In situ Growth of Ni$_x$Cu$_{1-x}$ Alloy Nanocatalysts on Redox-reversible Rutile (Nb,Ti)O$_4$ Towards High-Temperature Carbon Dioxide Electrolysis

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In this paper, we report the in situ growth of Ni$_x$Cu$_{1-x}$ (x = 0, 0.25, 0.50, 0.75 and 1.0) alloy catalysts to anchor and decorate a redox-reversible Nb$_{1.33}$Ti$_{0.67}$O$_4$ ceramic substrate with the aim of tailoring the electrocatalytic activity of the composite materials through direct exsolution of metal particles from the crystal lattice of a ceramic oxide in a reducing atmosphere at high temperatures. Combined analysis using XRD, SEM, EDS, TGA, TEM and XPS confirmed the completely reversible exsolution/dissolution of the Ni$_x$Cu$_{1-x}$ alloy particles during the redox cycling treatments. TEM results revealed that the alloy particles were exsolved to anchor onto the surface of highly electronically conducting Nb$_{1.33}$Ti$_{0.67}$O$_4$ in the form of heterojunctions. The electrical properties of the nanosized Ni$_x$Cu$_{1-x}$/Nb$_{1.33}$Ti$_{0.67}$O$_4$ were systematically investigated and correlated to the electrochemical performance of the composite electrodes. A strong dependence of the improved electrode activity on the alloy compositions was observed in reducing atmospheres at high temperatures. Direct electrolysis of CO$_2$ at the Ni$_x$Cu$_{1-x}$/Nb$_{1.33}$Ti$_{0.67}$O$_4$ composite cathodes was investigated in solid-oxide electrolyzers. The CO$_2$ splitting rates were observed to be positively correlated with the Ni composition; however, the Ni$_{0.75}$Cu$_{0.25}$ combined the advantages of metallic nickel and copper and therefore maximised the current efficiencies.

Solid oxide electrolyzers have demonstrated the tremendous advantages of electrochemical conversion of CO$_2$ into fuels with high efficiencies using renewable electrical energy$^{1-3}$. Oxide-ion-conducting solid oxide electrolyzers can directly electrolyse CO$_2$ into CO and pure oxygen under external applied potentials. At the cathode, CO$_2$ molecules are electrochemically split into CO while the generated O$^{2-}$ ions are transported through the electrolyte membrane to the anode compartment where pure O$_2$ gas is formed and released$^{4-6}$.

The conventional Ni/YSZ electrode has exhibited excellent steam-electrolysis performance under a reducing atmosphere; however, the Ni-cermets are not redox stable and require a significant concentration of reducing gas flowing over the Ni metal to avoid the oxidation of Ni to NiO$^{6-7}$. Similarly, the flowing of CO to the composite electrode is also necessary during electrolysis of CO$_2$ because the oxidation of Ni occurs at high temperatures$^8$. Furthermore, the catalytic activity of Ni metal toward the splitting of CO$_2$ is relatively high; carbon deposition most likely occurs and results in the degradation of cell performance. Some researchers have demonstrated that the deposition of carbon is likely caused by reactions that occur over the catalyst and favour to occur only when CO is present in the chemical reaction system$^{4-10}$. Cu/YSZ and Cu/SDC have also been considered as potential electrodes because of their ability to adsorb CO$_2$, resistance to carbon fouling and low cost; however, the catalytic activity of Cu toward CO$_2$ splitting is inferior to that of Ni$^{11,12}$. Cu similarly oxidises during the direct electrolysis of CO$_2$ or H$_2$O in the absence of a reducing gas flowing over the composite cathode at high temperatures.

High-temperature electrolysis based on the redox-stable LSCM or LSTO cathode has been reported for the direct electrolysis of H$_2$O, CO$_2$ or H$_2$O/CO$_2$, and promising electrode performances have also been observed$^{13-17}$. However, the LSCM, as a p-type conductor, is not well adapted to strong reducing potentials. LSCM exhibits lower conductivity than other cathode materials and undergoes adverse chemical changes under such extreme conditions; these changes lead to a large electrode polarisation resistance and to degradation of the electrolysis...
performance\textsuperscript{18,19}. Direct electrolysis of CO\textsubscript{2} with a current efficiency as high as approximately 50–60% has been achieved with LSCM cathodes, as reported in our previous work; however, rapid electrode degradation occurs at an external load of 2 V at 800 °C.\textsuperscript{20} By contrast, LSTO, which exhibits n-type conductivity upon reduction, has been considered a breakthrough in the development of redox-stable anode materials for SOFCs and has also been utilised for direct high-temperature electrolysis\textsuperscript{21}. However, this material’s insufficient catalytic activity still restricts the electrode polarisation and current efficiency during high-temperature electrolysis\textsuperscript{22}. To improve the performance of LSTO, metal catalysts have been introduced, which has resulted in a substantially enhanced electrode performance\textsuperscript{22,23}. However, control of the morphology of such catalysts on the substrate is difficult, and operation over a long period of time would risk catalyst agglomeration and, therefore, performance degradation. As documented in our previous work\textsuperscript{24–26}, steam electrolysis based on Ni- or Fe-impregnated LSCM or LSTO is stable during the first hour of operation at a load of 1.5–2 V, whereas an approximately 20–30% degradation in cell performance is observed when the operating time exceeds 5 h because of the agglomeration of metal nanoparticles on the surface of the composite cathode skeleton.

An alternative method is to incorporate the catalyst as a dopant within a host lattice during the synthesis of the catalyst in air, which is then exsolved at the surface in the form of catalytically active metallic nanoparticles or microparticles under reducing conditions\textsuperscript{27}. Upon re-oxidation, the dopant can be re-incorporated into the host lattice, yielding a regenerative catalyst. In this case, any possible agglomeration of exsolved metallic nanoparticles on the substrate surface can be avoided by periodically exposing the material to oxidising conditions. Fluorite oxide, Nb\textsubscript{Ti}0.5\textsubscript{Ni}0.5O\textsubscript{4} (NTNO), which is a single-phase rutile-type structure with the tetragonal (P4\textsubscript{2}/mm) space group, was first reported as a potential anode material for solid oxide fuel cells by Irvine et al.\textsuperscript{28–30}. Nanoparticles of metallic Ni can be exsolved at the surface of the highly-conducting Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} substrate after high-temperature reduction under a reducing gas. The Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} is a mixed conductor because of the edge sharing of NbO\textsubscript{6} octahedra along the c-axis, which result in Nb–Nb metal bond overlap with an inter-metallic distance of 3 Å. This high electronic conductivity is facilitated by the edge-sharing octahedra along the c-axis\textsuperscript{31}. In our previous work, the nanosized Ni/Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} composite exhibited promising electrode polarisation and current efficiencies for the direct steam electrolysis\textsuperscript{32}

Copper-based catalysts exhibit lower selectivity toward H\textsubscript{2} than toward CO or CO\textsubscript{2} because of their high over-potential of hydrogen evolution\textsuperscript{33}; however, their excellent CO\textsubscript{2}/monoxide adsorption properties and resistance to carbon fouling make copper-based catalysts appealing to many researchers\textsuperscript{34–36}. In contrast to copper, Ni metal exhibits high catalytic activity but probably tends to be prone to high coke formation; such a severe deactivation poses a serious obstacle to the future application of Ni-metal catalysts. Coke is favour to occur when CO and hydrocarbons are present for their chemisorption.\textsuperscript{37} Some researchers have taken a compromise approach by mechanocally mixing Ni and Cu particles to form a Ni + Cu composite and therefore utilise the respective catalytic activity by mechanically mixing Ni and Cu particles to form a Ni + Cu alloy with continuously tuned compositions an outstanding catalyst in many scientific fields\textsuperscript{38–40}. Here, we report the reversible in situ growth of Ni\textsubscript{x}Cu\textsubscript{1-x} (x = 0, 0.25, 0.50, 0.75 and 1.0) alloy catalysts to anchor and decorate the redox-reversible Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} ceramic substrate with the aim of tailoring the electrocatalytic activity of the composite materials through direct exsolution of metal particles from the crystal lattice of the ceramic oxide. The anchored interface is expected to enhance the electrocatalytic kinetics and the high-temperature stability of such nanoparticles. The electrical properties of the ceramic composite are investigated and further correlated to the electrochemical performance of their composite electrodes. Direct electrolysis of CO\textsubscript{2} is then performed using the Ni\textsubscript{x}Cu\textsubscript{1-x}/Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} composite cathode in a solid-oxygen electrolyser at high temperatures.

\textbf{Methods}

All the powders were purchased from SINOPHARM Chemical Reagent Co., Ltd (China) unless specified otherwise. The synthesis of \textit{Ni}, \textit{Cu}, \textit{Nb}, Ti, and O powders was carried out by a solid-state reaction using an appropriate mixture of Nb\textsubscript{2}O\textsubscript{5}, TiO\textsubscript{2}, CuO and NiO powders\textsuperscript{41,42}. The mixture was ball-milled in acetone, dried, pressed into pellets at room temperature and treated at 1300, 1150, 1100, 1050 and 1000 °C for the first cycle under a reducing atmosphere (5% H\textsubscript{2}/Ar) and Ni\textsubscript{x}Cu\textsubscript{1-x}/Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} and NTCO were sintered and then reduced in H\textsubscript{2}/Ar at 1300, 1250, 1150, 1100, 1050 and 1000 °C (2 °C/min) respectively, for 20 h to achieve the reduced form of the composite Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} + Ni\textsubscript{x}Cu\textsubscript{1-x}. The in situ growth of Ni\textsubscript{x}Cu\textsubscript{1-x} alloy nanocatalysts when all of the oxide forms were reduced in a reducing atmosphere (5% H\textsubscript{2}/Ar) at 1050 °C (3 °C/min) for approximately 20 h. The reduction-oxidation cycles of the composite materials were conducted for another three cycles under reducing or oxidising atmospheres (5% H\textsubscript{2}/Ar or static air).

The X-ray diffraction (XRD, 2\textsuperscript{θ}, 20 = 3°–110°, 20 = 10–90°, D/MAX2500V, Rigaku Corporation, Japan) analyses were performed to characterise the structural changes of the materials after the redox cycles. The microstructure of the Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} and Ni\textsubscript{x}Cu\textsubscript{1-x}/Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} were analysed using an ESCALAB250 spectrometer equipped with an Al Kα (1486.6 eV) radiation source. The thermogravimetric analysis (TGA, STA449F3, Germany) of the oxidised NTNO and Ni\textsubscript{x}Cu\textsubscript{1-x}/Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} samples was conducted from room temperature to 1000 °C and then back to room temperature under a reducing atmosphere: the heating rate was 2 °C/min, and the flow rate of 5% H\textsubscript{2}/Ar (99.99% purity). Transmission electron microscopy (TEM) analysis with selected-area diffraction was performed to observe the oxidised and reduced NTNO, Ni\textsubscript{x}Cu\textsubscript{1-x}/Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} powders; the analyses were performed on a JEOI 2100F field-emission transmission electron microscope operated at 200 kV.

Approximately 2.0 g of NTNO, NTNO, NTNO, NTNO, or NTNO powder was compacted into a bar at a pressure of 6 MPa (20.0 mm × 7.0 mm × 2.4 mm) and subsequently sintered at 1300, 1150, 1100, 1050 or 1000 °C for 10 h, respectively. The relative densities of all the samples were similar to each other, at approximately 80%. The bars were reduced completely at 1300, 1150, 1100, 1050 or 1000 °C, respectively, for 20 h in a reducing atmosphere (5% H\textsubscript{2}/Ar) for the conductivity tests. The conductivities of the reduced samples, Ni\textsubscript{x}Cu\textsubscript{1-x}/Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} were tested in 5% H\textsubscript{2}/Ar (99.99% purity) from room temperature to 800 °C using the DC four-terminal method; the conductivity was recorded at a step of 0.5 °C using an online system. The dependence of the conductivity on the oxygen partial pressure was tested at 800 °C under an oxygen partial pressure that ranged from 10\textsuperscript{−10} to 10\textsuperscript{−8} atm; the oxygen partial pressure was adjusted by variation of the flow rate of the dry 5% H\textsubscript{2}/Ar. The oxygen partial pressure (IgO\textsubscript{2}) and the conductivities were recorded using an online oxygen sensor (1231, ZrO\textsubscript{2}-based oxygen sensor, Noveltech, Australia) and an online multimeter (Keithley 2000 digital multimeter, Keithley Instruments, Inc., USA) respectively.

We prepared the 1 mm-thick YSZ disc electrolyte supports by dry-pressing the YSZ powder into green discs with a diameter of 20 mm and subsequently sintering the disks at 1500 °C (2 °C/min) for 1 h in air. The two surfaces of the obtained YSZ electrolyte support were mechanically polished and then ultrasonically cleaned in distilled water. The Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4}-SbDC composite electrode slurries were prepared by mixing the SDC powder with Nb\textsubscript{1.33}Ti\textsubscript{0.67}O\textsubscript{4} weight ratio of 35:65 in alpha-terpinene with cellulose as an additive\textsuperscript{43,44}. The electrode slurries were then coated onto the electrolyte in symmetric positions in an area of 1 cm\textsuperscript{2} to assemble the symmetric cells; the cells were subsequently subjected to a heat treat-
ment at 1000 °C (3 C min⁻¹) for 3 h in air. The current-collection layer was prepared using silver paste (SS-8060, Xinhui, Shanghai, China), which was printed onto both electrode surfaces. The external circuit was constructed using silver electrical wire (0.1 mm in diameter), which was then connected to both current collectors using silver paste (DAD87, Shanghai Research Institute for Synthetic Resins) followed by firing at 550 °C (3 °C min⁻¹) for 30 min in air. The AC impedance of the symmetric solid-oxide cells was tested at 800 °C with the two electrodes exposed to different hydrogen partial pressures at the open-circuit voltage (OCV) using an electrochemical station (IM6e, Zahner, Germany) with a frequency range of 4–0.1 Hz and a current strength of 10 mA in two-electrode mode. The electrode polarization resistance was calculated by modelling the spectra using the Zview software. The gas flow rate was controlled at 20 ml min⁻¹ using a mass flow meter (D+S 3F, Sevestan, China) to mix different ratios of H₂ (99.99%) and N₂ (99.99%).

The solid-oxide electrolyzers were constructed using NbTi₀.₅(NixCu₁-x)₀.₅O₄ as the cathode and LSM as the anode, with YSZ as the electrolyte. The two surfaces of the electrolyte were coated with NbTi₀.₅(NixCu₁-x)₀.₅O₄ SDC slurry and LSM-SDC slurry in symmetric positions with an area of 1 cm² and were subsequently subjected to the same heat treatment used for the symmetric solid-oxide cells, as previously described. The single solid-oxide electrolyser was sealed in a home-made testing jig using ceramic paste (JD-767, Judian, Dongguan, China) to determine the concentration of CO.

Results and Discussion

Fig. 1 (a) shows the XRD patterns of the single-phase rutile-type NbTi₀.₅(NixCu₁-x)₀.₅O₄ (x = 1, 0.75, 0.5, 0.25, 0), which confirms the homogeneous solid solution, i.e., even the composition of Ni and Cu changes in a wide range. The structures of the NbTi₀.₅(NixCu₁-x)₀.₅O₄ are tetragonal with the space group P42/mmm. Fig. 2 shows the parameters for NbTi₀.₅(NixCu₁-x)₀.₅O₄ (x = 1, 0.75, 0.5, 0.25, 0) calculated from the XRD data. We observed that the cell parameters a and c increase from 4.6944(8) Å and 3.0229(5) Å to 4.6974(8) Å and 3.0297(4) Å when the proportion of nickel is decreased from 1 to 0, respectively. However, a remarkable decrease of cell parameter a occurs, whereas the cell parameter c sharply increases from 3.0297(4) Å to 3.0387(7) Å and then decreases to 3.0316(2) Å when the Ni proportion, x, is decreased to 0. Notably, the cell volumes are distributed as a pyramid with the cell volume of x = 1 and 1 at the bottom, which may be related to the larger ionic radii of Ni²⁺ (0.69 Å) and Cu²⁺ (0.73 Å) compared with that of Ti⁴⁺ (0.605 Å) with the same coordination numbers. The incorporation of Cu²⁺ may play a leading role in the expansion of the cell parameters, especially the c-axis parameter, possibly because of an increase in lattice strength with Cu doping. Fig. 1 (b) shows the XRD patterns of reduced NbTi₀.₅(NixCu₁-x)₀.₅O₄ (x = 1, 0.75, 0.5, 0.25, 0), which confirms that the reduced NbTi₀.₅(NixCu₁-x)₀.₅O₄ are a mixture of two phases: NiₓCu₁-x + Nb₁.₃³Ti₀.₆₇. As shown in Fig. 1 (b), the NbTi₀.₅(NixCu₁-x)₀.₅O₄ changes into Nb₁.₃³Ti₀.₆₇O₄ (PDF No. 053-0293) and metallic NiₓCu₁-x alloy upon high-temperature reduction in 5% H₂/Ar (99.99%). This result confirms the phase change of NbTi₀.₅(NixCu₁-x)₀.₅O₄ to highly electrically conducting Nb₁.₃³Ti₀.₆₇O₄ and pure catalytically active metallic NiₓCu₁-x alloy.

To investigate the reversibility of the exsolution of the metallic NiₓCu₁-x, the composite powders were further treated for another three redox cycles at 1050 °C under a reducing atmosphere (5% H₂/Ar) and a oxidising atmosphere (static air) for 20 h. Fig. 1 (c) shows the XRD patterns of the composite after oxidation, which again confirms the successful integration of NiₓCu₁-x alloys into the Nb₁.₃³Ti₀.₆₇O₄ substrate and the formation of a single-phase NbTi₀.₅(NixCu₁-x)₀.₅O₄ solid solution. No phase impurities are observed in the case of NbTi₀.₅(NixCu₁-x)₀.₅O₄, thereby firmly verifying the superior redox reversibility of the NbTi₀.₅(NixCu₁-x)₀.₅O₄ ceramics. As shown in Fig. 1 (d), the corresponding XRD patterns confirm that the reduced NbTi₀.₅(NixCu₁-x)₀.₅O₄ (x = 1, 0.75, 0.5, 0.25, 0) are still composed of conducting ceramic Nb₁.₃³Ti₀.₆₇O₄ and metallic alloy powders, which further demonstrates the excellent reversible exsolution of the metallic NiₓCu₁-x from the lattice of the NbTi₀.₅(NixCu₁-x)₀.₅O₄ through a reversible phase transition. The three successive redox treatment cycles of NbTi₀.₅(NixCu₁-x)₀.₅O₄ solid solutions suggest that the parent material NbTi₀.₅(NixCu₁-x)₀.₅O₄ and the NiₓCu₁-x + Nb₁.₃³Ti₀.₆₇O₄ composite materials exhibit excellent redox reversibility. The metallic NiₓCu₁-x alloys can be repeatedly exsolved from the NbTi₀.₅(NixCu₁-x)₀.₅O₄ after the reduction and again integrated back into the Nb₁.₃³Ti₀.₆₇O₄ substrate to form a homogeneous phase.

To further validate the elemental valence change in redox cycles of the NbTi₀.₅(NixCu₁-x)₀.₅O₄ solid solution, we performed XPS on the oxidised and reduced NTN₅C₁₀ (NbTi₀.₅(Ni₀.₇₅Cu₀.₂₅)₀.₅O₄ and Nb₀.₇₅Ti₀.₂₅O₂₅ + Nb₁.₃³Ti₀.₆₇O₄) samples. All XPS patterns were fitted using a Shirley-type background subtraction function. The background functions for different the spectra of different elements were fitted using 80% Gaussian and 20% Lorentzian functions. As shown in Fig. 3 (a), only Nb⁵⁺ is observed in the oxidised NTN₅C₁₀ sample; however, the Nb⁴⁺ is reduced to Nb⁵⁺ in the Nb₁.₃³Ti₀.₆₇O₄ substrate when the sample is treated under a reducing atmosphere at 1200 °C for 20 h, as seen in Fig. 3 (b) and (c). The low valence of the Nb⁴⁺ ions favours the formation of Nb-Nb metal bonds, and the electronic conductivity is thus highly facilitated, resulting in enhanced electrical conductivity of Nb₁.₃³Ti₀.₆₇O₄. By contrast, element Ti, as exhibited in Fig. 3 (c), is completely in the Ti⁴⁺ state in the oxidised NTN₅C₁₀ sample; however, the low-valence Ti³⁺ is also observed in the reduced sample, Nb₁.₃³Ti₀.₆₇O₄ + Nb₀.₇₅Ti₀.₂₅O₂₅, as shown in Fig. 3 (d), due to the chemical reduction of Ti⁴⁺ to Ti³⁺ after the heat treatment under a reducing atmosphere. We reasonably speculated that the Nb₁.₃³Ti₀.₆₇O₄ is actually oxygen-deficient Nb₁.₃³Ti₀.₆₇O₄-δ according to the charge balance. The Ti³⁺ (2p1/2) and Ti⁴⁺ (2p3/2) peaks are observed at 462.80 eV and 457.80 eV, respectively, whereas the Ti³⁺ (2p1/2) and Ti⁴⁺ (2p3/2) peaks show peaks at 464.80 eV and 458.10 eV, respectively. Furthermore, the low-valence Ti³⁺ represents an approximately 0.174 mole ratio of all of the Ti according to this result, which indicates an oxygen deficiency of δ = 0.058 and a chemical formula of Nb₁.₃³Ti₀.₆₇O₄-δ. The Ni and Cu in the NTN₅C₁₀ are in the form of Ni²⁺ and Cu²⁺, as shown in Fig. 3 (e) and (f), respectively. In Fig. 3 (f), the Ni²⁺ (2p1/2) peaks are observed at 873.86 and 869.40 eV, whereas the Ni²⁺ (2p3/2) has three peaks at 861.0, 869.40 and 852.0 eV [16,29,48]. A similar change in the chemical state of elemental Cu is also observed in the NTN₅C₁₀ sample after reduction at high temperatures, as shown in Fig. 3 (h). The Cu²⁺ (2p1/2) and Cu²⁺ (2p3/2) peaks are observed at 951.88 and 932.20 eV, respectively. According to reports in the literature, the electronic potential energy of alloys of transition metals can be sensitively changed [46]. In this work, some peaks of binding energy change by approximately 0.2 to 0.3 eV in the case of Ni²⁺ and Cu²⁺ in the Ni₀.₅Cu₀.₅ alloy. The Ni²⁺ and Cu²⁺ exist in the form of metallic alloy nanoparticles in the reduced sample, which further confirms the exsolution of metallic Ni₀.₅Cu₀.₅ alloy on the ceramic substrate. The XPS results further confirm the reversible transformation between the oxidised NbTi₀.₅(NixCu₁-x)₀.₅O₄ solid solution and the reduced Nb₁.₃³Ti₀.₆₇O₄ ceramic electronic conductor loaded with metallic NiₓCu₁-x alloys.

TG and DTG of the oxidised NTN₅C₁₀ and NTNO samples was conducted from room temperature to 1000 °C at a heating rate of 4 °C min⁻¹ in a reducing atmosphere of 5% H₂/Ar. To ensure sufficient reduction of the powder sample, the predetermined temperature at 1000 °C is stabilised for as long as 3 h and then drifts to room temperature at the same rate, as previously stated. Fig. 4 (a) presents the percentage weight change of the oxidised NTNO powder as a function of temperature when heated under a 5% H₂/Ar atmosphere. The weight loss reaches 7.35% for the NTNO sample because of the loss of oxygen under such reducing conditions, which is in good agreement with the chemical change of the NbTi₀.₅(NixCu₁-x)₀.₅O₄ composite material. In
comparison, the weight loss of the studied NTNO powder reached approximately 7.59%, as seen in Fig. 4 (b), which is reasonably consistent with the theoretical value of 7.61% corresponding to the oxygen loss according to the chemical reaction presented in equation (1). Notably, the onset temperature of weight loss for the NTNO sample is approximately 750°C, as determined from the results in Fig. 4 (a), where the in situ exsolution of Ni metal is anticipated. Nevertheless, the weight loss of NTNO starts at temperatures as low as approximately 600°C to grow the metallic alloy. This growth may occur because the incorporation of copper reduces the chemical reaction barrier of metal exsolution and thus facilitates the reversible phase change to grow the metallic NiCu alloys. As evident in both Fig. 4 (a) and Fig. 4 (b), a small weight loss always occurred during the process of cooling. This weight loss is likely to exceed 7.40 and 7.61% for the NTNO and NTNO, respectively, if the samples experience longer reduction times at higher temperatures. Ultimately, the obtained reduced sample may be oxygen-deficient Nb1.33Ti0.67O4.8 + Ni or oxygen-deficient Nb1.33Ti0.67O4.8 + Ni0.5Cu0.5. Despite the different proportions, our conclusion through reasoning is that these results coincide with the aforementioned results, as shown in Fig 3.

$$4\text{NbTi}_{0.5}\left(\text{Ni}_{x}\text{Cu}_{1-x}\right)\text{O}_4 \rightarrow 4\text{Ni}_x\text{Cu}_{1-x} + 4\text{H}_2\text{O}$$

Figure 1 | XRD patterns of NbTi$_{0.5}$(Ni$_x$Cu$_{1-x}$)$_{0.5}$O$_4$ (a: patterns of the oxidised form; b: patterns of the reduced form; c: patterns of oxidised form after three redox cycles; d: patterns of the reduced form after three redox cycles).

Figure 2 | Cell parameters of the oxidised NbTi$_{0.5}$Ni$_x$Cu$_{1-x}$O$_4$ powder samples with $x = 0, 0.25, 0.5, 0.75$ and 1.0.
High-resolution transmission electron microscopy (HR-TEM) analysis of the oxidised NTN 1C1O reveals lattice spacings of 2.546 Å (101) and 3.322 Å (110), as shown in Figs. 5 (a) and (b), consistent with the separation spacing determined by the XRD analysis. As presented in Figs. 5 (c) and 5 (d), the corresponding lattice spacing of the parent material, Nb1.33Ti0.67O4, can be obtained as 2.537 Å (101) and 3.363 Å (110). Moreover, the interplanar spacing is 2.238 Å (111). These spacings can be demonstrated by the results of the XRD analysis, shown in Figs. 1 and 2. Furthermore, the reduction of the NTN 1C1O leads to the growth of Ni0.5Cu0.5 alloy nanoparticles on the Nb1.33Ti0.67O4 surfaces in Fig. 5 (d). The analysis results for the nickel copper alloy indicates a lattice spacing of 1.781 Å (200), consistent with the standard data for the alloy Ni1Cu1 data51. These TEM results further demonstrate and validate the reversible exsolution of metallic particles on the ceramic substrate through control of the phase transformation between the NbTi0.5(NixCu1−x)O4 solid solution and NixCu1−x/Nb1.33Ti0.67O4, as confirmed by the aforementioned XRD, XPS and TGA analyses. More importantly, the TEM results reveal that

Figure 3 | XPS results for Nb(a), Ti(c), Ni(e) and Cu(g) in the oxidised NbTi0.5(Ni0.75Cu0.25)0.5O4 and for Nb(b), Ti(d), Ni(f) and Cu(h) in the reduced NbTi0.5(Ni0.75Cu0.25)0.5O4.
the alloy particles are exsolved to in situ grow and anchor to the surface of the highly electronically conducting Nb$_{1.33}$Ti$_{0.67}$O$_4$ in the form of heterojunctions, which avoids any possible agglomeration of exsolved metallic nanoparticles on the substrate surface at high temperatures. The metal alloy nanoparticles can be re-incorporated or re-exsolved into/from the host material, yielding a catalyst that can be regenerated through periodic exposure of the material to oxidising/reducing conditions.

Fig. 6 shows the SEM and energy-dispersive X-ray spectroscopy (EDS) maps taken from the oxidised and reduced NbTi$_{0.5}$ (Ni$_{0.5}$Cu$_{0.5}$)$_{0.5}$O$_4$ pellets. The sintered samples were reduced in 5% H$_2$/Ar at 900°C for 17 h. As shown in Fig. 6 (a), the Ni and Cu are homogeneously dispersed in the oxidised NTN$_1$C$_1$O sample and the other elements are also well distributed in the bulk. Although the oxidised sintered NTN$_1$C$_1$O pellet is not highly dense, clear images are still observed for the sample with low sinterability and high porosity. In comparison, uniform exsolved nanoparticles anchor on the surface of the reduced NbTi$_{0.5}$ (Ni$_{0.5}$Cu$_{0.5}$)$_{0.5}$O$_4$ pellet, as shown in Fig. 6 (b), which is further confirmed by the EDS maps of the Ni and Cu. In addition, the Nb, Ti and O, which are components of the new phase of Nb$_{1.33}$Ti$_{0.67}$O$_4$, as previously discussed, are distributed evenly in the sample. The SEM and EDS results presented in Figure 6 (b) of the reduced NTN$_1$C$_1$O suggest the exsolution of Ni$_{0.5}$Cu$_{0.5}$ alloy nanoparticles to anchor on the substrate surfaces. The presence of Ni$_{0.5}$Cu$_{0.5}$ alloy nanoparticles is further confirmed by the SEM and EDS results in addition to the XRD, XPS and TEM results, as previously mentioned. These results indicate that the reversible exsolution of NiCu alloy nanoparticles from the parent NbTi$_{0.5}$ (Ni$_{0.5}$Cu$_{0.5}$)$_{0.5}$O$_4$ material to grow in situ and anchor the metal alloy nanocatalyst on the Nb$_{1.33}$Ti$_{0.67}$O$_4$ surface is successful. The dispersed Ni$_{0.5}$Cu$_{0.5}$ nanoparticles anchoring on the Nb$_{1.33}$Ti$_{0.67}$O$_4$ surface are expected to prohibit the agglomeration and improve the electrocatalytic activity of the composite cathode for high-temperature CO$_2$ electrolysis.

The dependence of the conductivity of the samples on the temperature and oxygen partial pressure was systematically investigated, as shown in Fig. 7. According to the literature, Nb$_{1.33}$Ti$_{0.67}$O$_4$ is a mixed conductor because of the edge sharing of NbO$_6$ octahedra along the c-axis, which results in Nb-Nb metal bond overlap with an inter-metallic distance of 3 Å. The reduced NbTi$_{0.5}$ (Ni$_{0.5}$Cu$_{0.5}$)$_{0.5}$O$_4$ ceramic samples (Nb$_{1.33}$Ti$_{0.67}$O$_4$ + Ni$_{0.5}$Cu$_{0.5}$) exhibit greater conductivity, as shown in Fig. 7 (a), because the metallic Ni$_{0.5}$Cu$_{0.5}$ nanoparticles dispersed on the substrate improve the electrical conductivity under a reducing atmosphere (5% H$_2$/Ar, 99.99% purity). The reduced NbTi$_{0.5}$Cu$_{0.5}$O$_4$ (Nb$_{1.33}$Ti$_{0.67}$O$_4$ + Cu) sample exhibits the highest conductivity, which reaches approximately 500 S·cm$^{-1}$ at 730°C. With increasing nickel composition, the conductivity of the reduced samples gradually decreases to...
...resistance is approximately 300 V under a series of different hydrogen partial pressures (0, 2, 5, 20, 40, V...
Figure 8 | AC impedance plots for the symmetrical cells based on NbTi_{0.5}(Ni_{x}Cu_{1-x})O_{4} electrodes with x = 1 (a, b, c), x = 0.75 (d, e, f), x = 0.5, (g, h, i), x = 0.25 (j, k, l) and x = 0 (m, n, o) tested at 800°C under different hydrogen partial pressures.
NTNxC1-xO composite cathodes for direct CO$_2$ electrolysis under applied voltages of 1.2, 1.3 and 1.4 V, respectively. As shown in Fig. 11 (a), the CO production rates gradually improve with increasing applied voltage for all of the electrolysers and exhibit the highest rates at a final applied voltage of 1.4 V because high voltages favour CO$_2$ splitting at the cathode. The CO production rate of the electrolyser with the NTN$_{3C1O( x \approx 0.75)}$ composite cathode is 0.1629 ml$^{-}\text{min}^{-1} \cdot \text{cm}^{-2}$ at 1.4 V, which is approximately three times greater than the rate of 0.04113 ml$^{-}\text{min}^{-1} \cdot \text{cm}^{-2}$ for the cell at the same applied voltage of 1.2 V. However, we note that the production rate of CO is strongly dependent on the nickel composition in the parent material, i.e., the NbTi$_{0.5}(\text{Ni}_{x}\text{Cu}_{1-x})_{0.5}$O$_4$ solid solution, which definitely determines the nickel concentration of the metallic $\text{Ni}_{x}\text{Cu}_{1-x}$ alloy nanocatalysts. The electrolyser produces CO at a rate of 0.07663 ml$^{-}\text{min}^{-1} \cdot \text{cm}^{-2}$ in the case of the NTNO composite cathode and was significantly enhanced to as high as 0.3866 ml$^{-}\text{min}^{-1} \cdot \text{cm}^{-2}$ in the case of the NTNO cathode at a voltage of 1.4 V. These results again verify the superior catalytic activity of the nickel catalyst toward electrochemical CO$_2$ splitting. Similar behaviour of the CO production rate versus the nickel composition was also observed at applied voltages of 1.2 and 1.3 V. Clearly, the CO production improves slowly when $x < 0.5$ and then increases rapidly in the interval of $0.5 \leq x \leq 1$. This behaviour can be attributed to the excellent catalytic activity of the $\text{Ni}_{x}\text{Cu}_{1-x}$ alloy when the nickel concentration is high.

Fig. 11 (b) shows the current efficiencies of the electrolysers versus the nickel composition for the case of NTN$_{3C1O}$ composite cathodes during direct CO$_2$ electrolysis under different applied voltages. The current efficiencies gradually improve with increasing copper content in the composition range of $0 \leq x \leq 0.75$ because of the adsorption of CO$_2$ onto copper. However, the current efficiencies begin to decrease when the copper content is in the range of $0.75 \leq x \leq 1$, although they are still greater than the current efficiencies of the cathode with $x = 0$. Copper with excellent CO$_2$/CO adsorption properties is expected to facilitate the electrochemical conversion of CO$_2$ to CO and to therefore improve the current efficiencies. The optimum composition of $\text{Ni}_{0.75}\text{Cu}_{0.25}$ alloy catalyst combines the advantages of both metallic nickel and metallic copper to maximise current efficiencies for the direct CO$_2$ electrolysis. The highest current efficiency of 74.29% are obtained in the case of the NTNO cathode at 1.4 V. Similarly, the current efficiencies are accordingly improved versus the applied voltage because the applied voltages electrochemically reduce/activate the composite cathodes to enhance the electrocatalytic activity. The in situ growth and anchoring of $\text{Ni}_{x}\text{Cu}_{1-x}$ alloy nanocatalysts on the Nb$_{1.33}\text{Ti}_{0.67}$O$_4$ surface combines the advantages of metallic nickel and copper and produces a synergistic effect to maximise the current efficiencies for the direct electrolysis of CO$_2$. The coupling of metal catalysts with the electronically conducting ceramic substrate offers possibilities for the direct CO$_2$ electrolysis at high temperatures.

**Conclusion**

In this work, the in situ growth of $\text{Ni}_{x}\text{Cu}_{1-x}$ ($x = 0, 0.25, 0.50, 0.75$ and $1.0$) alloy catalysts was achieved to anchor on the redox-reversible
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**Acknowledgments**

This work was financially supported by the Natural Science Foundation of China (NSFC), No. 21303037, the China Postdoctoral Science Foundation, No. 2013MS5150, the Ministry of Education of Overseas Returnees Fund, No. 20131792, and the Fundamental Research Funds for the Central Universities, No. 2012HGZY0001.

**Author contributions**

H.W. conducted the experiments. K.X., H.W., Y.Z., I.Y., J.C., Y.W.Y.Q. and J.Z. drafted the manuscript. K.X. and Y.W. supervised the experiments. All authors were involved in the data analysis and discussions.

**Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Wei, H.S. et al. *In situ* Growth of Ni$_x$Cu$_{1-x}$ Alloy Nanocatalysts on Redox-reversible Rutile (Nb,Ti)O$_x$ Towards High-Temperature Carbon Dioxide Electrolysis. *Sci. Rep.* 4, 5156; DOI:10.1038/srep05156 (2014).

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