore not desirable for heterogeneous catalysis.^{7,8} Increasing the contact area between the Cu and Ce species for an intimate synergistic effect needs complicated special control and hinders low-cost batch synthesis.⁹ Therefore, developing a strategy that can realize low-cost and high-yield growth of Cu-involved CeO₂ nanocrystals while achieving intimate synergistic interfaces without the assistance of surfactants is a long-standing challenge in low-temperature CO catalytic oxidation.

Due to the large surface-to-volume ratio and potentials in exposing certain crystal facets, one-dimensional (1D) nanowires have been shown to be great structures in heterogeneous catalysis, such as CO oxidation.¹⁰ In addition, the 1D quantum confinement effect in nanowires usually contributes to an enhanced electron transfer, which could facilitate the redox reactions in catalysis.¹¹ In this work, a highly active Cu doped CeO₂ 1D nanowire structure was established through intentional control over the composition of the precursor alloy (Al₉₀Cu_{2.5}Ce_{7.5}). The network of nanowires after dealloying was proved to be inherited in the Cu doped CeO₂ nanocrystals without any assistance from surfactants. The clean surface, intimate synergistic effects between Cu and Ce, and increased number of oxygen vacancies in this 1D structure result in a low activation energy of 55.4 kJ mol⁻¹ and are beneficial for excellent activity with a complete CO conversion temperature at around 100 °C and great performances in CO preferential oxidation (CO-PROX). More importantly, the tens of gram-scale laboratory synthesis strategy relying on dealloying offers a great opportunity for wide practical use in effective CO removal from automobile exhaust systems and PEMFC.

2. Experimental section

2.1. Catalysts preparation

A precursor alloy ingot of Al₉₀Cu_{2.5}Ce_{7.5} (at%, nominal concentration) was prepared from pure Al (99.9 wt%), Cu (99.9 wt%) and Ce (99.9 wt%) through a high-frequency induction furnace (Fig. S1a†). Alloy ribbons (around 20 to 50 μm in thickness and about 2 to 5 mm in width, Fig. S1b†) were then obtained by high-frequency induction heating of the alloy ingot and rapid solidification on a single roller melt-spinning apparatus under the protection of argon atmosphere. Dealloying was

carried out in 5 M NaOH aqueous solution until no bubbles were observed. The as-dealloyed powders were rinsed with ultrapure water and ethanol sequentially and dried overnight in a vacuum. Calcination of the as-dealloyed powders was performed in a muffle furnace at 300 and 500 °C. For comparison, alloy ribbons of Al₉₀Ce₁₀, Al₉₀Cu₅Ce₅ and Al₉₀Cu_{7.5}Ce_{2.5} were also dealloyed and calcinated using similar methods.

2.2. Materials characterization

X-ray diffraction (XRD, Rigaku D/max-rB) with Cu Kα radiation was employed to characterize the phase composition. A scanning electron microscope and a transmission electron microscope (SEM, Quanta FEG 250; TEM, FEI Tecnai G2) were used to investigate the microstructure. Surface elemental information was obtained by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The specific surface area was measured through N₂ adsorption-desorption on a V-sorb 2800P surface area analyzer. H₂-temperature programmed reduction (H₂-TPR) was performed to obtain an understanding of the profile of Cu distribution in the CeO₂ nanowires from room temperature to 900 °C at a rate of 8 °C min⁻¹. Raman spectra were obtained by using a Renishaw inVia Raman microscope (532 nm excitation wavelength).

2.3. Performance evaluations

CO catalytic oxidation performance evaluations were carried out in a fixed-bed quartz tube in which quartz sand (500 mg) and catalysts (300 mg) were well mixed. A gas mixture containing CO, O₂ and N₂ (volume ratio: 1:10:89) was purged into the reactor at a flow rate of 40 mL min⁻¹. Temperature control was programmed and a heating rate of 3 °C min⁻¹ was applied in the evaluation. CO conversion was computed through an on-line gas analyzer with ppm-precision. CO-PROX measurement was performed in the presence of an H₂ (50%), CO (1%), O₂ (1%) and N₂ balance at a flow rate of 100 mL min⁻¹ and heating rate of 3 °C min⁻¹. The O₂ selectivity can be calculated using the following equation: selectivity = 0.5([CO]_{in} - [CO]_{out}) / ([O₂]_{in} - [O₂]_{out}) × 100%.

3. Results and discussion

The synthesis route and structural evolution of the Cu doped CeO₂ nanowires are illustrated in a schematic (Fig. 1). As revealed by the XRD pattern in Fig. S1c,† Al₉₀Cu_{2.5}Ce_{7.5} is composed of Al and Al₃CuCe phases. When Al₉₀Cu_{2.5}Ce_{7.5} alloy ribbons were firstly immersed in an NaOH aqueous solution for the dealloying process, the electrochemically active Al was selectively etched to form soluble [Al(OH)₄]⁻ and at the same time the inert atoms Cu and Ce diffused along the electrolyte/solid interfaces. Specifically, the Al phase as well as the Al in Al₃CuCe results in a channel area after dealloying, and the diffusion of Cu and Ce contribute to the formation of the nanowire network indicated in the SEM image in Fig. 1. After annealing in air at 500 °C for 2 hours, the Cu doped CeO₂ nanocrystals (TEM image in Fig. 1, denoted as Cu_{2.5}Ce_{7.5}) are

Fig. 1 Schematic illustration of the synthesis of Cu doped CeO_2 (denoted as $\text{Cu}_{2.5}\text{Ce}_{7.5}$) ultrathin nanowires with appealing low-temperature CO catalytic oxidation performances.

obtained with the nanowire structural feature inherited from the as-dealloyed samples.

XRD results in Fig. S2a† and Fig. 2a further present the details in the phase transformation from dealloying to annealing. $\text{Ce}(\text{OH})_3$ (PDF# 54-1268) is found to be the only phase found in both as-dealloyed $\text{Al}_{90}\text{Cu}_{2.5}\text{Ce}_{7.5}$ and $\text{Al}_{90}\text{Ce}_{10}$. As shown in Table S1,† the actual atomic ratio of Cu to Ce obtained through SEM-EDX results is 1 to 2.27, which is equal to a Cu concentration of 31 at% in $\text{Cu}_{2.5}\text{Ce}_{7.5}$ and suggests a high Cu abundance. The disappearance of the Cu containing phase in the XRD suggests that a large portion of Cu should have been doped into the $\text{Ce}(\text{OH})_3$ lattice (Fig. S2a†). In fact, the radius of Cu^{2+} (0.073 nm) is a little smaller than that of Ce^{3+} (0.110 nm) and the substitutional doping is highly likely

to occur.^{6,12} This doping can also be confirmed from the peak shifting to higher 2 theta degrees for as-dealloyed $\text{Al}_{90}\text{Cu}_{2.5}\text{Ce}_{7.5}$, compared with standard $\text{Ce}(\text{OH})_3$ diffraction peak positions in Fig. S2a.† Subsequent to dealloying, the annealing process transformed Cu doped $\text{Ce}(\text{OH})_3$ to Cu doped CeO_2 (PDF# 43-1002), as reflected from the XRD pattern in Fig. 2a. XPS characterization shown in Fig. 2b–d and S2c† presents the valence and chemical environment profiles of Ce, Cu and O in the nanowire catalysts. The Ce 3d spectra in Fig. 2b show the characteristic peaks of Ce^{4+} located at 916.1 and 897.8 eV and of Ce^{3+} at 903.0 and 881.8 eV, indicating the mixed valence of Ce in the surface of CeO_2 .¹³ The shake-up peak at 940.0 to 945.0 eV and the 933.5 eV peak of the Cu 2p_{3/2} spectra in Fig. 2c demonstrate the presence of Cu^{2+} .¹⁴

Fig. 2 XRD pattern of $\text{Cu}_{2.5}\text{Ce}_{7.5}$ (a), XPS showing profiles of Ce 3d (b), Cu 2p and LMM Auger spectra (c–d) for the sample of $\text{Cu}_{2.5}\text{Ce}_{7.5}$.

However, the peak at 932.3 eV is close to the characteristic peaks of Cu^+ and Cu^0 . In order to differentiate the two valence states, a Cu LMM Auger spectrum (Fig. 2d) was obtained. The peaks at 570.9 and 569.2 eV confirm the existence of Cu^+ and Cu^{2+} .¹⁵ It has been reported that the $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ are important redox pairs during the CO oxidation, which can facilitate the adsorption of CO as well as the creation of oxygen vacancies.⁶ The O^{2-} species binding with Ce^{4+} and the surface adsorbed O^{2-} are found to be present at 531.8 and 529.3 eV in the O 1s spectrum (Fig. S2c†) for the as-prepared $\text{Cu}_{2.5}\text{Ce}_{7.5}$, well consistent with the formation of CeO_2 .¹⁶

The microstructures of the 1D nanowires are clearly observed in the SEM (Fig. S2d†) and low-magnification bright-field TEM in Fig. 3a. A dimension of around 20 nm for the diameter of the nanowires can clearly be seen (Fig. 3b). The selected area electron diffraction (SAED) pattern shows multiple diffraction rings (inset of Fig. 3a), which correspond to the (111), (200), (220), (311), (400) and (331) diffraction planes

of CeO_2 , in accordance with the XRD results. Even though SAED shows ‘polycrystalline rings’, the 1D nanowires are actually single crystalline and the bundles of single nanocrystals usually make a diffraction pattern similar to that of ‘polycrystalline rings’. As indicated in Fig. 3c–d, FFT results obtained from high-resolution TEM (HRTEM) images confirm that the nanowires grow along the [110] direction. HAADF-STEM and elemental mapping further confirm the homogeneous distribution of Cu and Ce in the nanowires (Fig. 3e), which demonstrates the feasibility of the dealloying method in realizing uniform atomic dispersion.

H_2 -TPR (Fig. 4a) reveals three special peaks present in the reduction process, as reflected by α (110 °C), β (145 °C) and γ (215 °C), which are associated with different states of Cu and Ce in $\text{Cu}_{2.5}\text{Ce}_{7.5}$. The peaks at relatively low temperatures (110 °C and 145 °C) are usually attributed to the fine dispersion of CuO, and Cu^{2+} doped in CeO_2 .⁴ Because bulk CuO is not present, the peak of γ at 215 °C could be due to the

Fig. 3 TEM images (a–b) and SAED (inset of a) revealing the microstructure of $\text{Cu}_{2.5}\text{Ce}_{7.5}$; HRTEM and associated FFT indicating [110] growth direction of the $\text{Cu}_{2.5}\text{Ce}_{7.5}$ nanowires (c–d); HAADF-STEM and elemental mapping (e) confirming the homogeneous dispersion of Cu in the nanowires.

Fig. 4 H₂-TPR curve of the as-prepared Cu_{2.5}Ce_{7.5} (a); N₂ adsorption-desorption isotherms of Cu_{2.5}Ce_{7.5} at 77 K (b).

reduction of surface Ce in oxidation states(III/IV), considering its high intensity.⁶ The H₂-TPR results are complementary to the XRD characterization, suggesting that CuO finely disperses on the surface of Cu doped CeO₂ nanowires. This heterogeneous structure is desirable in CO oxidation, as the interface between CuO and CeO₂ is regarded as providing active sites for synergistic effects, such as improved reducibility and electronic interaction.⁹ For example, during CO catalytic oxidation, Cu²⁺–O^{2–}–Ce⁴⁺ species can be simultaneously reduced by CO, resulting in an oxygen vacancy present between Cu⁺ and Ce³⁺.^{6,17} Cu⁺ and oxygen vacancies were found to act as the sites for CO and O₂ adsorption, respectively, which is significant for the subsequent reaction between adsorbed CO and O₂ to form

CO₂.⁶ Usually a large specific surface is necessary to guarantee a decent activity for catalysts. The N₂ adsorption-desorption isotherms of the as-prepared Cu_{2.5}Ce_{7.5} nanowires confirm that a high surface area of 66.4 m² g⁻¹ is obtained (Fig. 4b), boosting the possibility of exposing a large number of active sites in these fine 1D structures.

To evaluate the catalytic activity of the as-prepared Cu_{2.5}Ce_{7.5} nanowires towards CO oxidation, CO conversions at different temperatures were obtained and the data were compared with CeO₂ (Fig. 5a). Without doping, CeO₂ shows an inferior activity to Cu_{2.5}Ce_{7.5}, with a conversion of 5% achieved at a temperature of 90 °C and complete conversion of CO realized at around 180 °C. The performances of the CeO₂ syn-

Fig. 5 Catalytic performance comparison of Cu_{2.5}Ce_{7.5} and CeO₂ (a); the dependence of reaction rate on CO (b) and O₂ (c) concentrations (vol%) for CO oxidation over Cu_{2.5}Ce_{7.5}, and the corresponding Arrhenius plot (d).

thesized through dealloying already outperform those of many CeO₂ nanoparticles and are even comparable with Cu–CeO₂ catalysts reported recently, indicating the advantages of the dealloying strategy in creating catalytically active nanocrystals.^{4,5,18} However, a low-temperature CO oxidation close to 100 °C is always desirable to minimize energy input. As shown in Fig. 5a, the as-prepared Cu_{2.5}Ce_{7.5} is capable of converting around 5% CO at an extremely low temperature of 35 °C (near room temperature), indicating the highly intrinsic activity compared to the 5% CO conversion at 90 °C in the case of CeO₂. The 100% conversion of CO is achieved at 100 °C for Cu_{2.5}Ce_{7.5}, 80 °C lower than that of CeO₂. Also, the Cu doped CeO₂ nanowires in this work exhibit outstanding performances compared to state-of-the-art CO oxidation metal oxide catalysts, such as CuO–CeO₂, Cu/CuO_x/C, Co₃O₄ nanowires and the nanoporous Cu–O oxides system in which a temperature range from around 120 °C to more than 200 °C under the similar evaluation conditions was recorded for complete CO conversion.^{4,5,19–21} When the concentration of CO is decreased to 0.4% (Fig. S3†), the conversion is apparently promoted at the same temperature, with 12% conversion obtained at 35 °C and 100% conversion at 90 °C, indicating the sensitive response of the Cu_{2.5}Ce_{7.5}. Even compared with other low-temperature catalysts, such as KOH treated hopcalite (100% conversion at about 150 °C) at the same CO concentration, the 100% CO conversion at 90 °C for the Cu_{2.5}Ce_{7.5} shows its advantage in pushing down the upper limit of energy input.²² It is well understood that the low-temperature treatment of catalysts is usually desirable to retain their activity, as a high-temperature process is believed to anneal the active sites. For comparison, annealing of the as-dealloyed Al₉₀Cu_{2.5}Ce_{7.5} at a lower temperature of 300 °C was performed, with the same XRD pattern as that of Cu_{2.5}Ce_{7.5} treated at 500 °C, which demonstrates that Cu-doped CeO₂ can also be realized (Fig. S4a†). However, Cu_{2.5}Ce_{7.5}-300 °C exhibits an inferior activity to that of Cu_{2.5}Ce_{7.5}-500 °C, with a CO conversion of 3.4% obtained at 35 °C and 100% conversion at 115 °C (Fig. S4b†). It has been reported that in Raman spectra (Fig. S4c†) the ratio of the peak area of the band at 600 cm^{−1} (a band that is related to Cu doping in CeO₂ and is correlated with the formation of oxygen vacancies) to the peak area of another band at 450 cm^{−1} (induced by the F_{2g} vibration mode of the CeO₂) is used to reflect the concentration of oxygen vacancies.²³ The ratio is estimated to be 0.27 for Cu_{2.5}Ce_{7.5}-500 °C, three times higher than that of Cu_{2.5}Ce_{7.5}-300 °C (0.082), suggesting that the number of oxygen vacancies in the Cu_{2.5}Ce_{7.5} annealed at 500 °C is larger. And the increased oxygen vacancies should be responsible for the promoted activity in CO oxidation. In comparison, as-treated Cu₅Ce₅ and Cu_{7.5}Ce_{2.5} were also investigated. As can be seen from Fig. S5a–b,† the morphology of as-treated Cu₅Ce₅ and Cu_{7.5}Ce_{2.5} is actually a mixture of nanowires (Cu-doped CeO₂) and ligaments (CuO). The difference in morphology between the two samples and the Cu_{2.5}Ce_{7.5} is attributed to the different alloy precursors, and the increased Cu concentration in Al₉₀Cu₅Ce₅ and Al₉₀Cu_{7.5}Ce_{2.5} results in the presence of a

Cu-rich Al₈Cu₄Ce phase (Fig. S1c†), which can eventually evolve into bulk nanoporous CuO after dealloying and annealing (Fig. S5a–c†). The bulk nanoporous CuO is also believed to have a decent activity in CO oxidation, as reported in our previous work.²¹ Although the overall performance obtained for Cu₅Ce₅ is close to that of Cu_{2.5}Ce_{7.5} (both of them achieving 50% conversion at about 50 °C and 90% conversion at around 90 °C, Fig. S5d†), the catalytic efficiency with respect to moles for Cu₅Ce₅ is actually inferior to that of Cu_{2.5}Ce_{7.5}, considering that many more moles of Cu₅Ce₅ (CeO₂ and CuO) are involved in the CO oxidation than Cu_{2.5}Ce_{7.5} (CeO₂) at the same mass loading. The difference in performance is more apparent when the Cu concentration is further increased in Cu_{7.5}Ce_{2.5}, with an overall performance of 90% CO conversion achieved at 96 °C, almost 10 °C higher than that of Cu_{2.5}Ce_{7.5} for the same conversion (Fig. S5d†).

The excellent activity should be correlated with its favorable morphology and doped structure. For example, the 1D nanowires with high surface-to-volume ratio and high surface area have a large number of possible exposed active sites for CO oxidation. The naturally existing Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺ redox pairs in the nanowires can facilitate the redox reactions during CO oxidation by enhancing the CO adsorption on Cu sites and creating oxygen vacancies.⁶ In addition, the surfactant-free synthesis method is also believed to contribute to the appealing activity of Cu_{2.5}Ce_{7.5} nanowires in low-temperature CO oxidation. Activation energy is usually used to quantify the activity of CO oxidation catalysts and provides an objective value for comparison.²¹ The Arrhenius equation is used to quantify the activation energy of CO oxidation on the as-prepared Cu_{2.5}Ce_{7.5}, as follows:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (1)$$

where k represents the rate constant, A is the Arrhenius factor, E_a is the activation energy, R is the molar gas constant (8.314 J mol^{−1} K^{−1}) and T is the absolute temperature. Reaction orders and rate constant can be determined from the following equation:

$$R = k[\text{CO}]^a[\text{O}_2]^b \quad (2)$$

Temperatures from 313 K to 335 K and different CO or O₂ concentrations from 0.35 to 2.1% ([CO] or [O₂] representing vol%) are used to evaluate the reaction constant and the reaction orders. From Fig. 5b–c, the reaction orders of a and b are found to be 0.29 and −0.17, respectively. Based on this information, an activation energy of 55.4 kJ mol^{−1} is obtained, which is much smaller than the 113 kJ mol^{−1} for the reported Cu–Ce–O catalysts.²⁴ It also shows an absolute advantage when compared with the noble metals such as Pd (111), which has a high activation energy of 133 kJ mol^{−1}.²⁵ The minimized activation energy represents a low energy barrier that the CO oxidation reaction should overcome, further confirming the highly active feature of the as-prepared Cu_{2.5}Ce_{7.5} nanowires. In addition to the promoted activity, the Cu doped CeO₂ nano-

Fig. 6 CO-PROX test in excess of H₂ over Cu_{2.5}Ce_{7.5}.

wires also exhibit great stability at 100% conversion (100 °C) during 24 hours of continuous function without any performance decay (Fig. S6†).

The excellent low-temperature CO oxidation performances of the Cu_{2.5}Ce_{7.5} nanowires show a great potential for application in a PEMFC in which the operating temperature usually ranges from 80 °C to 200 °C.² In order to explore its potential to be used in PEMFC, the influence of H₂ (O₂ selectivity) should be considered. Fig. 6 reveals that the Cu_{2.5}Ce_{7.5} nanowires can achieve both high CO conversion (96%) and O₂ selectivity (96%) at around 88 °C, indicating their superior selective CO oxidation ability compared to previous reports in which the same conversion/selectivity level was achieved but a higher temperature from 100 °C to 200 °C was required.^{26–28}

4. Conclusions

To conclude, in this work we synthesized Cu doped CeO₂ nanowires in high yield through a dealloying-annealing strategy. The as-synthesized nanowires have been characterized as growing along the [110] direction. The surfactant-free synthesis feature, the Cu doped CeO₂ lattice structure along with favorable 1D nanowires, and the synergistic effect between Cu and Ce redox cycles together contribute to the excellent CO oxidation activity, with complete CO conversion achieved at 100 °C. The minimized activation energy of 55.4 kJ mol⁻¹ as well as facilitated CO adsorption after Cu doping suggest that the catalysts have great potential to replace noble metal based CO oxidation catalysts. CO-PROX evaluation indicates that the active Cu doped CeO₂ nanowires are capable of converting 96% CO and retaining 96% O₂ selectivity at a very low temperature of 88 °C, exhibiting a promising future in applications in energy conversion devices. Last but not least, the dealloying-dependent large-scale preparation strategy not only provides a great chance for the widely practical use of inexpensive but active metal oxides, but also lays the foundations for future excellent property-oriented alloys-nanowires transformation studies.

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