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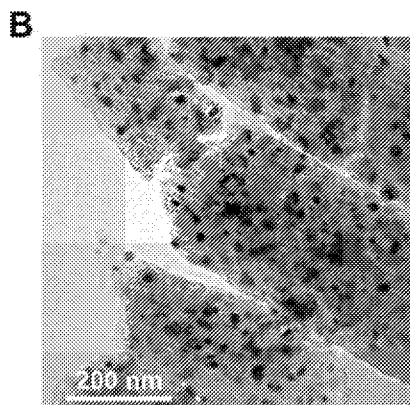
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Figures 1



(57) Abstract: The invention provides a highly selective catalyst containing transition metal atoms or clusters coordinated in electrically conductive support materials. These materials can be employed as active centers for CO₂ reduction to carbon monoxide (CO) within a liquid medium or in the gas phase, with a high Faradaic efficiency and higher current-per-mass catalyst values and fast turnover frequencies. The catalyst can be paired with an oxygen evolution reaction (OER) catalyst and powered by a solar cell for an artificial photosynthesis system, allowing the production of CO from CO₂ in a liquid medium, e.g., at neutral, acidic, or basic pH, or in the gas phase, e.g., via gas diffusion electrode.

METAL-DOPED CATALYST, METHODS FOR ITS PRODUCTION AND USES THEREOF**FIELD OF THE INVENTION**

The invention is directed to the field of supported metal catalysis during electrochemical processes.

5 BACKGROUND OF THE INVENTION

Effectively converting clean solar energy into carbon fuels via electrocatalytic carbon dioxide (CO₂) reduction and water oxidation, a mimic process of photosynthesis in nature, can potentially play a critical role in sustaining global energy demands and in reducing further CO₂ emissions (1-5). However, practical application is currently challenged by the low activity and selectivity of CO₂ reduction due to high kinetic
10 barriers and also competition with hydrogen evolution reactions (HER) in aqueous media (6-8). Strategies including exploring novel catalysts (7-9), or using non-aqueous electrolytes such as ionic liquids (9-11), have been extensively studied to reduce reaction barriers or suppress HER. Highly selective CO₂ reduction reaction (CO₂RR) requires catalysts to have specific electronic structures which could facilitate the CO₂ activation process and also properly bind reaction intermediates, not too strong nor too weak
15 (12). A representative example is a transition metal (TM) catalyst such as Au, which has been demonstrated to convert CO₂ to carbon monoxide (CO) with high selectivity (13-15), while Pt, with one fewer d-band electron, generates H₂ exclusively and can be easily poisoned by CO (16,17).

Other Earth-abundant TMs such as Fe, Co, and Ni are rarely studied as CO₂ reduction catalysts, mainly due to their high HER activities as well as the strong bonding between CO and the metal surfaces (16-
20 20). Therefore, how to effectively tune the catalytic electronic properties plays a critical role in searching for active CO₂ reduction catalysts.

SUMMARY OF THE INVENTION

We have developed a highly selective catalyst containing transition metal atoms or clusters coordinated in electrically conductive support materials. These materials can be used as active centers for CO₂
25 reduction to carbon monoxide (CO) within a liquid medium or in the gas phase, with a high Faradaic efficiency and higher current-per-mass catalyst values and fast turnover frequencies. The catalyst can be paired with an oxygen evolution reaction (OER) catalyst and powered by a solar cell for an artificial photosynthesis system, allowing the production of CO from CO₂ in a liquid medium, e.g., at neutral, acidic, or basic pH, or in the gas phase, e.g., via gas diffusion electrode.

30 One aspect of the invention features a composition that includes an electrically conductive support material and a transition metal atom or cluster which is incorporated within the electrically conductive support material. In some embodiments, the electrically conductive support material is carbon particles (e.g., activated), carbon powder (e.g., activated), graphene, reduced graphene oxide, graphene oxide, or a carbon nanotube. In one embodiment, the electrically conductive support material is graphene. In
35 another embodiment, the electrically conductive support material is graphene oxide. In other embodiments, the transition metal atom is Ni, Co, Fe, Mn, Rh, Pt, Cu, Mo, or W, in particular Ni. In further embodiments, the electrically conductive support material includes a dopant atom incorporated

within. The dopant atom is, for example, from Group 13, Group 15, or Group 16 of the periodic table, such as N, P, B, O, or S, in particular N. In one embodiment, the composition includes a core of the transition metal surrounded by a shell of transition metal atoms or clusters in the electrically conductive support material. In other embodiments, the composition does not include a core of the transition metal.

5 For example, the composition may include a uniform distribution of transition metal atoms or clusters in the electrically conductive support material. For example, the composition is in the form of a nanosheet, e.g., with single atoms of the transition metal.

In one embodiment, the composition includes Ni incorporated into graphene, optionally further including N incorporated within the graphene. In one embodiment, the composition includes Ni incorporated into
10 graphene oxide, optionally further including N incorporated within the graphene oxide.

In other embodiments, the composition includes a transition metal nanoparticle (e.g., 5 to 50 nm, such ~ 20 nm) surrounded by the support material, where the nanoparticle is not solvent accessible. For example, the nanoparticle may include several layers, e.g., 2 to 50, of the support material, e.g., graphene, surrounding it where the outermost layer contains transition metal atoms or clusters
15 incorporated within.

Another aspect of the invention features a method for fabricating a catalyst. A transition metal salt, carbon source, and optionally a dopant source are mixed together, and the mixture is heated to form an electrically conductive support material having a transition metal atom and optionally a dopant atom incorporated within.

20 In some embodiments of the method, the morphology of the mixture is that of fibers, nanosheets, particles, or powders. In one embodiment, the morphology is particles. In another embodiment, the morphology is nanosheets. In yet another embodiment, the morphology is fibers. In some embodiments, the fibers can be produced from electrospinning. In any of the above embodiments, the source of the dopant and carbon can be the same material.

25 In a further aspect, the invention features a method for the reduction of CO₂ in a liquid medium, where a composition of the invention contacts CO₂ in a liquid medium, and a voltage potential is applied to the composition sufficient to cause the reduction of CO₂.

In some embodiments of the method, the liquid medium is aqueous. In other embodiments, the liquid medium is non-aqueous. The method of the invention further includes a step for the oxidation of water
30 into O₂ including water contact with a second catalyst, where the second catalyst is separated from the catalyst composition of the invention by an ion permeable membrane, with the second catalyst and catalyst composition of the invention electrically connected. In some embodiments of the method, the second catalyst is an oxygen evolution reaction catalyst such as Co₃O₄ doped with Li⁺ ions, a transition metal oxide, a transition metal sulfide, a transition metal phosphide, Ir, or Ru, in particular Co₃O₄ doped
35 with Li⁺ ions. In some embodiments, the voltage potential may be supplied by a photovoltaic cell.

In a related aspect, the invention features a method for the reduction of CO₂ in a gas (e.g., humidified CO₂), where a composition of the invention contacts CO₂ in the gas, and a voltage potential is applied to the composition sufficient to cause the reduction of CO₂. In some embodiments, the composition is in a

membrane electrode. Gaseous CO₂ may have any suitable humidity, e.g., 0.01% to 100%, such as 0.1% to 50%.

In some embodiments of any method of the invention, the CO₂ is reduced to CO, a hydrocarbon, or an alcohol. The method may further include a corresponding oxidation reaction, e.g., oxidizing water, formic acid, methanol, ethanol, or SO₃. The corresponding oxidation, e.g., of water, formic acid, methanol, ethanol, or SO₃, occurs at an electrode separated from the composition of the invention by an ion permeable membrane, and the electrode and composition of the invention are electrically connected. In some embodiments, the electrode includes an oxygen evolution reaction catalyst such as Co₃O₄ doped with Li⁺ ions, a transition metal oxide, a transition metal sulfide, a transition metal phosphide, IrO₂, or Ru, in particular, IrO₂.

As used herein, the term “cluster” refers to a group of atoms having no cross-sectional dimension greater than 1 nm.

As used herein, “incorporated within” refers to the incorporation of individual atoms or a cluster within the support layer. Incorporation may be by coordination or other bond formation.

As used herein, graphene and similar monolayer materials may refer to a single layer of a multilayer structure.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A-1D: Characterization of NiN-GS catalysts. **(A)** Scanning electron microscopy (SEM) image of carbonized electrospun polymer NFs. **(B)** TEM image of ball-milled NiN-GS catalyst. **(C)** Aberration-corrected STEM image of a Ni NP tightly wrapped by a few graphene layers. The Ni NP is ~ 20 nm in diameter. The GS is ~ 10 nm thick. The layer spacing is measured to be 0.34 nm. **(D)** EDS mapping of NiN-GS catalyst.

Figures 2A-2D: **(A)** TEM image of Ni-NG nanosheet. No Ni NPs were observed. **(B)** Aberration-corrected HAADF-STEM image of Ni-NG nanosheet. The uniformly distributed bright dots represent Ni atoms due to the high mass compared to C or N. **(C)** A zoom-in STEM image of Ni-NG. Isolated Ni single atoms (brighter dots) were observed, and a few representatives were indicated by circles. **(D)** Elemental mapping of Ni-NG nanosheet confirming the co-existence of C, N, and Ni atoms.

Figures 3A-3E: **(A)** OER CVs of pristine Co₃O₄, Li-Co₃O₄, and IrO₂ at a scan rate of 5 mV/s in pH 7.5 solution under a catalyst loading of 4 mg/cm² on carbon fiber papers. **(B)** Long-term OER stability and O₂ FE test of Li-Co₃O₄ under 5 mA/cm² current. **(C)** Schematic of the artificial photosynthesis system, with the triple junction solar cell and the electrosynthetic cell directly wired together. **(D)** I-V curves of the 1 cm² triple junction solar cell under illumination and in the dark, with the electrosynthetic full cell I-V curve overlapped. **(E)** Faradaic efficiency and Solar-to-fuel efficiency curves of NiN-GS catalyst in the currently adapted electrosynthetic cell.

Figures 4A-4E: **(A)** Schematic of the anion MEA, with a cathode of Ni-NG for CO₂RR and an anode of IrO₂ for oxygen evolution reaction. The Ni-NG catalyst does not directly contact liquid electrolyte. **(B)** The steady-state current of Ni-NG (0.5 mg/cm²) on the 4-cm² electrode. **(C)** Corresponding FEs of H₂ and

CO. The error bars represent three independent samples. **(D)** Long-term electrolysis under a full-cell voltage of 2.78 V and a current of ~ 200 mA (~ 50 mA/cm²). The CO selectivity maintained above 90% over the course of 8-h continuous operation. **(E)** The accumulated CO production during the 8-h continuous electrolysis.

5 Figures 5A-5B: **(A)** Measurement of graphene layer spacing by STEM with the arrows indicating the region for spacing analysis. **(B)** Integrated pixel intensities of graphene layers along (001) spacing directions (perpendicular to the facets). The peaks and valleys represent the atoms and gaps, respectively. The layer spacing of 0.34 nm is averaged over 6 atomic layers for high accuracy and is close to the literature value of 0.335 nm (21).

10 Figures 6A-6E: EDS mapping of NiN-GS. **(A)** STEM image of NiN-GS. **(B)** EDS mapping of Ni, N and C. **(C, D)** The corresponding EDS spectra of selected areas in Ni mapping (rectangular area in **(B)**). **(E)** Enhanced Ni EDS signals in the GS region after tuning of the image contrast.

Figure 7: Raman spectra of NiN-GS, Ni-GS, and CoN-GS catalysts. The distinguished peaks at ~ 1350 and 1580 cm⁻¹ are assigned to defected graphite (D band) and graphite (G band) features, respectively.

15 Figures 8A-8B: TEM characterizations of Ni-GS. The graphene layers in **(B)** shows less curvatures and defects compared with NiN-GS in Figure 1C and Figure 6A.

Figures 9A-9D: EDS mapping of Ni-GS. **(A)** STEM image of Ni-GS. **(B)** EDS mapping of Ni and C. **(C, D)** Corresponding EDS spectra of selected areas in Ni mapping (red rectangles of **(B)**).

Figures 10A-10C: **(A)** Normalized XPS survey spectra of NiN-GS, VAL-NiN-GS, Ni-GS, CoN-GS, FeN-GS, and N-CNF. **(B)** XPS spectra of Ni 2p regions of NiN-GS, VAL-NiN-GS, and Ni-GS. The Ni 2p_{3/2} peak in Ni-GS indicated by the dash line is consistent with Ni metals, which is contributed by the embedded Ni NPs. (22, 23). **(C)** XPS spectra of N 1s regions of NiN-GS, VAL-NiN-GS, and Ni-GS. The ratio of pyridinic N in N-CNF is slightly more than that of NiN-GS and VAL-NiN-GS.

Figures 11A-11H: EDLC measurements for bare glassy carbon electrode **(A, B)**, NiN-GS **(C, D)**, Ni-GS **(E, F)**, and N-CNF **(G, H)**.

Figures 12A-12E: Electrocatalytic CO₂ reduction performance of NiN-GS. **(A)** CVs of NiN-GS in CO₂ and N₂ saturated electrolyte, suggesting a different reaction pathway when CO₂ is in present. **(B)** FEs of H₂ and CO under different applied potentials for NiN-GS. The error bars are based on three identical samples. **(C)** Partial currents of H₂ and CO. **(D)** Long-term electrolysis test under -0.7 V overpotential. **(E)** The cumulative TON of CO₂ to CO conversion on the Ni active sites based on the electrolysis in Fig. 2D.

Figures 13A-13D: TEM images of NiN-GS catalysts after acid leaching **(A, B)** and violent acid leaching **(C, D)** processes. The embedded Ni NPs cannot be leached away until the CNF was broken into small pieces with pin holes introduced to graphene shells as shown in **(C)**. This shell protection can prevent the direct contact between Ni NPs and water.

Figures 14A-14D: Catalytic performance of Ni-GS and N-CNF indicating the dominant product for both is H₂.

Figures 15A-15D: EDLC measurements for AL-NiN-GS (**A, B**), and VAL-NiN-GS (**C, D**). The significantly increased capacitance of VAL-NiN-GS is due to the violent ball milling which greatly increases the surface area of the catalysts with the same mass loading on electrode.

Figures 16A-16D: Catalytic performance of catalysts before and after acid leaching processes.

- 5 Figures 17A-17D: TEM images of CoN-GS (**A, B**) and FeN-GS (**C, D**) catalysts, which present similar core-shell structures with NiN-GS.

Figures 18A-18D: Catalytic performance of CoN-GS and FeN-GS compared with NiN-GS indicating the CO FEs of Co and Fe catalysts are much lower than that of Ni.

- Figures 19A-19F: (**A**) Ni K-edge XANES of Ni-NG catalyst as well as Ni metal and NiO as the
 10 references. (**B**) Charge density distribution of the Ni single atoms confined in graphene vacancies (Ni-NG in single vacancy configuration, *vide infra*). The pronounced delocalization observed in both charge density difference plots indicates a strong interaction and a significant charge transfer between coordinated C or N atoms and single Ni atom. (**C**) *in situ* electrochemical XANES spectra of Ni-NG under different potentials during CO₂RR electrolysis. (**D**) Ni K-edge Fourier transformed EXAFS spectra in R
 15 space of Ni-NG catalyst in comparison to other Ni-based control samples. (**E**) N K-edge and (**F**) C K-edge XAS spectra for Ni-NG and reference samples.

- Figures 20A-20D: (**A**) TEM image of Ni single atoms and N co-doped carbon powder catalyst. (**B**) HAADF-STEM image and elemental mapping of Ni-N-C. (**C**) Recorded steady-state current of Ni-N-C catalyst cast on the anion membrane electrode assembly, together with the partial currents of CO and
 20 H₂. (**D**) Long-term electrolysis performance.

- Figures 21A-21F: GC measurement set up and a representative example to demonstrate the whole process of FE measurement. (**A**) 1. Mass flow control (MFC) for an accurate 50 sccm CO₂ flow rate. 2. CO₂ gas flows into the cell. 3. CO₂ gas flows out of the reactor bringing gas products together. 4. The gas mixture fills the sampling loop of GC continuously. 5. The continuous gas flow is monitored by the
 25 bubbles generated in the glass. (**B**) Chronoamperometry of CO₂ reduction under -0.82 V vs RHE. (**C, D**) TCD and FID responses to the gas products. (**E, F**) TCD and FID standard gas calibration.

Figure 22: FID spectra of 20 sccm CO₂ flow through H-Cell without potential control (black line) and with potential hold at 0.35 V vs RHE (red line) of NiN-GS sample.

- Figure 23: Linear sweep voltammetry of 2 mg cm⁻² NiN-GS on high surface area carbon fiber paper
 30 substrate at a scan rate of 5 mV s⁻¹ in 0.5 M KHCO₃. The inset is the FEs of H₂ and CO under different potentials using the current NiN-GS catalyst deposited on the carbon fiber paper substrate.

Figure 24: GC-MS spectra recorded during isotope ¹³CO₂ electrolysis over NiN-GS at - 0.82 V vs RHE. The main peak at ca. 2.2 min arises from ¹³CO₂ background, and the shoulder peak at ca. 1.9 min can be ascribed to the generation of ¹³CO as reduction product.

- 35 Figure 25: Tafel slope of CO evolution on NiN-GS catalyst. Currents are averaged over electrolysis currents.

Figures 26A-26B: **(A)** Typical GC-FID spectrum recorded during CO₂ electrolysis over NiN-GS at - 0.82 V vs RHE (red line) together with a reference spectrum of standard mixture gas (black line at bottom) containing 101 ppm of C₂H₄, 100 ppm of C₂H₆, 100 ppm of C₂H₂, 100 ppm of CH₄, and 100 ppm of CO. Insert is a zoomed-in region of working sample indicating no other gas products were detected. **(B)** ¹H NMR spectra of any reduction product after 2h of electrolysis at - 0.82 V vs RHE over NiN-GS, together with a standard sample of 0.1 M KHCO₃ containing a mixture of species at low concentrations.

Figures 27A-27D: TEM images of NiN-GS before **(A and B)** and after **(C and D)** 20 h continuous electrolysis under - 0.7 V CO₂ to CO overpotential indicating the robustness of the graphene shell after long-term electrolysis.

Figures 28A-28E: **(A)** FE of H₂ and the corresponding steady-state current densities of Ni-NG on a glassy carbon electrode (GCE) in CO₂-saturated 0.5 M KHCO₃. The catalyst mass loading is 0.2 mg/cm². The error bars represent three independent samples. **(B)** FE of CO and the corresponding steady-state current densities of Ni-NG on GCE in CO₂-saturated 0.5 M KHCO₃. The catalyst mass loading is 0.2 mg/cm². The error bars represent three independent samples. **(C)** FE of H₂ and the corresponding steady-state current densities of Ni-NG on carbon fiber paper (CFP) in CO₂-saturated 0.5 M KHCO₃. The catalyst mass loading is 1 mg/cm². All gas products were sampled into on-line GC after a continuous electrolysis of ~ 15 min under each potential. **(D)** FE of CO and the corresponding steady-state current densities of Ni-NG on CFP in CO₂-saturated 0.5 M KHCO₃. The catalyst mass loading is 1 mg/cm². All gas products were sampled into on-line GC after a continuous electrolysis of ~ 15 min under each potential. **(E)** The CO₂RR stability test of current density and CO FE of Ni-NG on CFP under 0.64 V overpotential for more than 20 h continuous operation. The error bars represent two independent samples.

Figure 29A-29B: Electrocatalytic CO₂ reduction performance of NiN-GS in 0.5 M KHCO₃ solutions under a current density of ~5 mA cm⁻² under a catalyst mass loading of 0.2 mg cm⁻².

Figure 30: The galvanostatic cycling profile of Co₃O₄ NPs on CFP electrode. The Li⁺ charging and discharging process helps to create active boundaries and surface areas in Co₃O₄ catalysts.

Figures 31A-31D: SEM images of Co₃O₄ NPs before **(A, B)** and after **(C, D)** the Li⁺ tuning process revealing the reduction of the NP grains after Li⁺ tuning.

Figure 32: XRD patterns of Co₃O₄ and Li-Co₃O₄. No peaks can be detected after the Li⁺ tuning process, suggesting the NPs created by the Li⁺ tuning method are substantially smaller.

Figure 33A-33C: The 3D-printed electrosynthetic cell for artificial photosynthesis. **(A)** An expanded view of the 3D-printed cell. **(B)** A photograph of the 3D-printed electrosynthetic cell. The cathodic chamber is filled with 0.5 M KHCO₃ and the anodic chamber is filled with 0.5 M KHCO₃ + 0.5 M K₂HPO₄/KH₂PO₄ buffer solution. The pH is balanced at 7.5 under CO₂ saturation. The cathode catalyst is NiN-GS for CO₂ reduction to CO, and anode catalyst is Li⁺-Co₃O₄ for OER. **(C)** The solution resistance across the two electrodes was measured to be ~15 Ω.

Figures 34A-34D: **(A)** Photograph of the triple junction solar cell used in a device containing the invention. **(B)** P-V curve of the triple junction solar cell, with a maximal solar to electricity efficiency of 27.2 % under

AM 1.5G 0.5 Sun illumination. (C) The solar cell voltage remains stable at ~ 2.4 V. (D) The accumulated CO volume during the 10-h continuous artificial photosynthesis.

DETAILED DESCRIPTION OF THE INVENTION

Different methods, such as metal oxidation and metal alloying, have been demonstrated to be successful in engineering TM electronic states for improved CO₂ reduction activities (6, 7, 15, 24, 25). However, these engineering processes on TM catalysts usually result in complicated atomic structures and complex coordination, making it difficult to study and understand the possible catalytic active sites. Instead, introducing TM atoms into a well-established material matrix could open up new opportunities to: 1) tune the electronic properties of TMs as CO₂ reduction active sites, and 2) at the same time maintain relatively simple atomic coordination for fundamental mechanism studies (8). In addition, TM atoms trapped in a confined environment cannot be easily moved around during catalysis, which prevents the nucleation or reconstruction of surface atoms observed in many cases (26-29). Graphene layers, including graphitized carbon, are of particular interest as hosts for TM atoms due to their high electron conductivity, chemical stability, and inertness to both CO₂ reduction and HER catalytic reactions (30). TM atoms can be trapped in the naturally or chemically formed defects of the graphene such as single vacancies (SVs) and double vacancies (DVs), presenting distinctively different properties from bulk metal materials (31-33). By introducing dopants, defects can be generated in graphene, which could significantly increase the concentration of TM atoms coordinated within the layers (34).

The invention provides compositions containing transition metal atoms or clusters for use as catalytic materials in electrochemical reactions; e. g., the electrochemical reduction of carbon dioxide (CO₂) into carbon monoxide (CO) in a liquid medium or gas, e.g., by in a membrane electrode assembly. The compositions are advantageous as they use Earth-abundant transition metals as the active site of the catalyst, have high Faradaic efficiency, high current-per-mass values, and fast turnover rates (TOR). Methods of producing the compositions are also provided by the invention.

The invention also provides compositions containing single Ni atoms uniformly dispersed in a two-dimensional (2D) graphene layer as highly active and selective centers for electrocatalytic CO₂ to CO conversion. As a result of this single atom within layers structure, more than 90% of the CO selectivity was delivered within a wide electrochemical potential in aqueous solution, with a maximal CO Faradaic efficiency (FE) of more than 95 % under an overpotential of 550 mV. The single Ni atomic sites also have excellent stability and are able to maintain a stable CO selectivity of ~ 90 % for over 20 hours of continuous electrolysis. A CO evolution current of more than 200 mA (50 mA/cm²) under a 97 % FE was demonstrated on a 4 cm² anion membrane electrode assembly using Earth-abundant catalytic materials.

In one embodiment, the composition includes a core of the transition metal surrounded by a shell of transition metal atoms or clusters in the electrically conductive support material. In other embodiments, the composition does not include a core of the transition metal. In particular, the invention provides compositions containing single transition metal atoms dispersed in a two-dimensional (2D) electrically conductive support material, e.g., a layered electrically conductive support material. The transition metal atoms may be distributed uniformly in the electrically conductive support material or may be distributed

randomly in the electrically conductive support material. For example, the composition is in the form of a nanosheet, e.g., with single atoms of the transition metal.

The invention also provides methods for using the composition in an electrochemical cell for reducing CO₂, e.g., into CO. The described methods provide CO or other carbon compounds, which can be collected.

Compositions

A composition of the invention includes an electrically conductive support material and a transition metal atom or cluster incorporated within the support material.

Suitable electrically conductive support materials include carbonaceous materials such as carbon powder (e.g., activated), carbon particles (e.g., activated), graphene, reduced graphene oxide, graphene oxide, and carbon nanotubes. Exemplary electrically conductive support materials are graphene and graphene oxide. Support materials may be a single layer of material or part of a multilayer structure. For example, graphene or graphene oxide can be a single-layer material or a multi-layer material (two-layer, three-layer, etc.).

Transition metals useful for the compositions include, but are not limited to, Ni, Co, Fe, Mn, Rh, Pt, Cu, Mo, and W. An exemplary transition metal is Ni.

Clusters incorporated into the support material has no cross-sectional dimension of greater than 1 nm. For example, a cluster incorporated into the support material may include 2, 3, 4, 5, 6, 7, 8, 9, or 10 atoms.

The composition may also include dopant atoms, for example, that create defects for incorporation of transition metal atoms in the support material. Examples of dopants include elements selected from Group 13, Group 15, and Group 16 of the periodic table, e.g., N, P, B, O, and S. An exemplary dopant atom is nitrogen (N).

Figures 1A-1D and 2A-2D show representative images of an exemplary catalyst with graphene (Figs. 1A-1D) and graphene oxide (Figs. 2A-2D) as the support material, Ni as the transition metal, and N as the dopant atom.

Methods of production

The invention features a method for producing an electrically conductive support material containing transition metal atoms or clusters and optionally dopant atoms incorporated within the support material.

The method involves mixing together a solution of a transition metal salt, a source of carbon, and optionally a source for the dopant. This mixture is then heated via a furnace to produce a solid electrically conductive support material having a transition metal atom or cluster and optionally a dopant atom incorporated within.

Useful morphologies of compositions include fibers, nanosheets, particulate materials, e.g., particles, and powders. An example of a composition morphology is fibers (e.g., nanofibers, (NFs)). NFs can be produced by electrospinning. Other fiber production methods include, but are not limited to,

electrospray, extrusion, and solution dry spinning. Nanosheets, particulates, and powders can be formed by methods known in the art.

Suitable transition metal salts for incorporation within the support material generally include salts of any counterion (e.g., Cl^- , NO_3^- , or SO_4^{2-}).

5 The sources of carbon include polymeric and non-polymeric materials. Examples include poly(alkylene oxides), e.g. polyethylene glycol, polypropylene oxides, polyacrylic polymers (e.g., polyacrylonitrile, polyacrylamide), polypyrrolidone, polyvinyl alcohol, amorphous carbons, and halogenated aromatics. Examples of non-polymeric materials include carbohydrates (e.g., glucose and sucrose). The carbon source may also be a support material, e.g., graphene oxide that has defects for incorporation of
10 transition metal atoms or clusters.

The source of the dopant atom can be one of the carbon source materials, such as the nitrogen containing polymers, or can be a separate material. Other sources for dopant atoms are known in the art. For example, sources of nitrogen include ammonia and urea.

To form the support material from a liquid mixture, the mixture is heated, e.g., under graphitization
15 conditions, using methods known in the art. The heating process can be done in the presence of air, an inert gas (e.g., H_2 or Ar), or under vacuum to produce the composition. In one example, transition metal atoms or clusters can be incorporated into a support material that already contains atomic-scale defects, e.g. graphene oxide. For example, a transition metal salt can be dispersed over the surface of graphene oxide, and the mixture can be annealed to incorporate the transition metal atom or cluster within the
20 support.

For example, a particulate material can be formed by mixing metal salts, activated carbon particles, and N-atom dopants and annealing the mixture in a furnace with a flow of an inert gas (e.g., H_2 or Ar). Carbon particles can be activated by acids or other oxidation method and dispersed in water or other solvent. Metal salts can be dissolved into a solvent to facilitate adsorption onto the surface of the carbon
25 materials, e.g., particles. The mixture can be centrifuged and dried and can be further mixed with dopants, e.g., N-atom dopants, e.g., urea or NH_3 , during the annealing process.

Methods of use

The invention features a method for using a composition of the invention as a catalyst for electrochemical reactions performed in a liquid medium or in the gas phase, e.g., via a membrane
30 electrode assembly. Chemical reactions which can be catalyzed by a catalyst of the invention include, but are not limited to, the reduction of CO_2 into CO, the hydrogenation of CO_2 , and the hydrogenation of CO useful for producing carbon-based chemical feedstocks and fuels such as methane, linear and branched hydrocarbons, and alcohols.

One use for the catalyst of the invention is for producing CO from the reduction of CO_2 in a liquid
35 environment. CO produced can further be used as a feedstock for carbon-based fuels. The composition can be used as a material in an electrode in an electrocatalytic cell, where the electrode is immersed in a liquid medium. The composition can be deposited on electrodes, e.g., glassy carbon, by methods known in the art. Gaseous CO_2 can be bubbled through the liquid medium, which is reduced when a voltage

potential is applied to the composition. The liquid media can be an aqueous solution (e.g. buffered salt solution or pure water) or a non-aqueous solution (e.g. ionic liquid, alcohols, or nitriles). Liquids for electrochemical CO₂ reduction reactions are known in the art and include carbonate-based solutions, including CO₃²⁻, HCO₃⁻, and H₂CO₃ and alkali metal salts thereof. In one embodiment of the invention, the liquid is a solution of KHCO₃.

Another use for the catalyst of the invention is for producing CO from the reduction of CO₂ directly in the gas phase. The composition can be used as a material in an electrode in an electrochemical cell, where the electrode, such as a membrane electrode assembly, is configured to act as a gas diffusion layer. The composition can be deposited on electrodes, e.g., carbon fiber paper (CFP), by methods known in the art. Gaseous CO₂ can be delivered to the electrochemical cell through the gas diffusion layer, which is reduced when a voltage potential is applied to the composition.

Whether performed in liquid medium or in the gas phase, protons for the electrochemical reduction of CO₂, e.g., into CO, can be produced by an oxidation reaction coupled with the CO₂ reduction reaction. Examples of oxidation reactions that can be coupled with CO₂ reduction include water oxidation, formic acid oxidation, methanol oxidation, ethanol oxidation, and SO₃ oxidation. An exemplary oxidation reaction which releases protons is the oxidation of water; water oxidation also releases molecular oxygen (O₂). For example, water is in contact with a second catalyst separated from the CO₂ reduction catalyst by an ion permeable membrane (e.g., Nafion). Catalysts for oxygen evolution reactions (OER) are known in the art; examples include Co₃O₄ doped with Li⁺ ions, a transition metal oxide, a transition metal phosphide, iridium (Ir), and ruthenium (Ru). An example of an OER catalyst is Co₃O₄, where the surface of the catalyst has been tuned using Li⁺ ions. In one embodiment of the invention, this Li-Co₃O₄ catalyst is dissolved and deposited onto a suitable material to form an electrode for an electrocatalytic cell. Other OER catalysts include Ir, e.g., IrO₂, deposited on a carbon, e.g., CFP, substrate.

In one embodiment of the invention, the catalyst of the invention and the OER catalyst form the cathode and anode, respectively, of an electrocatalytic cell designed to mimic photosynthesis. A schematic of such a system and related performance metrics are shown in Figures 3A-3E. In another embodiment, the catalyst of the invention and the OER catalyst form the cathode and anode, respectively, of a membrane electrode assembly (MEA). A schematic of such a system and related performance metrics are shown in Figures 4A-4E. In a MEA, an ion permeable membrane, e.g., anion exchange membrane, e.g., PSMIM, is held between two gas diffusion electrodes to separate the chambers of the MEA. On the cathode side of the MEA, a channel, e.g., a metallic channel, may supply humidified CO₂ gas to the cathode. The anode side of the MEA may have a circulating aqueous electrolyte useful for CO₂ reduction. Liquids for electrochemical CO₂ reduction reactions are known in the art and include carbonate-based solutions, including CO₃²⁻, HCO₃⁻, and H₂CO₃ and alkali metal salts thereof.

In some embodiments, the electrocatalytic cell contains a photovoltaic device providing a sufficient voltage potential to drive the reactions. Such photovoltaic devices include, but are not limited to, semi-conductor-based single junction arrays, semi-conductor-based multi-junction arrays, dye-sensitized solar cells, thin-film solar cells, quantum dot solar cells, and/or combinations thereof.

EXAMPLES

Example 1 – Preparation of a Graphite-Supported Fiber Catalyst

A catalyst containing Ni as the transition metal and N as the dopant atom in a graphite support (NiN-GS catalyst) was prepared by dissolving 0.5 g polyacrylonitrile (PAN, MW=150,000), 0.5 g polypyrrolidone (PVP, MW=1,300,000), 0.5 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 0.1 g dicyandiamide (DCDA) in 10 mL of dimethylformamide (DMF) under 80 °C with constant stirring. The solution was then electrospun using a conventional electrospinning set-up with the following parameters: 15 kV of static electric voltage, 15 cm of air gap distance, 5 mL solution and 1.2 mL h⁻¹ flow rate. A carbon fiber paper (CFP) substrate (8 × 8 cm) was used as the collection substrate with – 4 kV electric voltage. The electrospun polymer nanofibers (NFs) on the CFP was then heated up to 300 °C in 1.5 h in the box furnace, and kept under the temperature for 0.5 h to oxidize the polymers. After the oxidization process, the NFs were self-detached from the carbon paper resulting in the freestanding film. Those NFs were further carbonized and graphitized under forming gas (5% H₂ in Ar) atmosphere, with 10 min ramping to 300 °C, and 2 h ramping to 750 °C, where it was maintained for another 1 h and followed by the natural cooling down. Considering the starting mass of 0.1 g Ni (in 0.5 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and a 60% mass loss of polymers observed during the oxidation and carbonization processes, the overall Ni to C ratio in NiN-GS catalyst should be more than 5%. The as-synthesized NiN-GS catalyst was then ball milled (5 min, Mixer/Miller 5100) to nano-powders for catalysis and characterizations. Co and Fe catalysts were synthesized with the same method. N-CNF was prepared without the addition of metal salts. Ni-GS catalyst was prepared by electrospinning of poly(vinyl alcohol) (PVA, MW=85,000) and Ni solution without N (1 g of PVA and 0.5 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 5 mL H₂O and 5 mL ethanol mixer), followed with the same carbonization process of NiN-GS. The acid leaching was performed by ultra-sonicating the NiN-GS sample in concentrated HCl (37 wt%) solution for 4 h, followed by repeated centrifuging and water rinsing until neutralization. To further remove the embedded Ni NPs, the violent acid leaching process was performed by ball milling the NiN-GS catalysts for 1 h where each 10 min was stopped for remixing the sample in the vial set, and followed with ultra-sonicating the sample in concentrated HCl acid for more than 8 h.

Example 2 – Preparation of a Graphene Oxide-Supported Catalyst

A catalyst containing Ni as the transition metal and N as the dopant atom in a graphene oxide support (Ni-NG) was prepared by the impregnation and reduction method. A 3 mg/mL nickel nitrate stock solution was first prepared by dissolving $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Puriss, Sigma-Aldrich) in Millipore water (18.2 MΩ·cm). A carbon suspension was prepared by mixing 50 mg graphene oxide sheets (GO, purchased from CYG and used as received) with 20 mL of Millipore water, and tip sonicated (Branson Digital Sonifier) for 30 min until a homogeneous dispersion was produced. 800 μL of Ni²⁺ solution was dropwise added into GO solution under vigorous stirring, followed by quickly freezing the solution in liquid nitrogen to produce an “ice cube” having a Ni:C atomic ratio of ~ 0.4 atomic percent. The “ice cube” was freeze-dried using a RVT4104 lyophilizer (Thermo) at -100 °C and below 0.2 Torr. The as-prepared $\text{Ni}(\text{NO}_3)_2/\text{GO}$ powder was heated in a tube furnace to 750 °C under a gas flow of 50 sccm NH₃ (anhydrous, Airgas) + 150 sccm Ar (UHP, Airgas) within 3 h, and kept at same temperature for another hour before cooling down to room temperature. N

doped graphene (NG) was prepared in a similar way but the absence of Ni precursor. To prepare Ni atoms doped graphene (Ni-G) and graphene supported Ni nanoparticles (Ni NPs/G), a forming gas (5% UHP H₂ balanced with UHP Ar, Airgas) flow was used during the annealing process, and 8 mL Ni²⁺ solution was added in the latter case. Other Metal-NG (Co, Fe, Cu, Mn) samples were prepared in a similar way with Ni-NG except to vary metal salt precursors of Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·2.5H₂O and Mn(NO₃)₂·4H₂O (Puriss or ACS Grade, Sigma-Aldrich), respectively.

Example 3 – Preparation of an Oxygen Evolving Reaction (OER) Catalyst

The oxygen evolving reaction (OER) catalyst Co₃O₄ NPs were directly synthesized on CFP electrode (AvCarb MGL270, FuelCellStore) by a previously developed dip-coating method (16). The solution of cobalt nitrate was first prepared by dissolving 40 wt% Co(NO₃)₂·6H₂O (Sigma-Aldrich) and 4 wt% PVP (MW=360,000, Sigma-Aldrich) into 56 wt% deionized water. Specifically, 2 g of Co(NO₃)₂·6H₂O and 0.2 g of PVP were dissolved into 2.8 mL of deionized water. O₂ plasma-treated CFP was then dipped into the solution and dried in the vacuum. The Co(NO₃)₂/CFP was then heated up to 350 °C in 1 h in air and kept there for another 1 h, where the Co(NO₃)₂ decomposed into Co₃O₄ NPs. The mass loading of Co₃O₄ was measured to be ~ 4mg cm⁻². The as-grown Co₃O₄ on CFP was made into a pouch cell battery with a piece of Li metal and 1.0 M LiPF₆ in 1:1 w/w ethylene carbonate/diethyl carbonate (BASF Chemicals) as the electrolyte. The galvanostatic cycling current is set at 0.2 mA cm⁻² and cycle between 0.4 and 3 V vs Li⁺/Li. The cutoff voltage of the last discharging step is 4.3 V for thoroughly delithiation. The galvanostatic cycled Co₃O₄ on CFP was then washed by ethanol and H₂O for SEM, XRD, and electrocatalytic characterizations. The IrO₂ benchmark catalyst ink was prepared with the same method of NiN-GS and drop casted onto CFP electrode with the same mass loading of Co₃O₄.

Example 4 – Physical Characterization of NiN-GS Catalysts

STEM characterization of the NiN-GS catalyst shown in Fig. 1C was carried out using a JEOL ARM200F aberration- corrected scanning transmission electron microscope under 80 kV. All other TEM images were obtained by using a JEOL 2100 transmission electron microscope operated under 200 kV. EDS analysis was performed on a JEOL ARM200F at 60kV, using an EDAX Octane Plus windowless detector. Drift correction was applied during acquisition. Raman spectroscopy was carried out using a WITEC CRM200 confocal Raman microscope with a 532 nm laser source. Typically, a dispersion grating of 600 grating lines per mm and a co-adding of 64 scans were applied in the spectral tests. X-ray photoelectron spectra were obtained with a Thermo Scientific K-Alpha ESCA spectrometer, using a monochromatic Al K α radiation (1486.6 eV) and a low energy flood gun as neutralizer. The binding energy of C 1s peak at 284.6 eV were used as reference. The elemental ratio on the surface of the NiN-GS catalyst is shown in Table 1. The quantification method is based on measuring the peak area of each element on the sample surface, since the number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the XPS sampling volume. To generate atomic percentage values, each raw XPS signal will be further corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF), and normalized over all of the elements detected. Thermo Advantage V5 program were employed for surface componential content analysis as well as peaks fitting for selected elemental scans. Powder X-ray diffraction data were collected using a Bruker D2 Phaser diffractometer

in parallel beam geometry employing Cu K α radiation and a 1-dimensional LYNXEYE detector, at a scan speed of 0.02° per step and a holding time of 1 s per step.

Graphitized carbon NFs (CNFs, ~ 200 nm in diameter) catalyzed by uniformly dispersed Ni NPs (~ 20 nm in diameter) were obtained after the carbonization process of polymers (Figs. 1A and 1B) (35-37). A closer observation of the Ni NPs by aberration-corrected scanning transmission electron microscopy (STEM) in Fig. 1C reveals that, the NP is tightly encapsulated by a few layers (~ 10 nm) of graphene as confirmed by the averaged layer spacing of ~ 0.34 nm (NiN-GS, Figs. 5A-5B). No Ni clusters were observed within the GS. This shell prevents the Ni NP from a direct contact with the aqueous electrolyte and can thus dramatically suppress HER. The existence of Ni atoms in the surface shell was confirmed by energy-dispersive X-ray spectroscopy (EDS) mapping in Fig. 1D, with EDS spectra of the area highlighted in the dashed line circle shown in Figs. 6A and 6B. The Z-contrast STEM image on the left panel shows three bright areas representing three Ni NPs, with one of them pointed out by the yellow circle. In the Ni mapping image (marked by green dots), in addition to the NP regions with concentrated signals, Ni peaks was also detected in the neighboring carbon areas (Figs. 6C-6E), demonstrating the successful incorporation of Ni atoms in the GS.

N doping here plays a critical role in creating defects in the graphene layers, which helps to trap and bond a significant number of Ni atoms in the GS (34). This is evidenced by both Raman and TEM characterizations where the graphene layers in NiN-GS present a defective nature compared with the sample without N incorporation (Ni-GS, Figs. 7 and 8A, 8B) (38). In addition, no Ni signals were detected in the GS outside of the Ni NP in Ni-GS, due to the high-quality of graphene synthesized (Fig. 9A-9D). Coordinated Ni atoms within the graphene layers in NiN-GS showed distinctively different oxidation states from Ni NPs covered below by X-ray photoelectron spectroscopy (XPS, Fig. 10A-10C, Table 1), suggesting the successful tuning of Ni electronic structures and thus the possible tuning of its catalytic activities.

Table 1. Atomic ratio of prepared NiN-GS catalyst surface characterized by XPS measurements.

Name	Peak B.E. (eV)	FWHM eV	Area (P) CPS (eV)	Atomic %
C 1s	285.28	3.10	1858162.16	88.44
O 1s	532.52	3.96	287062.59	5.65
N 1s	400.33	4.50	161996.11	4.97
Ni 2p	855.32	5.17	251638.19	0.93

Example 5 - Physical Characterization of Ni-NG Catalysts

The STEM characterization in Figures 2A-2D was carried out using a JEOL ARM200F aberration-corrected scanning transmission electron microscope under 80 kV. All other TEM images were obtained by using a JEOL 2100 transmission electron microscope operated under 200 kV. EDS analysis was performed on a JEOL ARM200F at 60kV, using an EDAX Octane Plus windowless detector. Drift correction was applied during acquisition.

X-ray photoelectron spectroscopy was obtained with a Thermo Scientific K-Alpha ESCA spectrometer, using a monochromatic Al K α radiation (1486.6 eV) and a low energy flood gun as neutralizer. The binding energy of C 1s peak at 284.6 eV were used as reference. Thermo Advantage V5 program were employed for surface componential content analysis as well as peaks fitting for selected elemental scans.

- 5 Ex situ XAS spectra on Ni, N, and C K-edge were acquired using the SXRMB beamline of the Canadian Light Source. The SXRMB beamline used a Si(111) double crystal monochromator to cover an energy range of 2–10 keV with a resolving power of 10000. The XAS measurement was performed in fluorescence mode using a 4-element Si(Li) drift detector in a vacuum chamber. The powder sample was spread onto double-sided, conducting carbon tape. Ni foil was used to calibrate the beamline energy. In situ electrochemical XAS measurement on Ni K-edge was carried at Beamline 8-ID, National Synchrotron Light Source II, Brookhaven National Laboratory, using a Si(111) monochromator and a Lytle detector. For in situ spectroelectrochemical tests, continuous CO₂ flow was delivered into an in-house TEFLON® H-cell filled with CO₂-saturated 0.5 M KHCO₃. A KAPTON® film covered carbon fiber paper (Ni-NG/CFP) working electrode served as the X-ray window for synchrotron radiation. Analyses of both the near edge (in energy scale) and extended range (in *R* space) XAS spectra were performed using Athena software.

Layered graphene oxide (GO) nanosheets were selected as the matrix material for Ni single atoms due to the following reasons: 1) a high density of defects have been created in GO; 2) the high-area, negatively-charged surface helps to uniformly absorb a monolayer of positive metal cations for single atom dispersion; 3) the density of single atom active sites can be maximized on the 2D surface for higher catalytic activities; 4) the single atomic site can be clearly characterized on the well-defined 2D structure. By controlling the amount of incorporated Ni ions followed by a high temperature annealing process with ammonia as the reducing reagent and the source of N dopants, atomically dispersed Ni atoms coordinated in graphene vacancies (Ni-NG) were obtained as shown in Figures 2A-2D. While no Ni NPs or clusters were observed in the 2D Ni-NG nanosheet in Figure 2A by transmission electron microscopy (TEM), the elemental mapping (Figure 2D) by energy-dispersive X-ray spectroscopy (EDS) suggests the existence and uniform distribution of Ni atoms. The atomic ratio was determined to be ~ 0.44 wt.% by X-ray photoelectron spectroscopy (XPS), consistent with the estimation from material synthesis. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with Z-contrast can differentiate Ni atoms out of the surrounding light elements for detailed characterization. Ni atoms with high contrast were observed to be homogeneous on the graphene layer (Figure 2B), which under a higher magnification suggests the atomically dispersed morphology in Figure 2C. The circles in Figures 2A-2D point out a few representative single Ni atoms in graphene.

Example 6 – Electrochemical Characterization Methods

All electrochemical measurements were run at 25 °C in a customized gastight H-type glass cell separated by Nafion 117 membrane (Fuel Cell Store). A BioLogic VMP3 work station was employed to record the electrochemical response. A specific amount of KHCO₃ (Sigma-Aldrich, 99.95 %) was dissolved in Millipore water to prepare the 0.1 M and 0.5 M electrolyte, which was further purified by electrolysis between two graphite rods at 0.1 mA for 24 h to remove any trace amount of metal ions. In a typical 3-electrodes test system, a platinum foil (Beantown Chemical, 99.99 %) and a saturated calomel electrode

(SCE, CH Instruments) were used as the counter and reference electrode, respectively. A fresh (electrochemically) polished glassy carbon (HTW GmbH, 1cm x 2cm), with its backside covered by an electrochemically inert, hydrophobic wax (Apiezon wax W-W100), or an a O₂ plasma treated CFP (cut into 1cm x 2cm, AcCarb MGL270, Fuel Cell Store) were used as the working electrode substrate.

Typically, 5 mg of as-prepared catalyst was mixed with 1 mL of ethanol and 10 μ L of Nafion 117 solution (Sigma- Aldrich, 5%), and sonicated for 20 min to get a homogeneous catalyst ink. 80 μ L of the ink was pipetted onto 2 cm² glassy carbon surface (0.2 mg cm⁻² mass loading), or 400 μ L pipetted onto CFP toward a mass loading of 1.0 mg/cm², and vacuum dried prior to usage. For a long-term stability test, 50 μ L instead of 10 μ L Nafion solution was added into the catalyst ink. Additionally, after the catalyst was vacuum dried to form a uniform layer on the glassy carbon substrate, another 4 μ L of binder (diluted in ~80 μ L ethanol) was coated on top of the catalyst layer to further enhance the stability. All potentials measured against SCE was converted to the reversible hydrogen electrode (RHE) scale in this work using $E \text{ (vs RHE)} = E \text{ (vs SCE)} + 0.244 \text{ V} + 0.0591 \cdot \text{pH}$, where pH values of electrolytes were determined by an Orion 320 PerpHecT LogR Meter (Thermo Scientific). Solution resistance (R_u) was determined by potentiostatic electrochemical impedance spectroscopy (PEIS) at frequencies ranging from 0.1 Hz to 200 kHz, and manually compensated as $E \text{ (}iR \text{ corrected vs RHE)} = E \text{ (vs RHE)} - R_u \cdot I$ (amps of average current). OER tests were performed in 0.5 M KHCO₃ + 0.5 M K₂HPO₄/KH₂PO₄ buffer solution with pH of 7.5 under CO₂ saturation.

For the anion membrane electrode assembly test, 0.5 mg/cm² Ni-NG and IrO₂ were air-brushed onto two 2x2 cm² Sigracet 35 BC gas diffusion layer (Fuel Cell Store) electrodes as the CO₂RR cathode and the OER anode, respectively. A PSMIM anion exchange membrane (Dioxide Materials) was sandwiched between the two gas diffusion layer electrodes (Fig. 4A) to separate the chambers. On the cathode side, a titanium gas flow channel supplied 50 sccm humidified CO₂ while the anode was circulated with 0.1 M KHCO₃ electrolyte at 2 mL/min flow rate. The cell voltages in Fig. 4B have been iR -corrected.

The calculation of turnover frequency (TOF) and turnover number (TON) per site was based on the estimation of the numbers of Ni active sites in NiN-GS catalysts. First, the surface area of the graphene layers in NiN-GS catalyst can be estimated by the electrochemical double layer capacitance (EDLC). Based on previous literature, the EDLC of graphene is measured to be ~ 21 μ F cm⁻² on one side (39, 40). This is very close to the glassy carbon electrode capacitance (24 μ F cm⁻², Fig. 11A and 11B) we measured here. Since the EDLC of NiN-GS catalyst is 1.57 mF (0.2 mg loading on 1 cm² geometric electrode area), and regardless of the effects of the trace amount of Ni or N in the graphene layers (the EDLC of Ni-GS is quite similar to NiN-GS, confirming our hypothesis), we could estimate the surface area of graphene layers in NiN-GS to be ~75 cm². Therefore, the moles of carbon atoms on the electrochemical surface can be calculated to be $75/10000 \text{ m}^2 / 2600 \text{ m}^2 \text{ g}^{-1} / 12 \text{ g mol}^{-1} = 2.4 \cdot 10^{-7} \text{ mol}$, where 2600 m² g⁻¹ is the theoretical specific surface area of graphene (39). Based on the XPS measurement where signals from surface Ni atoms in the graphene shell become dominant in NiN-GS (Fig. 10B), the atomic ratio of Ni atoms is ~1% (Table 1). Since the small contribution from Ni NPs embedded below cannot be completely ruled out, this atomic ratio could be a slightly overestimation of the Ni atom concentrations in the graphene shell, which could result in an underestimation of the TOF and TON per site. This yields the moles of Ni sites in the surface graphene layers to be ~2.4*10⁻⁹ mol.

The partial current of CO₂ reduction to CO on NiN-GS under an overpotential of $\eta = -0.7$ V is ~ 4 mA, which yields a TOF of Ni active site to be $4/1000 \text{ C s}^{-1} / 105 \text{ C mol}^{-1} / 2 / 2.4 \times 10^{-9} \text{ mol} = 8 \text{ s}^{-1} = 28800 \text{ h}^{-1}$. The cumulative TON was calculated based on the long-term electrolysis in Fig. 12D and 12E.

Example 7 – Control Experiments for NiN-GS Activity

Control experiments were performed to provide important clues to the possible active sites in NiN-GS for this highly selective CO₂ reduction. First, it is unlikely that the Ni NP cores are in contact with the electrolyte to participate into the gas reduction reactions. This is confirmed by the TEM images of NiN-GS after an acid leaching process (AL-NiN-GS, Fig. 13A and 13B) (41), which show the Ni NPs to be well-protected from concentrated protons by the tightly surrounded GSs. Only by violent ball-milling followed with acid leaching can the core-shell structures fracture enough to allow acids to attack Ni NPs (VAL-NiN-GS, Fig. 13C and 13D). In addition, Ni-GS with Ni NPs embedded presents practically no activity towards CO formation (Figs. 11C-11H and 14A-14D). Secondly, the dramatically decreased CO evolution activity per electrochemical surface area (ECSA, Fig. 15A-15D) after acid leaching processes suggest that Ni atoms in the surface GS play a more important role than the N dopants (Fig. 16A-16D) (42-44). Finally, Co and Fe catalysts with the same core-shell structure and N doping (Fig. 17A-17D), however, presents lower activity and selectivity towards CO formation compared with NiN-GS (Fig. 18A-18D), indicating that the high CO FE is related to the specific electronic structure of Ni sites in the GS. Therefore, the Ni sites in GS should be the active centers for electrocatalytic CO₂ to CO conversion, which exhibits a high turnover frequency (TOF) of $\sim 8 \text{ s}^{-1}$ and a cumulative turnover number (TON) of up to 454,000 under -0.7 V overpotential (Fig. 12E).

Example 8 – Characterization of Ni Bonding Environment within Ni-NG Catalyst

Ex-situ and *in-situ* X-ray characterizations were performed to further probe the atomic and electronic structure of Ni single atomic sites as well as their surrounding coordination environment. The XPS study of Ni-NG and Ni-G shows more positive Ni 2p_{3/2} binding energies than Ni metal (852.6 eV) (45), suggesting the positive oxidation states of Ni single atoms are in different coordination environments. In addition, the Ni 2p binding energy of Ni-NG is slightly higher than that of Ni-G (Ni-C coordination), indicating the possible Ni-N coordination which further levels up the Ni oxidation states (46, 47). The coordination environment of Ni atomic sites can be readily studied using synchrotron-based X-ray absorption spectroscopy (XAS), with the results shown in Figures 19A-19F. Fig. 19A shows the typical X-ray absorption near-edge structure (XANES) of Ni K-edge in Ni-NG catalyst, with Ni metal and NiO as references. The near-edge of Ni-NG sits in between Ni metal and NiO, indicating that the average oxidation states of those Ni single atoms are between the metallic and the fully oxidized states. This is because the neighboring C (or possibly N) atoms partially deplete Ni free electrons through the valence bond, as shown in the simulated charge density distribution (Fig. 19B). The *in-situ* XAS test of Ni-NG during the CO₂RR electrolysis shows no obvious changes in Ni XANES under different potentials applied (Fig. 19C), suggesting the high stability of Ni single atoms confined in graphene vacancies and thus ensuring practical use in long-term electrolysis.

The possible coordination environment around Ni single atoms was further analyzed using the k^2 -weighted Fourier transforms of extended X-ray absorption fine structure (EXAFS) at the Ni K-edge in Fig.

19D, where Ni-NG catalyst as well as other model references such as Ni phthalocyanine (Ni-Pc) were included. Ni metal exhibits a typical first shell Ni-Ni pair at ~ 2.20 Å, while Ni-O interaction in NiO locates at 1.62 Å. The R-space characteristics of Ni-N bonding can be studied using Ni-Pc due to its well-defined structure, which suggests a 1.40 Å bonding length of Ni-N. Ni-G exhibits a distinguished peak, assigned as Ni-C coordination, at the same position of 1.40 Å, suggesting that it is difficult to fully differentiate Ni-C and Ni-N coordination due to their very close bonding length (48, 49). In addition, another peak at ~ 2.06 Å indicates the possible presence of Ni-Ni bonding from small Ni clusters, which is in consistent with STEM observations. These observations are supported by the data presented in Figures 20A-20D, which show additional physical characterization and CO₂RR performance metrics of the Ni-NG (Ni-N-C) catalysts. The coexistence of Ni single atoms in graphene vacancies and Ni clusters explains the comparable CO₂RR and HER processes on Ni-G, and further confirms the CO₂-to-CO activity on atomic sites of Ni@vacancy (Fig. 20A). When N dopants was introduced during the sample synthesis, the morphology and coordination environment of Ni atoms were changed. Different from Ni-G, our Ni-NG catalyst shows negligible Ni-Ni interaction with most of the Ni atoms in single atomic morphology as suggested by EXAFS (Fig. 19D). In addition, the XANES and EXAFS of both Ni and N in Ni-NG show distinguished differences with that of Ni-Pc, ruling out the possibility that those single Ni atoms are coordinated with N only such as a Ni porphyrin structure, and thus suggesting an environment of mixed Ni-C and Ni-N coordination (48). Since there are a variety of different sizes of vacancies in graphene oxide nanosheets due to its violent synthesis process (50), it is believed that different types of Ni atomic sites could exist. Small vacancies such single vacancy (SV) or double vacancy (DV) with one or two C atoms missing can fit a single Ni atom for Ni@vacancy active sites (Fig. 20A) (46). For slightly larger vacancies, due to their more negative surface charges, they could adsorb more Ni ions and thus result in small Ni clusters in the Ni-G catalyst in the absence of a N dopant. Our assumption is that the incorporation of N could potentially help to isolate the Ni atoms by forming Ni-N in addition to Ni-C bonds in Ni-NG catalyst, with representative atomic sites such as Ni-N@SV or Ni-N@DV illustrated in Fig. 20A (46). The Ni-Ni bonding was dominant in Ni NPs/G, which was significantly weakened in Ni-G sample with the coexistence of Ni-C signal, and was further eliminated in Ni-NG sample with a dominate Ni-C/N peak. As a result, the Ni NPs generate exclusively H₂, Ni-G presents nearly 40 % selectivity of CO₂ reduction, and Ni-NG shows more than 95 % CO selectivity. This trend provides a strong evidence that the Ni single atomic sites are responsible for CO₂ reduction. Furthermore, the N K-edge XAS in Ni-NG exhibits strong signals in both π^* (398.1 eV) and σ^* (407.2 eV) bands, which is similar to NG (Fig. 19E) but different from Ni-Pc and Ni₃N, indicating that the majority of N dopants is coordinated with carbon to form pyridine- and pyrrole-ring structure (51). Additional C K-edge XAS in Ni-NG and NG (Fig. 19F) shows similar graphene matrix structure as evidenced by the similar π^* band intensities at ~ 285.4 eV, but more defects within macrocyclic pyrrolic carbon structure in Ni-NG catalyst (51, 52).

Example 9 – NiN-GS Activity for CO₂ Reduction

The electrocatalytic CO₂ reduction performance of NiN-GS catalyst, drop casted on glassy carbon current collector, was performed in 0.1 M potassium bicarbonate (KHCO₃) electrolyte in a customized H-cell as described in Example 6.

During electrolysis, CO₂ gas (Airgas, 99.995 %) was delivered into the cathodic compartment containing CO₂-saturated electrolyte at a rate of 50 standard cubic centimeters per minute (sccm, monitored by an Alicat Scientific mass flow controller) and vented into a gas chromatograph (GC, Shimadzu GC-2014) equipped with a combination of molecular sieve 5Å, Hayesep Q, Hayesep T, and Hayesep N columns. A thermal conductivity detector (22TCD) was mainly used to quantify H₂ concentration, and a flame ionization detector (FID) with a methanizer was used to quantitative analysis CO content and/or any other alkane species. The detectors are calibrated by two different concentrations (H₂: 100 and 1042 ppm; CO: 100 and 496.7 ppm) of standard gases (Fig. 21E and 21F). The gas products were sampled after a continuous electrolysis of ~ 15 min under each potential. The partial current density (j_i) for a given gas product was calculated as below:

$$j_i = x_i \times v \times \frac{n_i F p_0}{RT} \times (\text{electrode area})^{-1}$$

where x_i is the volume fraction of certain product determined by online GC referenced to calibration curves from two standard gas samples (Scott and Airgas), v is the flow rate of 50 sccm, n_i is the number of electrons involved, $p_0 = 101.3$ kPa, F is the Faraday constant and R is the gas constant. The corresponding Faradaic efficiency (FE) at each potential is calculated by $FE = (j_i/i_{\text{total}}) \times 100$ %. A representative example to demonstrate the whole process of FE measurement is shown in Fig. 21A. The potential was held at -0.82 V vs RHE (the highest CO FE) for a continuous electrolysis with a 50 sccm CO₂ gas flow. The chronoamperometry current is shown as Fig. 21B with a current density ~ 4.34 mA/cm² (1 cm² electrode for test). The 50 sccm CO₂ gas, mixed with continuously produced H₂ and CO, continuously flowed through the sampling loop (1 mL) of GC during the electrolysis. At ~ 15 min the GC machine automatically switched valves to inject the gas sample in the sampling loop into packed columns for analysis. H₂ was detected by TCD at ~5.5 min (Fig. 21C), and CO was first converted into CH₄ by the methanizer and then detected by FID at ~ 11 min (Fig. 21D). Based on the GC calibration curve (Figs. 21E and 21F) and the integrated peak areas of H₂ and CO, the concentration of H₂ was calculated to be ~ 74 ppm and that of CO was ~ 616.7 ppm. With a 50 sccm CO₂ flow, the gas products were therefore produced at a rate of 2.57×10^{-9} mol/s of H₂ and 2.14×10^{-8} mol/s of CO, which corresponds to a partial current density of 0.49 mA/cm² H₂ and 4.13 mA/cm² CO. The corresponding FEs were finally obtained as 11.3% of H₂ and 95.2% of CO. The cumulated gas volume during the 15-min electrolysis is 0.055 mL for H₂ and 0.462 mL for CO.

A few advantages of the CO₂ gas flow cell method for GC measurements are: 1) the gas product concentration can be tuned by changing the CO₂ gas flow rate and therefore the FE measurements can be accurate even for small currents; 2) the gas sample injection by auto GC valve switching can be highly dependable with small error ranges; 3) by programming the GC auto valve switching every certain amount of time, the electrolysis can be continuously operated and analyzed for long-term stability test unattended.

1-D ¹H NMR spectra were collected on an Agilent DD2 600 MHz spectrometer to test if any liquid products present during the CO₂ reduction over NiN-GS catalyst. Typically, 900 μL of electrolyte after electrolysis (or 0.1 M KHCO₃ containing certain chemicals of interest) were mixed with 100 μL of D₂O

(Sigma-Aldrich, 99.9 at% D) and 0.05 μL dimethyl sulfoxide (Sigma-Aldrich, 99.9 %) as an internal standard.

The cyclic voltammograms (CVs) in CO_2 and N_2 saturated electrolyte suggests that reactions other than the hydrogen evolution reaction (HER) occur when CO_2 is present (Fig. 12A). Gas products were

analyzed by gas chromatography (GC) at potential steps of 100 mV and further zoomed into 50 mV

around the FE peak (Fig. 12B, Fig. 21B). Detectable CO signals start at -0.35 V vs. reversible hydrogen electrode (RHE), suggesting the onset overpotential of CO_2 to CO to be less than 230 mV (Fig. 22). As the potential becomes more negative, the FE of CO increases with that of HER decreases (Fig. 12B). The overall Faradaic efficiency under different potentials ranges from 91.2 to 105.8% (Fig. 12B, Table 2).

The highest FE of CO_2 to CO reaches to 93.2% at 0.7 V overpotential, with a CO evolution current density of $\sim 20 \text{ mA cm}^{-2} \text{ mg}^{-1}$ (4 mA cm^{-2} at 0.2 mg cm^{-2} mass loading, Fig. 12C). The geometrical current density can be significantly improved by loading more NiN-GS catalysts onto carbon fiber paper (CFP) substrate while maintaining a high CO FE of $\sim 90\%$ in 0.5 M KHCO_3 electrolyte. (Fig. 23)

An isotope $^{13}\text{CO}_2$ labeling experiment was performed using GC-MS to confirm that the gas product of CO comes from CO_2 reduction (Fig. 24). ^{13}C isotope measurements were run on an Agilent 7890A GC-MS equipped with a thermal conductivity detector (TCD) and an Agilent 5975C inert Triple-Axis quadrupole mass selective detector. $^{13}\text{CO}_2$ (Sigma-Aldrich, 99% at ^{13}C) stream was delivered into the cathodic compartment containing $0.1 \text{ M NaHCO}_3\text{-}^{13}\text{C}$ (Sigma-Aldrich, 98 at% ^{13}C) at a rate of 20 sccm and was routed into the GC-MS with He as the carrier gas.

The Tafel slope plotted with electrolysis currents and overpotentials, was 138.5 mV/decade (Fig. 25) (8, 38, 43, 53). No other gas or liquid products were detected by GC-FID (Fig. 26A) or ^1H nuclear magnetic resonance (NMR, Fig. 26B). Whether these surrounded GS will be stable under long-term operations is our concern, because if the protection layer breaks, the Ni NPs will be exposed to water and may produce H_2 heavily (19). Around 80% FE of CO was still maintained after more than 20 hours continuous

electrolysis under 0.7 V overpotential (Fig. 12D), suggesting the excellent stability of the catalytic sites. A pre- (Figs. 27A and 27B) and post-catalysis (Figs. 27C and 27D) TEM examination also confirms that the core-shell structure remains intact to prevent contact between Ni NPs and water.

Table 2. Faradaic efficiencies of evolved gas products using the NiN-GS catalyst under different applied potentials.

E vs RHE (V)	H ₂ FE (%)	CO FE (%)	Overall FE (%)
-0.35	97	4	101
-0.45	84.8	8.1	92.9
-0.55	75	16.2	91.2
-0.64	50.6	42.5	93.1
-0.71	39.8	63.2	103
-0.75	21.5	81.8	103.3
-0.78	15.1	85.9	101

E vs RHE (V)	H ₂ FE (%)	CO FE (%)	Overall FE (%)
-0.82	12.6	93.2	105.8
-0.86	24.3	77	101.3
-0.92	40.8	59.6	100.4
-0.98	61.2	39.1	100.3

Example 10 – Comparison of CO₂RR Performance Using Different Electrode Substrates

The CO₂RR catalytic activity of Ni-NG catalyst, drop-casted onto mirror polished glassy carbon electrode (GCE), was evaluated in a standard three-electrode H-cell configuration with CO₂-saturated 0.5 M KHCO₃ as the electrolyte. H₂ and CO are the major gas products detected by on-line gas chromatograph, with their FEs under different potentials as well as the corresponding partial currents shown in Figs. 28A and 28B, respectively. CO₂-to-CO conversion starts from -0.31 V vs. RHE (ca. 190 mV overpotential), which rapidly increases to an 83 % of CO FE at 480 mV overpotential, and maintains a high plateau of more than 90 % CO until -0.87 V. The competitive HER was dramatically suppressed with FEs less than 10 %, in sharp contrast to the supported Ni nanoparticle catalyst. The Tafel slope, which is used to analyze the kinetic behavior of CO₂RR on Ni single atomic sites, is ~ 110 mV/dec and comparable to Au- and Ag-based electrocatalysts (15, 54) suggesting a rate-limiting step of initial CO₂ activation. (46, 55). The CO production turnover frequency (TOF) per active Ni site is calculated to be 6.8 s⁻¹ at an overpotential of 0.57 V, based on electrochemical surface area determination from double layer capacitance measurements, and increases to 21.2 s⁻¹ at an overpotential of 0.75 V. Geometrical current density can be further improved with a high surface area current collector (carbon fiber paper, CFP) and more mass loading of catalysts (1 mg/cm²). Compared to the CO₂RR performance on a GCE, the current density of the catalyst on a CFP electrode was significantly improved while maintaining a similar trend of CO selectivity. A maximal CO FE of ~ 95% (Fig. 28C) with a current density of ~ 11 mA/cm² was achieved under an overpotential of 620 mV (Fig. 28D). It is noted that the current density was not linearly improved with the catalyst loading, which is possibly due to the overlap of graphene layers on CFP. Long term CO₂RR stability is a particularly important measure for single atom catalysts due to the potential atom aggregation during catalysis. The Ni-NG catalyst maintains a stable current of ~ 12 mA/cm² and CO selectivity of ~ 90 % for more than 20 hours of continuous operation, demonstrating excellent electrocatalytic durability. Ni atoms are largely maintained as isolated features in the support structure, as observed in the post-catalysis TEM image and X-ray fine structure characterization, suggesting the stable confinement of Ni single atoms in graphene vacancies. The electrolyte before and after 20 h electrolysis were examined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and no detectable Ni species were observed (detection limit of ~ 100 ppb) in both cases, suggesting negligible Ni leaching.

Other TM atomic sites, such as Co, Fe, and Mn, exhibit different reaction pathways, especially for Co which generates hydrogen exclusively. Density functional theory (DFT) calculations suggest that, the

weaker CO binding and higher HER barrier account for the superior CO₂-to-CO selectivity of Ni single atoms than that of Co.

Example 11 – Artificial Photosynthesis using NiN-GS and OER Catalyst

A practical electrosynthetic cell for CO₂ reduction to fuels requires an active and stable oxygen evolution reaction (OER) catalyst to efficiently oxidize water and free the protons (10, 35). Considering the significant energy loss by the low ionic conductivity in 0.1 M KHCO₃ electrolyte, the salt concentration was increased to 0.5 M (pH 7.5 under CO₂ saturation) in the full cell system to reduce the *iR* drop while maintaining a high FE of CO₂ to CO on NiN-GS catalyst (Fig. 29A and 29B). Relatively small OER overpotentials in alkaline solutions have been achieved by transition metal catalysts (19, 56), which however do not work well in neutral pH (44). Co-based catalytic materials are known to perform better than other transition metals in a neutral pH liquid medium, but still require ~ 500 mV overpotential to deliver 5 to 10 mA cm⁻² current (4, 24, 57, 58). Inspired from studies in transition metal oxide Li ion batteries, where electrode materials gradually fracture due to the cyclic Li⁺ insertion and extraction, a Li⁺-tuned Co₃O₄ catalyst (Li-Co₃O₄) was utilized to create additional grain boundaries and active sites for neutral pH OER (Fig. 30) (19). The size of pristine Co₃O₄ NPs (~ 100 nm) was significantly reduced after the Li⁺ tuning process as observed by SEM images (Fig. 31A-31D). In addition, the X-ray diffraction (XRD) pattern of Co₃O₄ disappears in Li-Co₃O₄ (Fig. 32), which confirms that ultra-small grains below the detection limit of XRD have been created within the NPs (19). As a result, the OER catalytic activity of Li-Co₃O₄ was dramatically improved from the pristine sample (Fig. 3A) (35). An OER electrolysis of Li-Co₃O₄ under 5 mA cm⁻² current, which matches the current of the best CO FE of NiN-GS catalyst (Fig. 28A), can be continuously operated at ~ 1.6 V vs. RHE (370 mV overpotential) for more than 20 hours with negligible degradation (Fig. 3B). Considering the NiN-GS CO₂ reduction catalyst with a – 0.74 V vs. RHE potential for ~ 83 % CO FE, the full-cell reaction can be operated under 2.34 V (without considering the *iR* drop) and deliver a ~50 % electricity to CO energy conversion efficiency. This optimized operation voltage, added with additional ohmic loss, can be powered by a single cell of commercialized GaInP₂/GaAs/Ge triple junction photovoltaic which delivers an open-circuit voltage of greater than 2.5 V (Figs. 3C and 3D) (59). An artificial photosynthesis system was therefore built by integrating a 1 cm² triple junction solar cell with the NiN-GS and Li-Co₃O₄ catalysts in a 3D-printed electrosynthetic cell (Figs. 3C, 33A, 33B, 33C and 34A), under simulated solar illumination without any external power input. Fig. 34B-34D show the solar to electrical efficiency (Fig. 34B), stability of the cell over 10 h of continuous use (Fig. 34C), and CO conversion performance of the setup (Fig. 34D). Trace amount of Co ions from the OER catalyst surface could be leached out into the electrolyte due to the local pH decrease during long-term OER electrolysis. Trace amount of Co ions diffusing across the Nafion membrane can be deposited as Co metal onto the cathode due to the negative potential applied (60), which poisons the CO₂ reduction catalyst and decreases the CO FE and thus the overall STF. Therefore, the electrolyte in the electrosynthetic cell was refreshed via exchange every few hours (shown as the spikes in the current density in Fig. 3E) to avoid metal ion contaminations in CO₂ reduction. The efficiency of solar-to-fuel (STF) is calculated by the equation of $\text{STF} = j_{\text{tot}} \times \text{FE}_{\text{CO}} \times 1.35 \text{ V} / P_{\text{solar}}$, where 1.35 V represents the thermodynamic energy of CO₂ to CO conversion and P_{solar} is the input power of solar energy. Around 10 % artificial photosynthesis efficiency can be achieved with Earth-abundant electrocatalysts (Fig. 3E) over

10-hour continuous operation, exceeding that of biological photosynthesis in nature (61). The STF efficiency can likely be further improved with more advanced integrated system (instead of the direct wiring here) to ensure the optimized operation voltage for both the photovoltaic device and electrolytic cell.

- 5 In the 3D-printed electrosynthetic cell (Fig. 33A and 33B) for fuel production, 0.5 M KHCO_3 and 0.5 M $\text{KHCO}_3 + 0.5 \text{ M K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ buffer solution (both saturated with CO_2 with pH of 7.5) were used in the cathodic compartment for CO_2 reduction and anodic compartment for OER, respectively. The mass loadings of NiN-GS and Li- Co_3O_4 are 0.3 and 8 mg on a 1 cm^2 glassy carbon and CFP electrode, respectively. The 1 cm^2 $\text{GaInP}_2/\text{GaAs}/\text{Ge}$ triple junction solar cell was illuminated under AM 1.5G 0.5
- 10 Sun solar simulator (Newport, calibrated by Newport reference cell) to match the current density of the electrosynthetic cell ($\sim 5 \text{ mA}/\text{cm}^2$ working current). The positive electrode of the solar cell was connected with Li- Co_3O_4 and the negative with NiN-GS, respectively. One channel of electrochemical working station was wired in parallel to monitor the voltage and another one was wired in series (with 0 V applied) to monitor the current. A mini-magnet stirring bar was added in the cathode chamber of the 3D-printed
- 15 electrosynthetic cell to dramatically facilitate the electrolyte mass transport. As described above, the electrolyte was refreshed every few hours to avoid metal ion deposition onto CO_2 reduction catalyst. Both the mass transport and the cross-contamination issues can be further improved by designing a flow cell for real applications in the future.

Example 12 – Gas Phase Reduction of CO_2 Using Ni-NG and OER Catalyst

- 20 One feature that was evident in our liquid CO_2 reduction system was that the CO evolution current on the Ni-NG catalyst was limited in the H-cell system. Due to the direct contact between the catalyst and water, the HER would easily take off under a significant overpotential needed to boost the current (Figs. 28B and 28D). An anion membrane electrode assembly (MEA) can prevent the catalyst from contacting with water and facilitate the CO_2 mass transport as well (Fig. 4A) (11, 62, 63), greatly suppressing the competing
- 25 HER even under large overpotentials. More than 200 mA current was achieved on a 4 cm^2 electrode for demonstration ($50 \text{ mA}/\text{cm}^2$), with a high CO selectivity of $\sim 97 \%$ and H_2 of only $\sim 4 \%$ (Figs. 4B and 4C). Fig. 4D exhibits a stable CO selectivity of $> 90 \%$ under a significant current of $\sim 200 \text{ mA}$ ($50 \text{ mA}/\text{cm}^2$) over the 8-h continuous electrolysis, which represents an unprecedented CO evolution rate of 3.81 mmol/h using earth-abundant electrocatalysts and a record TOF of $\sim 59 \text{ s}^{-1}$ (or ca. $2.1 \times 10^5 \text{ h}^{-1}$) at a cell
- 30 voltage of 2.78 V. More than 630 mL of CO gas was accumulated during this electrolysis (Fig. 4E), which can be further scaled up by extending the size of the gas diffusion layer, increasing the catalyst loading, or by stacking multiple cells together.

- To better probe the active sites in Ni-NG toward this superb CO_2RR performance, control experiments on Ni-coordinated graphene without the incorporation of N (Ni-G), N-doped graphene (NG) and Ni_3N
- 35 catalysts were carried out. First, the possibility that Ni_3N was responsible for the high CO selectivity on Ni-NG catalyst was ruled out due to the extensive observed HER (H_2 FE is $\sim 80\%$). In addition, NG without the incorporation of Ni atoms showed a poor CO_2 -to-CO selectivity, suggesting that neither the N dopants nor if any metal impurities (64) in graphene (our XPS survey spectrum and energy dispersive X-ray spectrum suggests a negligible metallic impurity) directly contribute to the high CO selectivity of Ni-

NG. Finally, without the incorporation of N, Ni-G catalyst exhibited a maximal CO FE of ~ 41% at – 0.80 V. This reasonable selectivity agrees well with our previous demonstration that, single Ni atoms coordinated with C in graphene vacancies (Ni@vacancy), such as Ni@SV and Ni@DV, are active sites for CO₂-to-CO conversion. However, when N dopants were incorporated during the synthesis process to obtain Ni-NG catalyst, the CO selectivity was further boosted with greatly suppressed HER.

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- 20 62. H.-R. M. Jhong, F. R. Brushett and P. J. A. Kenis, *Adv. Energy Mater.*, 2013, 3, 589-599.
63. R. B. Kutz, Q. M. Chen, H. Z. Yang, S. D. Sajjad, Z. C. Liu and I. R. Masel, *Energy Technol.*, 2017, 5, 929-936.
64. Y. Lum, Y. Kwon, P. Lobaccaro, L. Chen, E. L. Clark, A. T. Bell and J. W. Ager, *ACS Catal.*, 25 2016, 6, 202-209.

Other embodiments are in the claims.

What is claimed is:

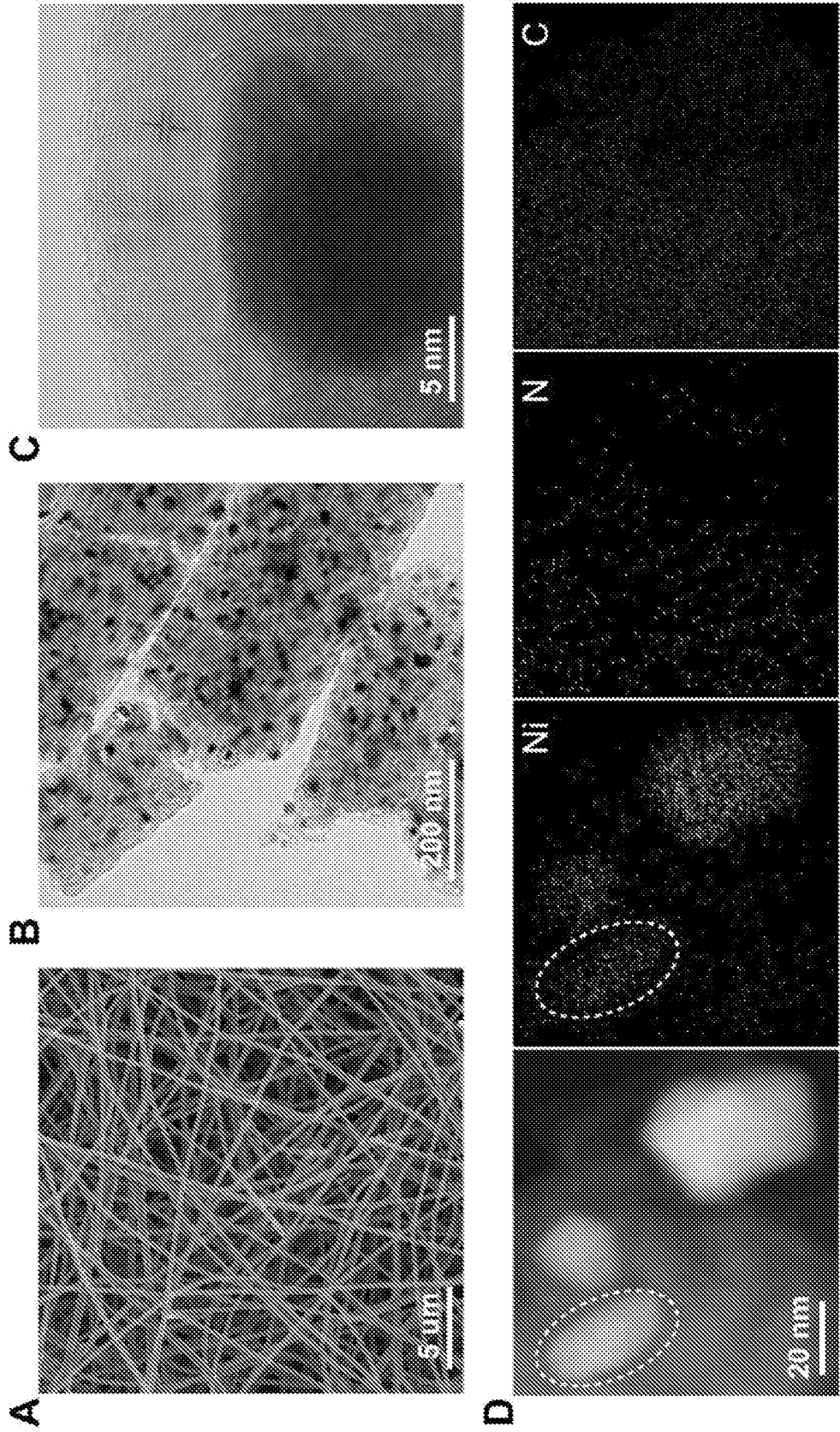
CLAIMS

1. A composition comprising an electrically conductive support material and a transition metal atom or cluster, wherein the transition metal atom or cluster is incorporated within the electrically conductive support material.
2. The composition of claim 1, wherein the electrically conductive support material is selected from the group consisting of carbon particles, carbon powder, graphene, reduced graphene oxide, graphene oxide, and carbon nanotubes.
3. The composition of claim 2, wherein the electrically conductive support material is graphene.
4. The composition of claim 2, wherein the electrically conductive support material is graphene oxide.
5. The composition of claim 1, wherein the transition metal is selected from the group consisting of Ni, Co, Fe, Mn, Rh, Pt, Cu, Mo, and W.
6. The composition of claim 5, wherein the transition metal is Ni.
7. The composition of claim 1, further comprising a dopant atom incorporated in the electrically conductive support material.
8. The composition of claims 7, wherein the dopant atom is selected from the group consisting of elements from Group 13, Group 15, and Group 16 of the periodic table.
9. The composition of claim 8, wherein the dopant atom is selected from the group consisting of N, P, B, O, and S.
10. The composition of claim 9, wherein the dopant atom is N.
11. The composition of claim 1, wherein the composition comprises a core of the transition metal surrounded by a shell of transition metal atoms or clusters in the electrically conductive support material.
12. The composition of claim 1, wherein the composition does not comprise a core of the transition metal.
13. A method of fabricating a catalyst, the method comprising:
 - a) mixing together a transition metal salt, carbon source, and optionally a dopant source;
 - b) heating the mixture to form an electrically conductive support material having a transition metal atom or cluster and optionally a dopant atom incorporated therein, thereby fabricating the catalyst.

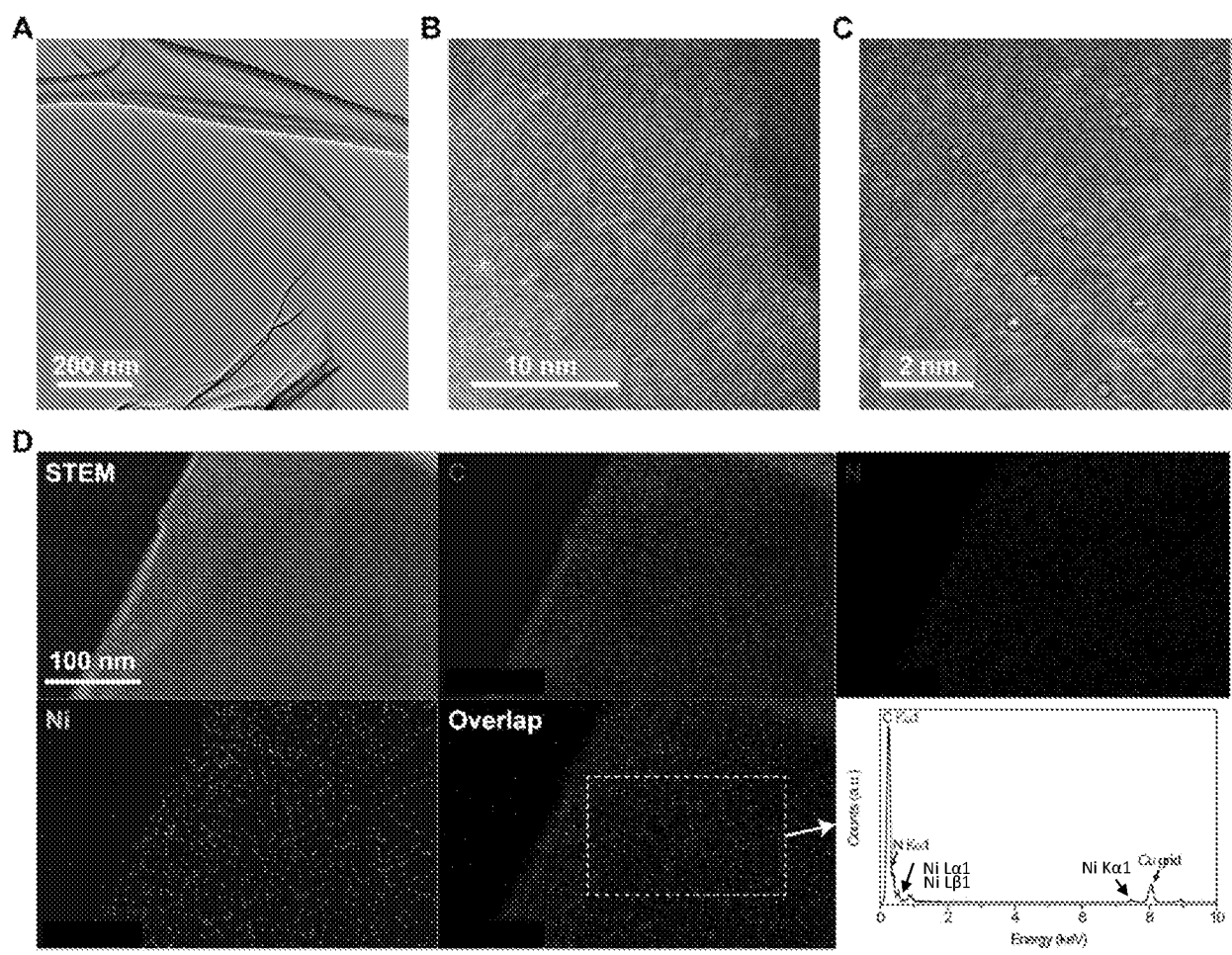
14. The method of claim 13, further comprising forming the mixture of (a) into a morphology selected from the group consisting of fibers, nanosheets, particles, and powders.
15. The method of claim 14, wherein the mixture is in the form of fibers.
16. The method of claim 14, wherein the mixture is in the form of nanosheets.
17. The method of claim 14, wherein the mixture is in the form of particles.
18. The method of claim 15, wherein the fibers are produced via electrospinning.
19. The method of claim 13, wherein dopant source is present, and the carbon source and dopant source are the same material.
20. A method of reducing CO₂ in a liquid medium, the method comprising:
 - a) providing the composition of any one of claims 1-12;
 - b) contacting CO₂ with the composition in the liquid medium; and
 - c) applying a voltage potential to the composition sufficient to reduce CO₂.
21. The method of claim 20, wherein the liquid medium is aqueous.
22. The method of claim 20, wherein the liquid medium is non-aqueous.
23. The method of claim 20, further comprising oxidizing water into O₂, wherein the water is in contact with a second catalyst, the second catalyst is separated from the catalyst of (a) by an ion permeable membrane, and the second catalyst and catalyst of (a) are electrically connected.
24. The method of claim 23, wherein the second catalyst comprises an oxygen evolution reaction catalyst selected from the group consisting of Co₃O₄ doped with Li⁺ ions, a transition metal oxide, a transition metal sulfide, a transition metal phosphide, Ir, or Ru.
25. The method of claim 24, wherein the second catalyst comprises Co₃O₄ doped with Li⁺ ions.
26. The method of claim 20, wherein the voltage potential is supplied by a photovoltaic cell.
27. The method of claim 20, wherein the CO₂ is reduced to CO, a hydrocarbon, or an alcohol.
28. The method of claim 20, further comprising oxidizing formic acid, methanol, ethanol, or SO₃, wherein the formic acid, methanol, ethanol, or SO₃ is in contact with an electrode separated from the catalyst of (a) by an ion permeable membrane, wherein the electrode and catalyst of (a) are electrically connected.
29. A method of electrochemically reducing gaseous CO₂ into CO, the method comprising:

- a) providing the composition of any one of claims 1-12;
 - b) contacting gaseous CO₂ with the composition deposited on at least one electrode; and
 - c) applying a voltage potential to the composition sufficient to reduce gaseous CO₂.
30. The method of claim 29, wherein the electrode is a membrane electrode.
31. The method of claim 29, further comprising oxidizing water into O₂, wherein the water is in contact with a second electrode separated from the composition of (a) by an ion exchange membrane, and the second electrode and composition of (a) are electrically connected.
32. The method of claim 31, wherein the second electrode comprises an oxygen evolution reaction catalyst selected from the group consisting of Co₃O₄ doped with Li⁺ ions, a transition metal oxide, a transition metal sulfide, a transition metal phosphide, IrO₂, and Ru.
33. The method of claim 32, wherein the second catalyst comprises IrO₂.
34. The method of claim 29, wherein the voltage potential is supplied by a photovoltaic cell.

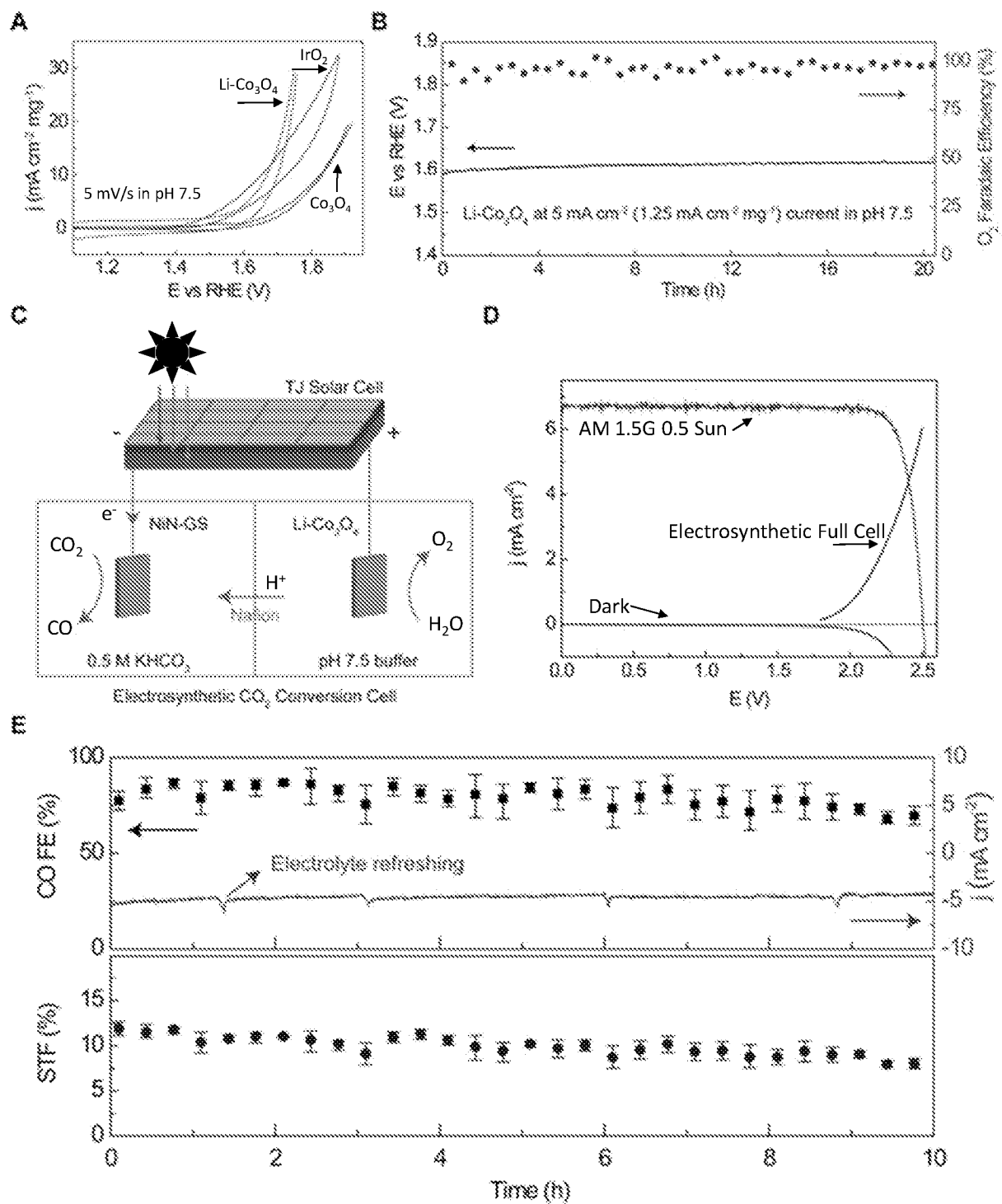
Figures 1A-1D



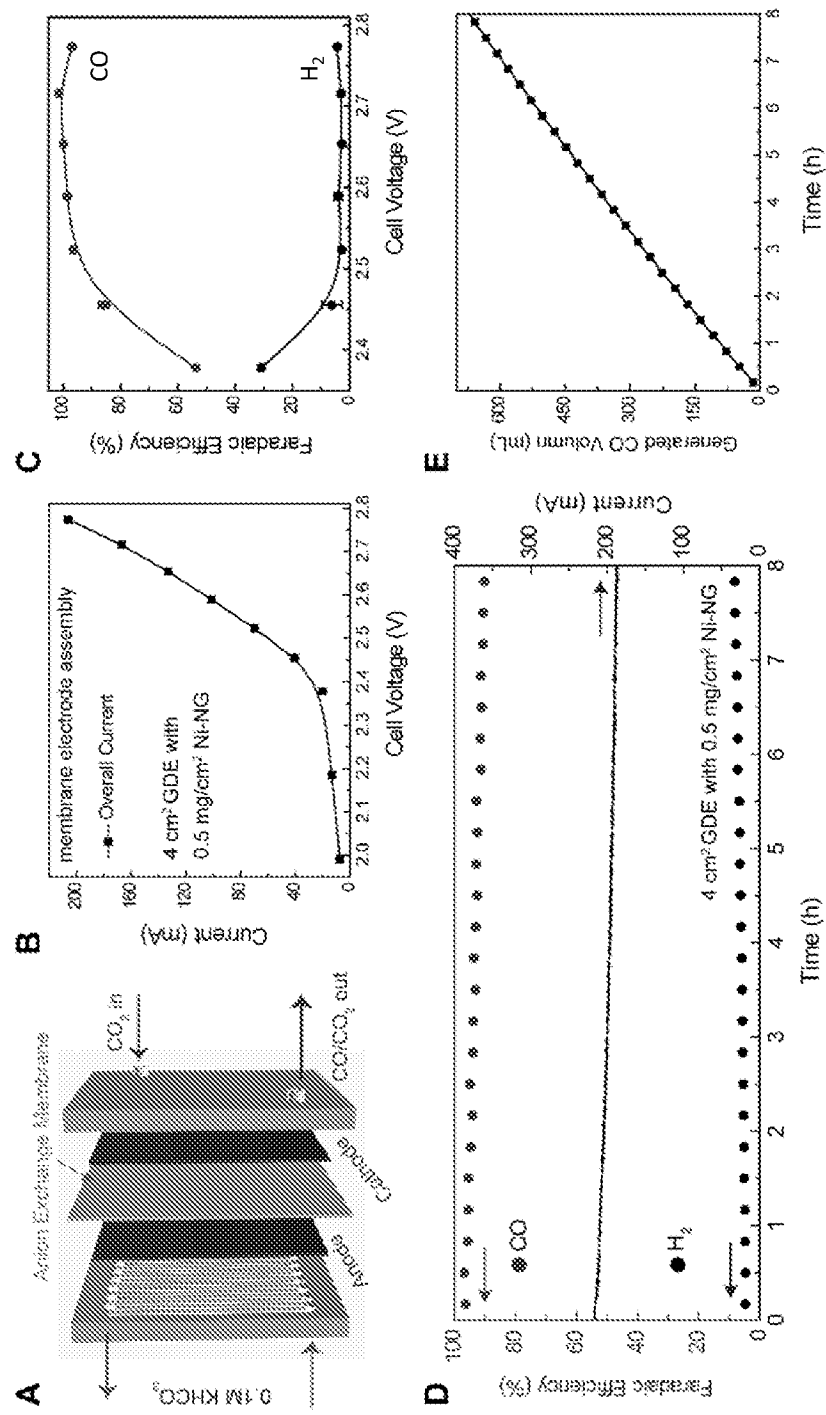
Figures 2A-2D



Figures 3A-3E

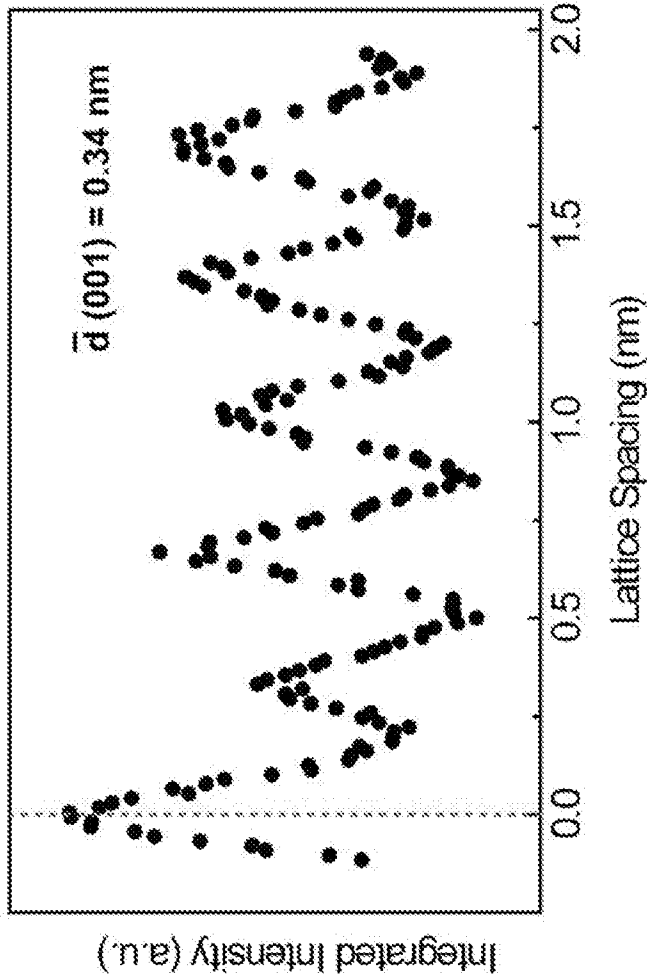


Figures 4A-4E

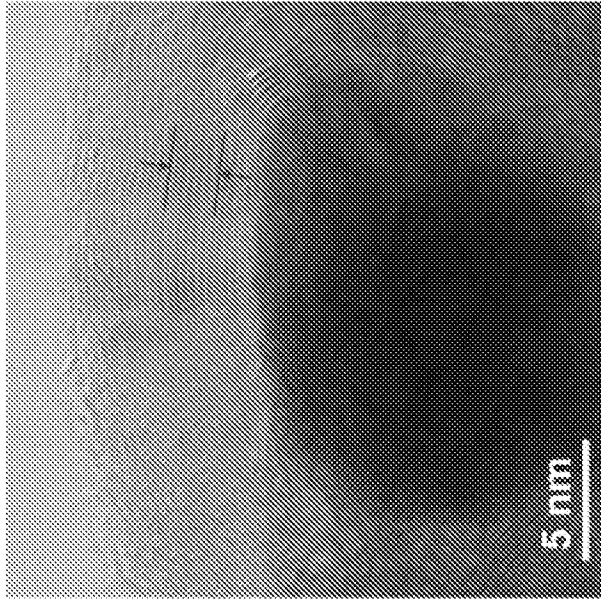


Figures 5A-5B

B



A



Figures 6A-6E

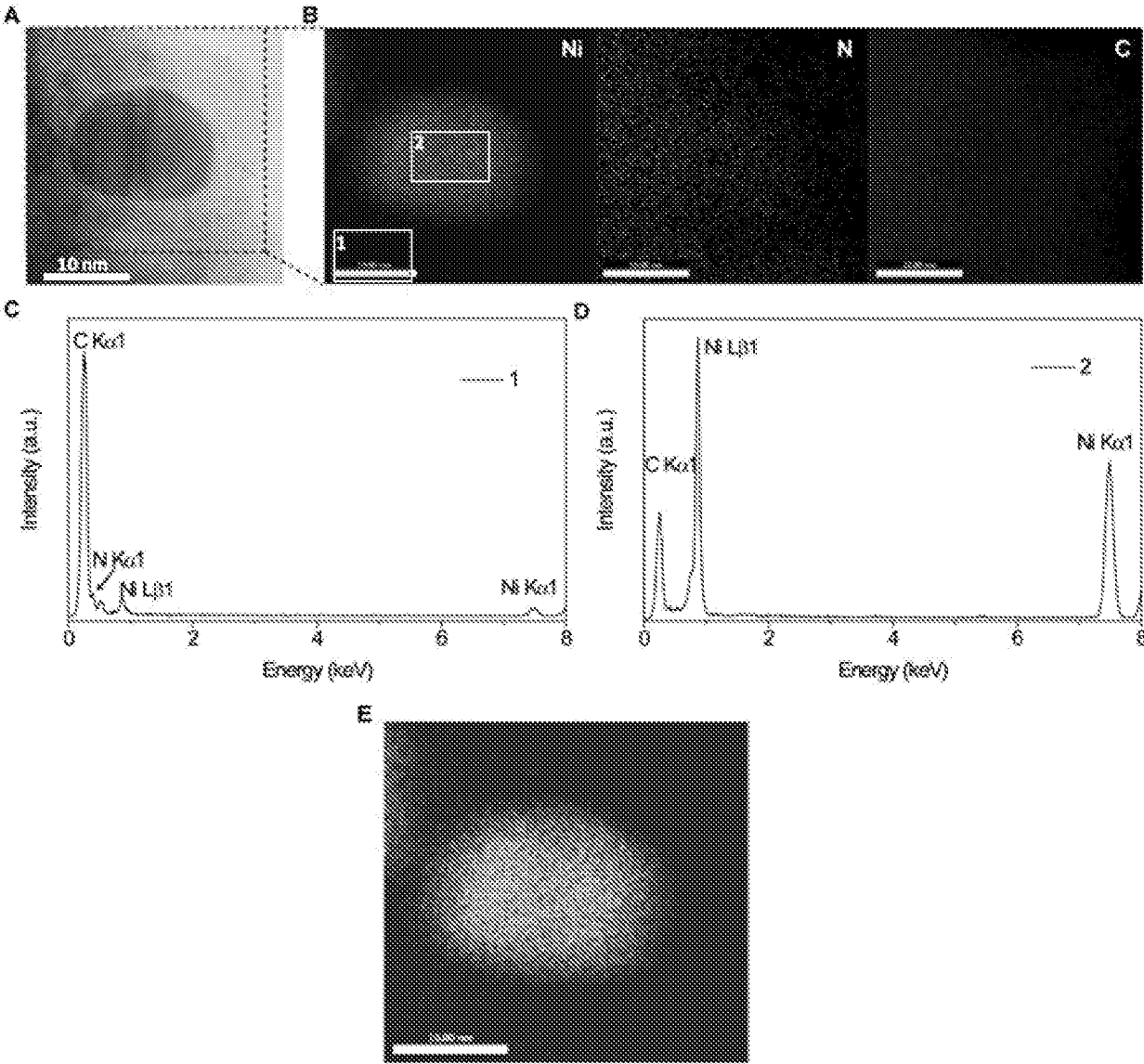
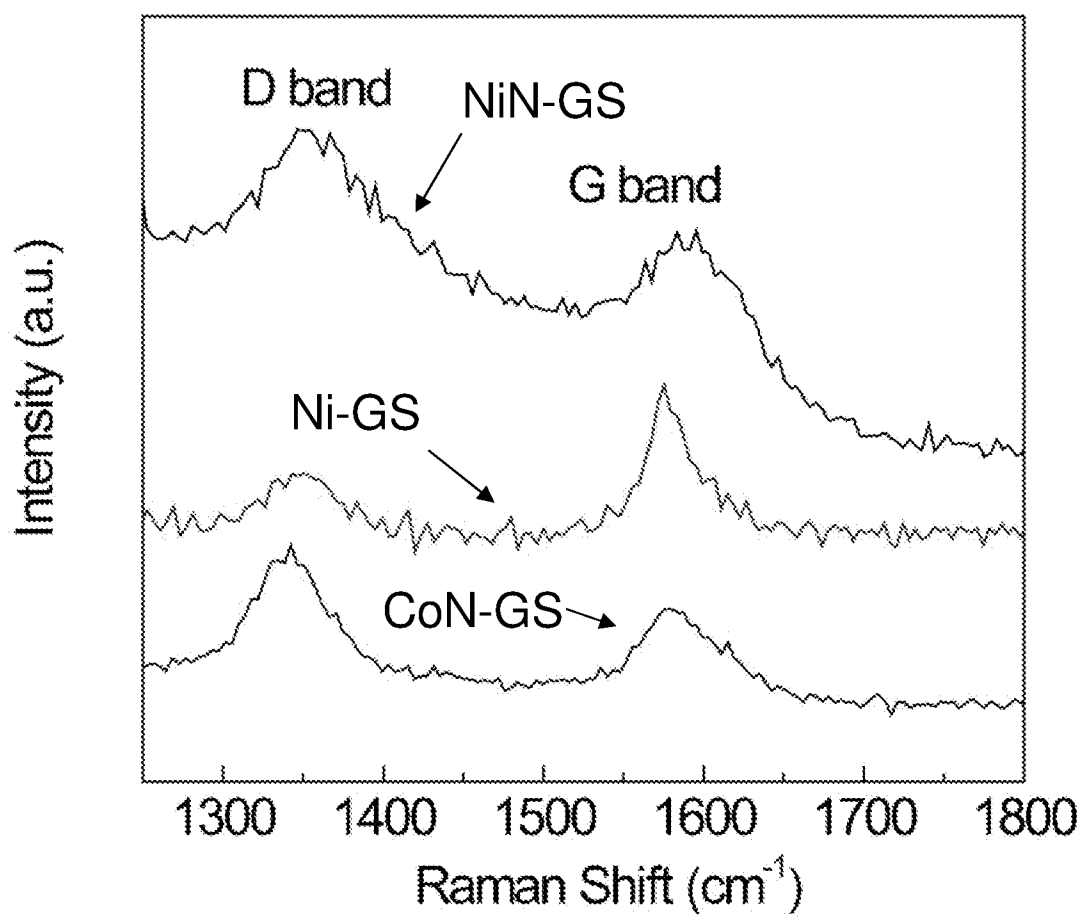
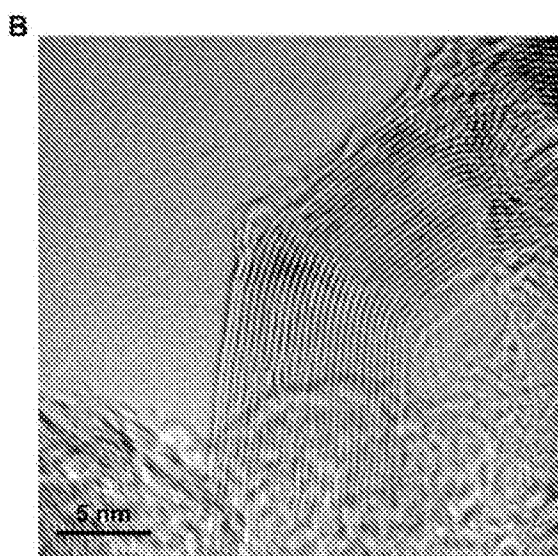
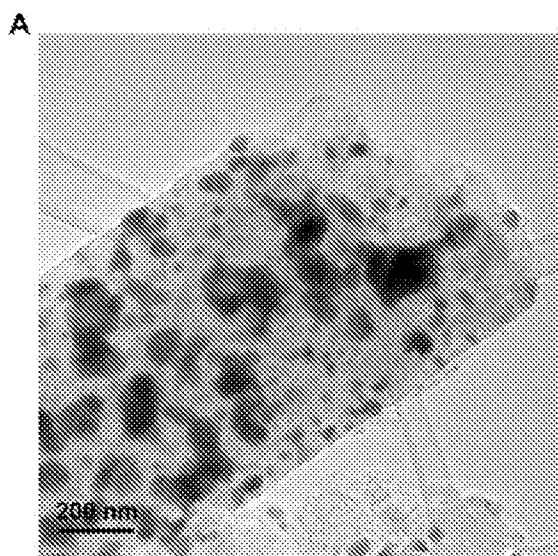


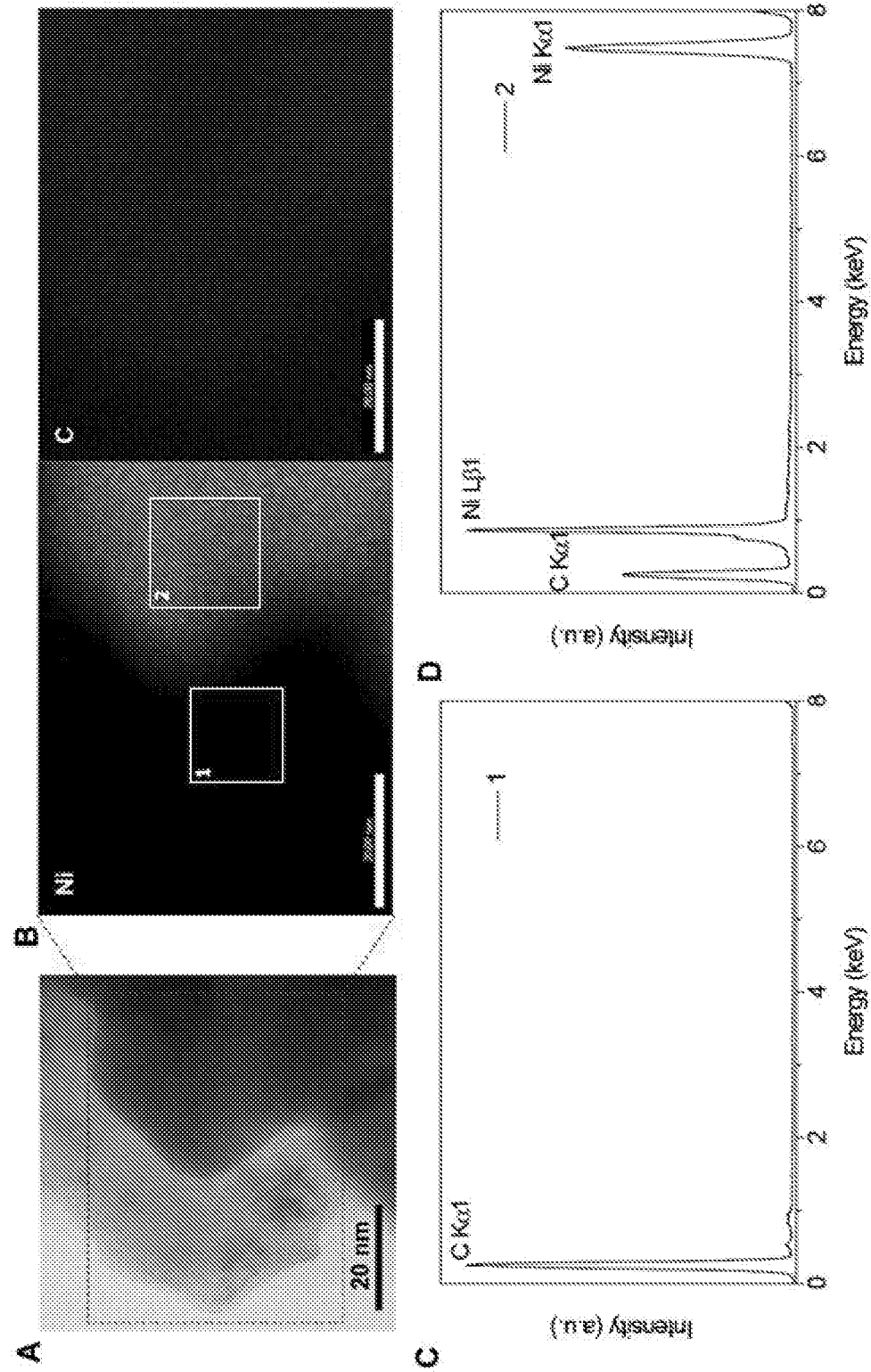
Figure 7



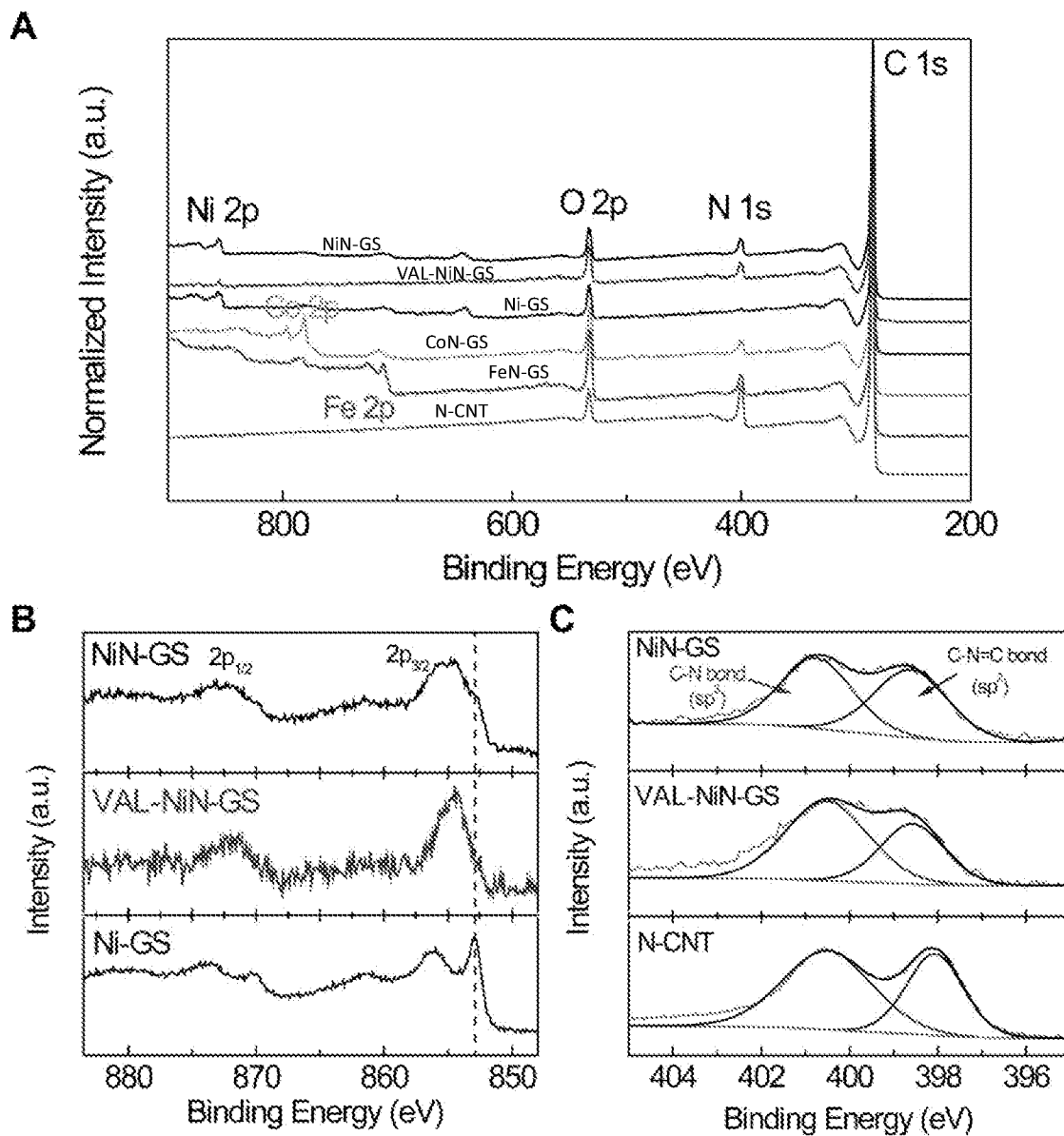
Figures 8A-8B



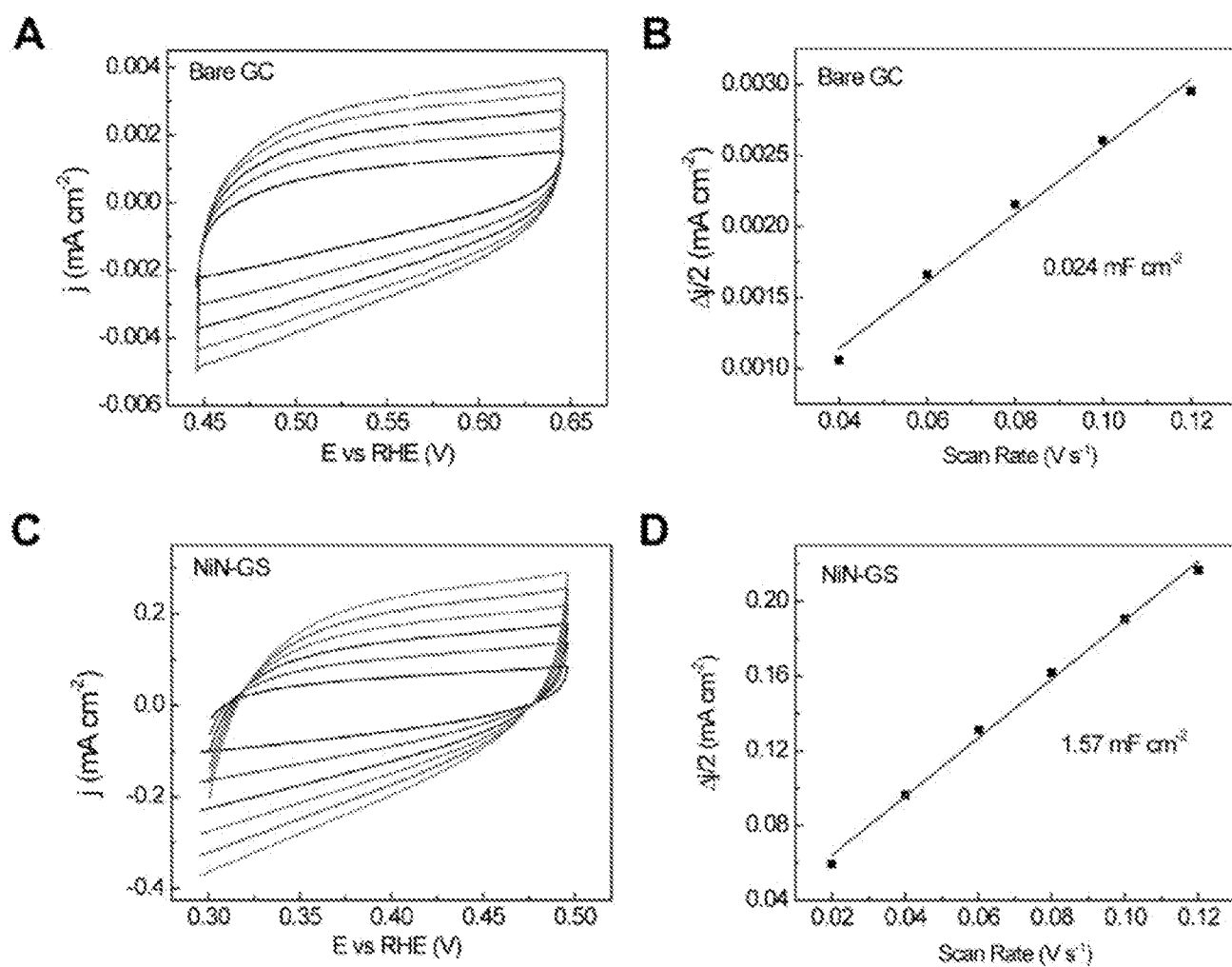
Figures 9A-9D



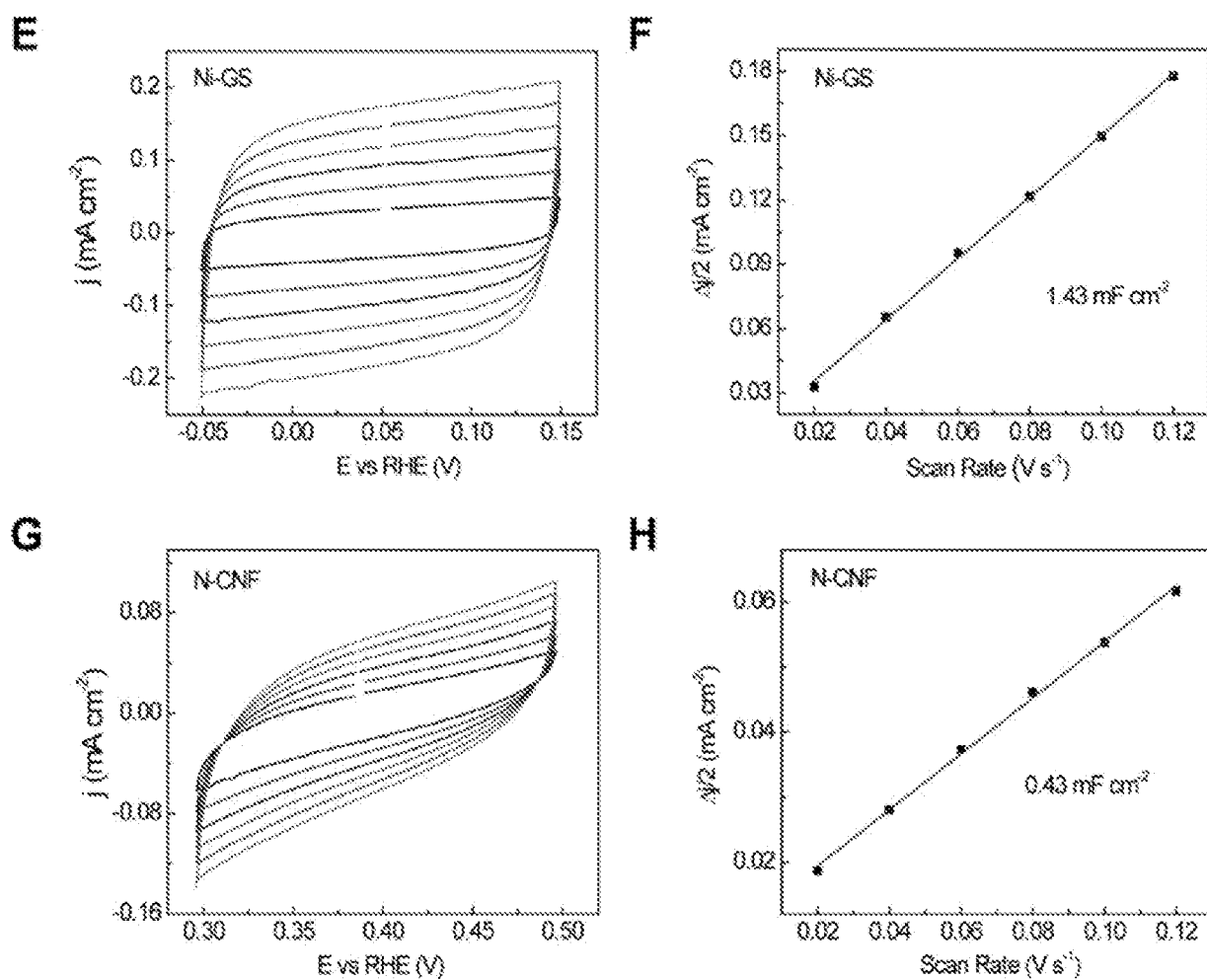
Figures 10A-10C



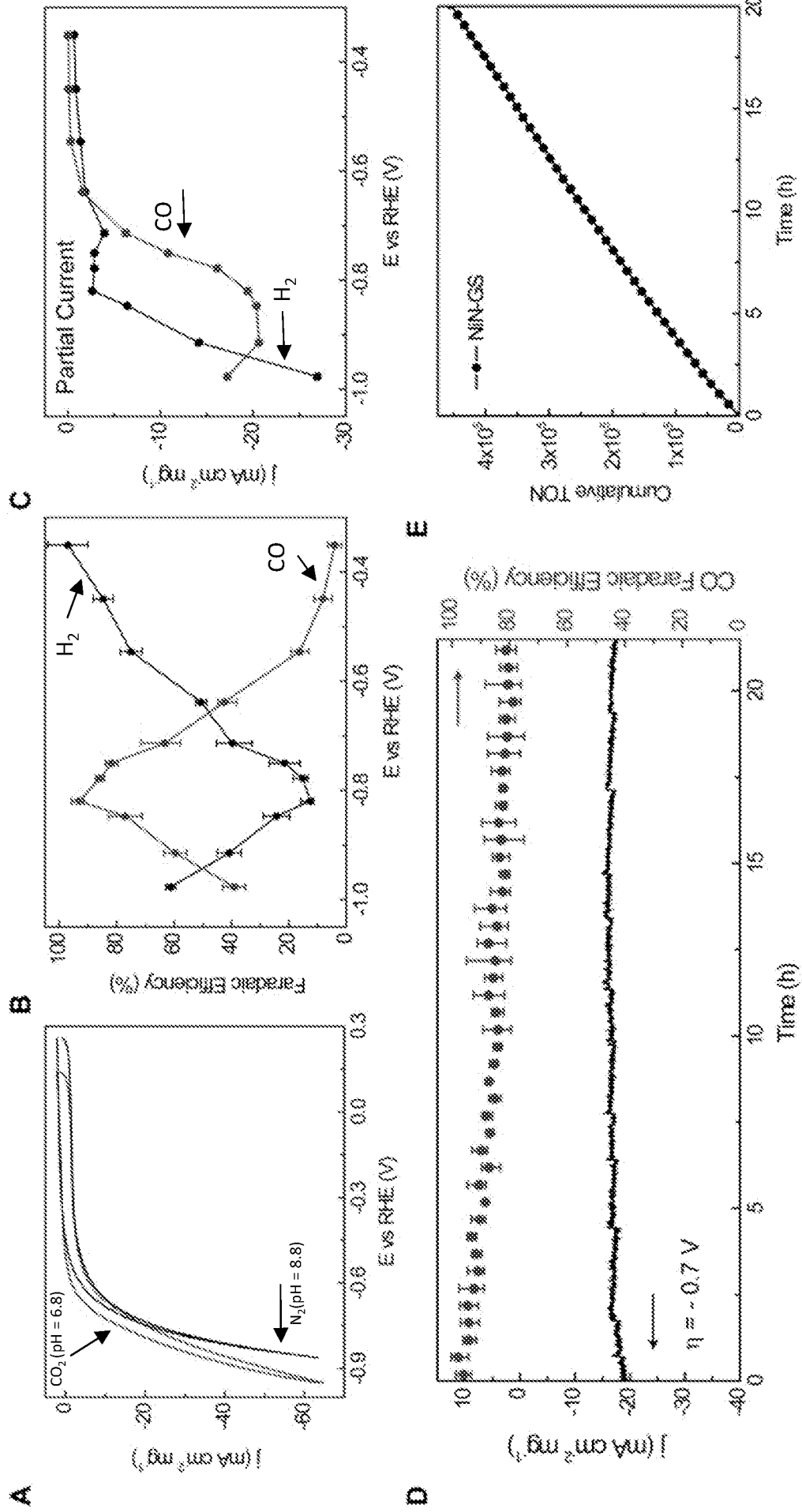
Figures 11A-11D



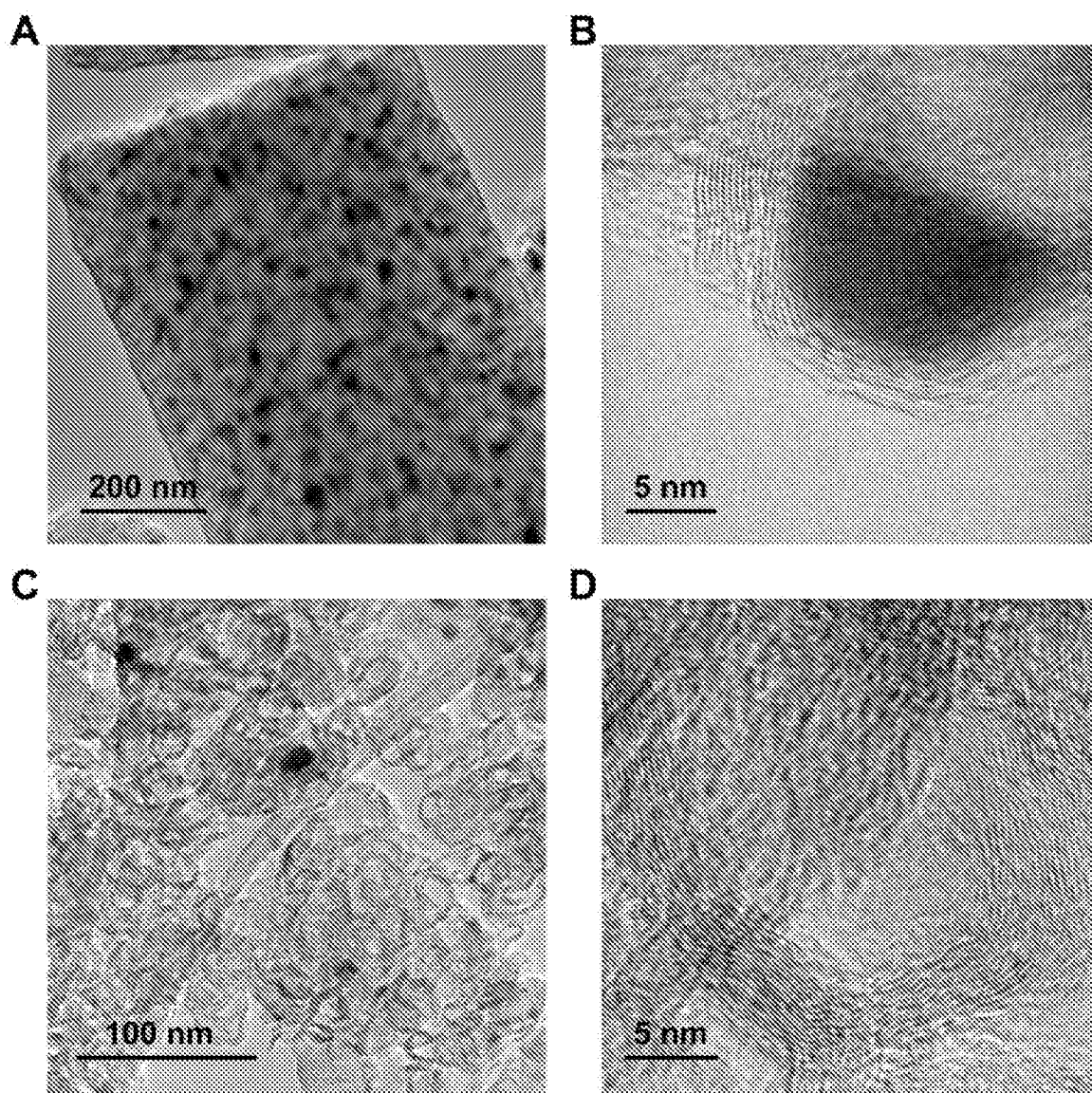
Figures 11E-11H



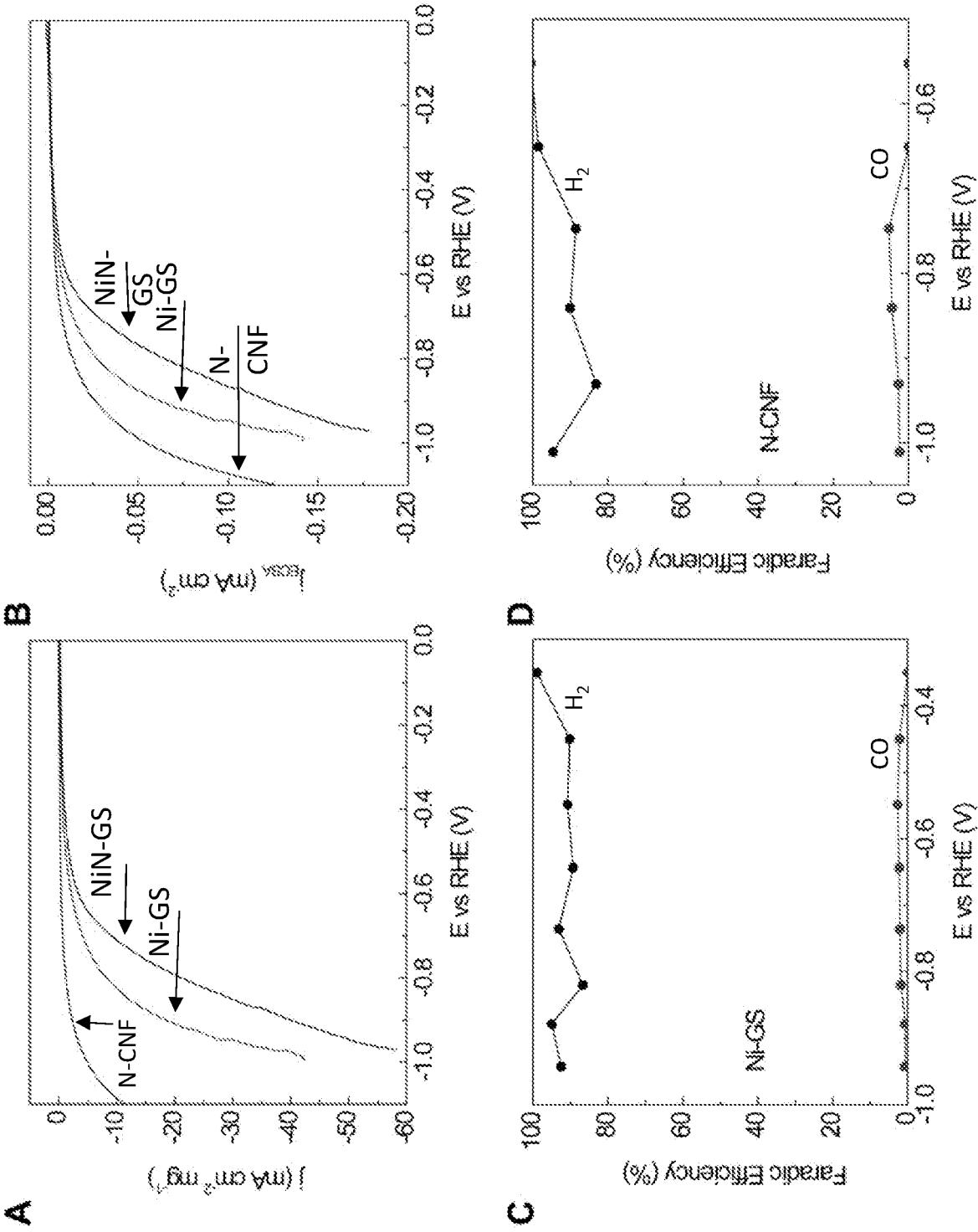
Figures 12A-12E



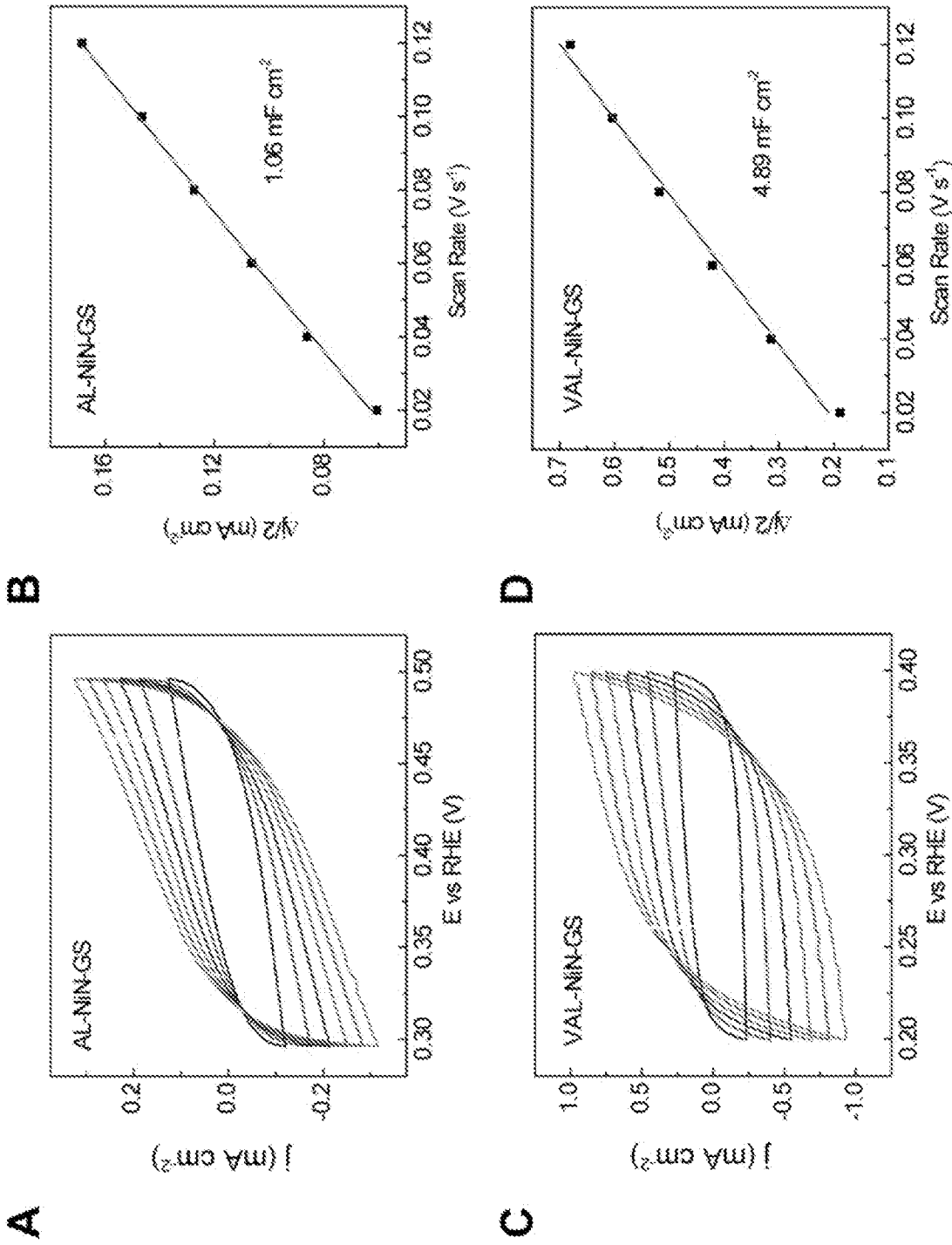
Figures 13A-13D



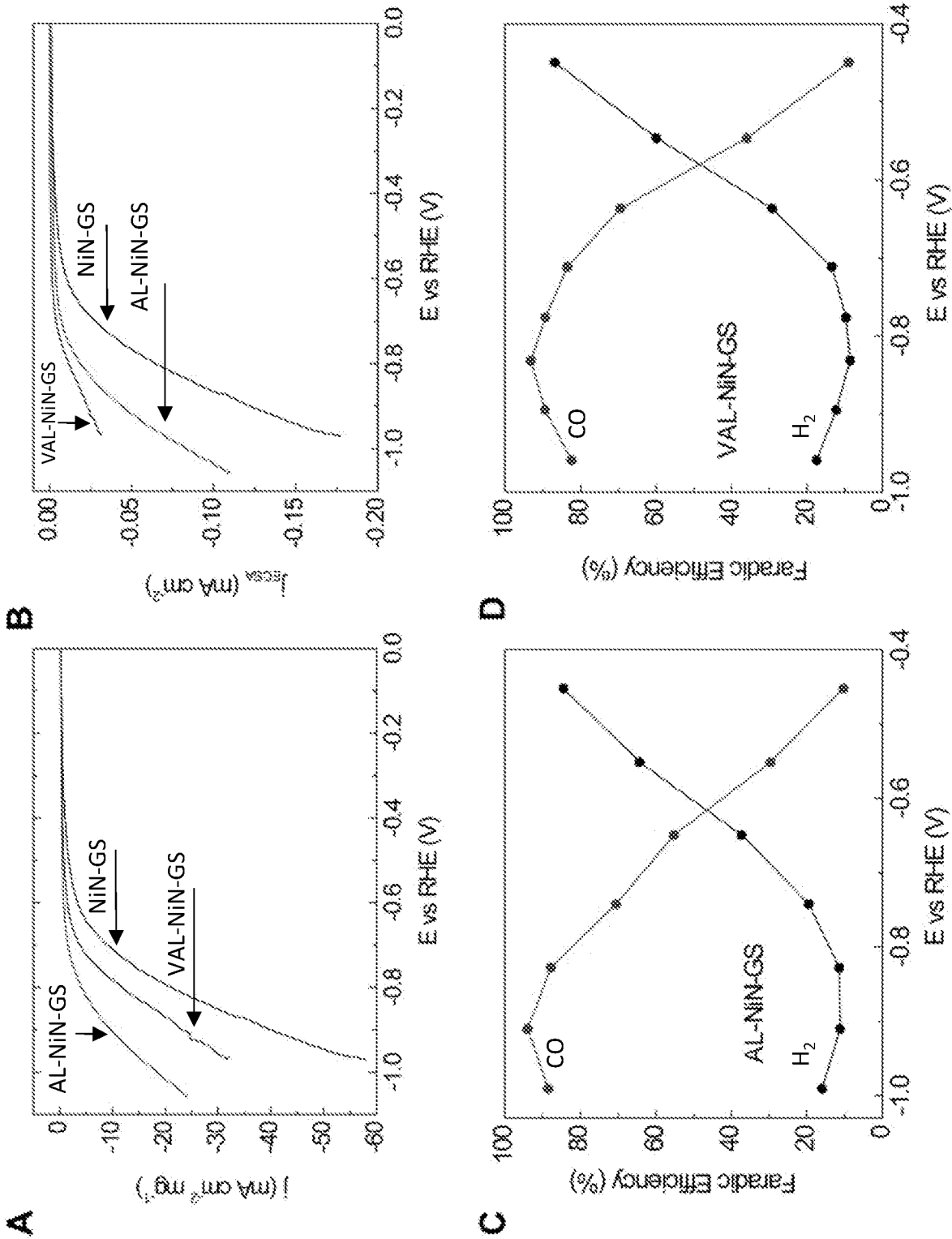
Figures 14A-14D



Figures 15A-15D



Figures 16A-16D



Figures 17A-17D

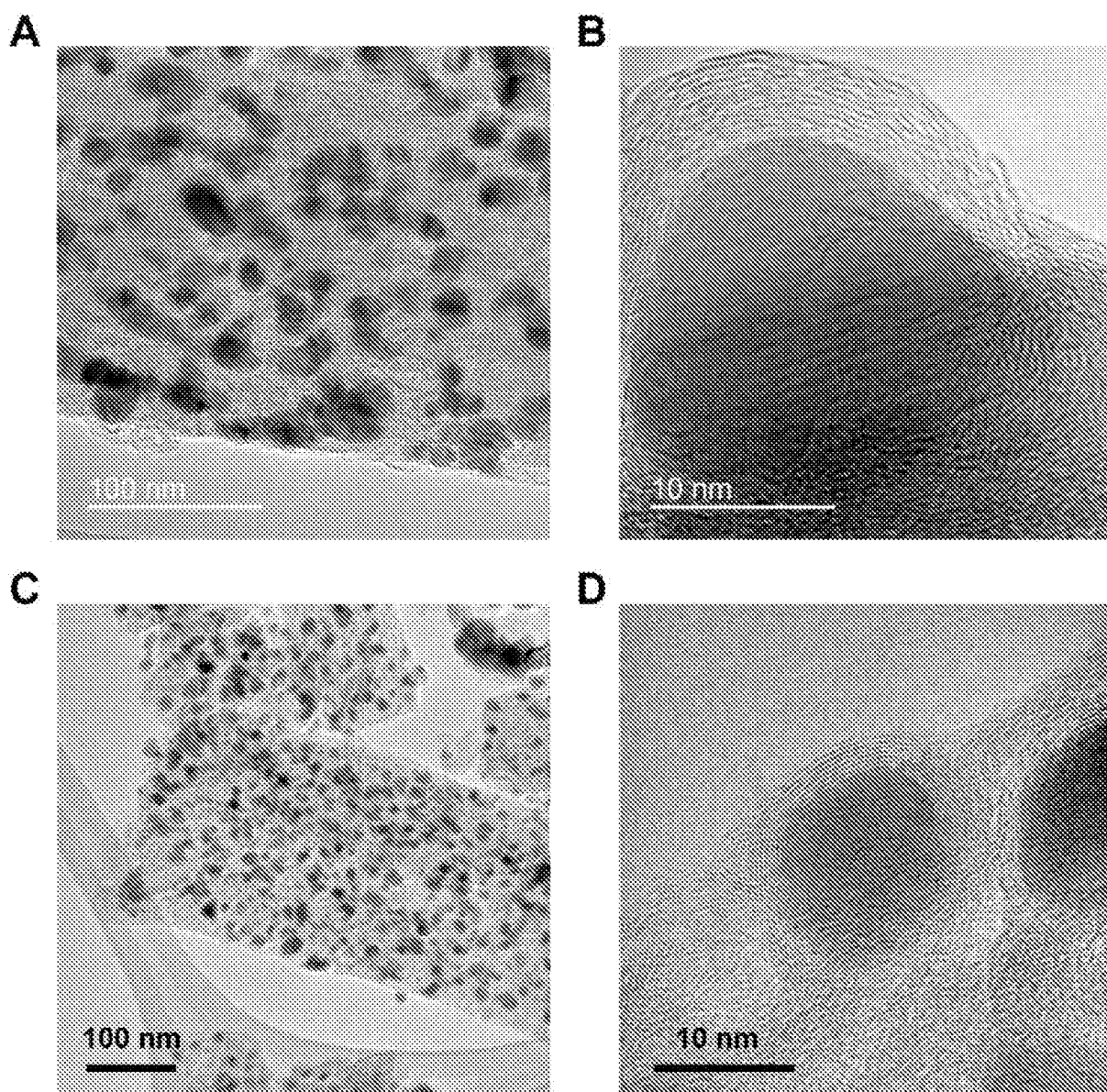
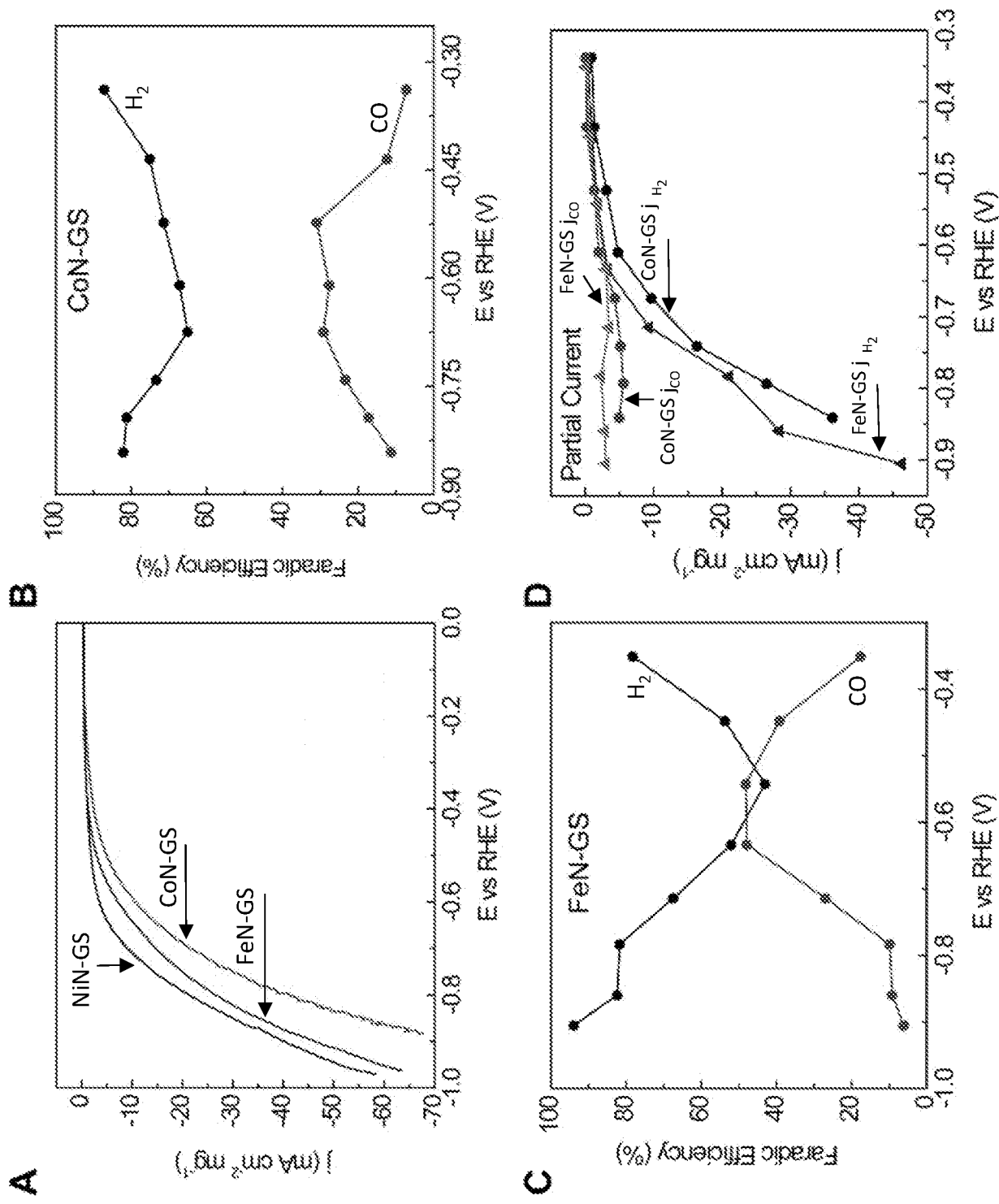
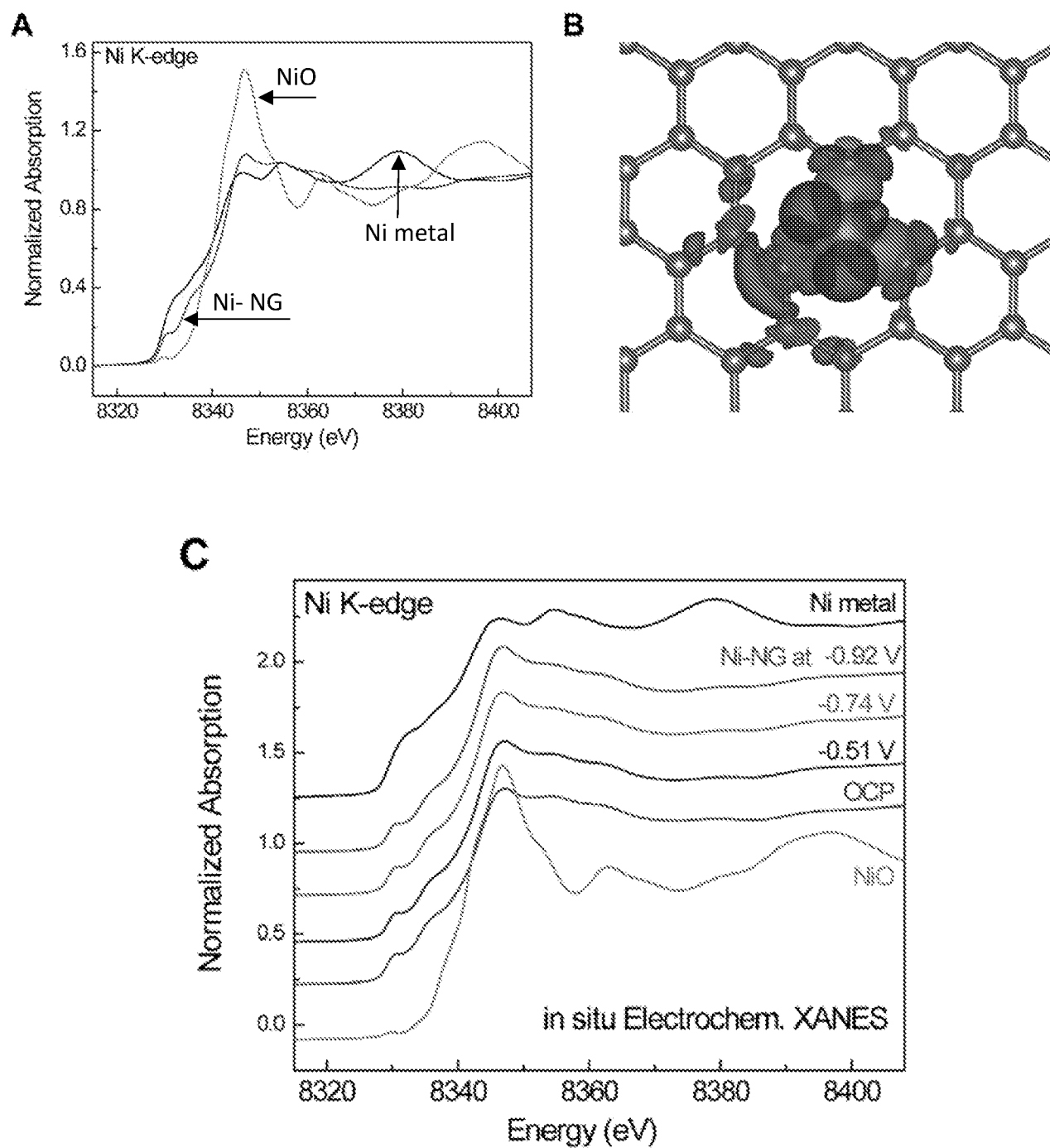


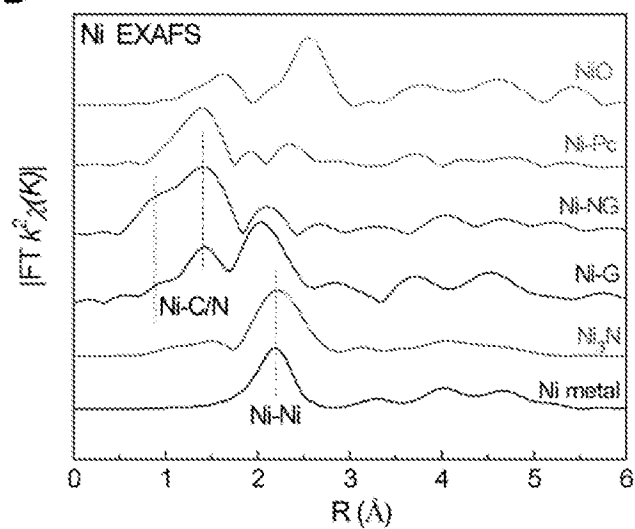
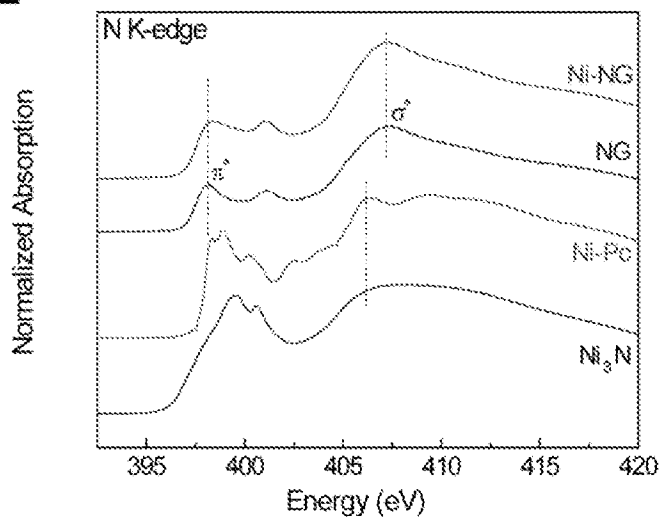
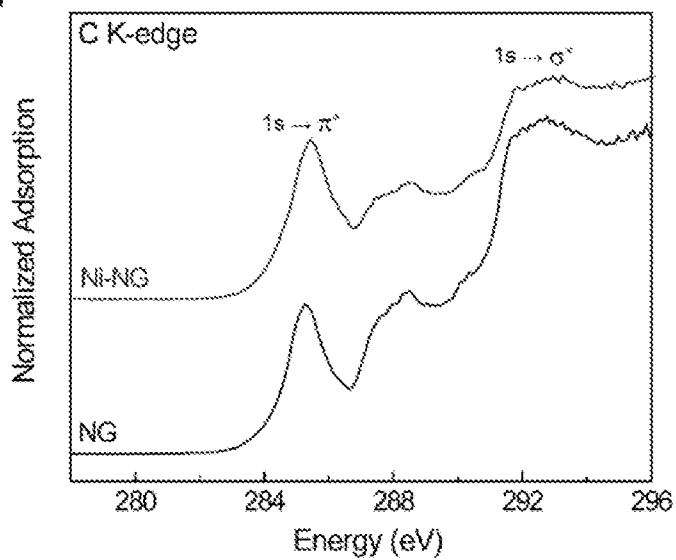
Figure 18A-18D



Figures 19A-19C



Figures 19D-19F

D**E****F**

Figures 20A-20B

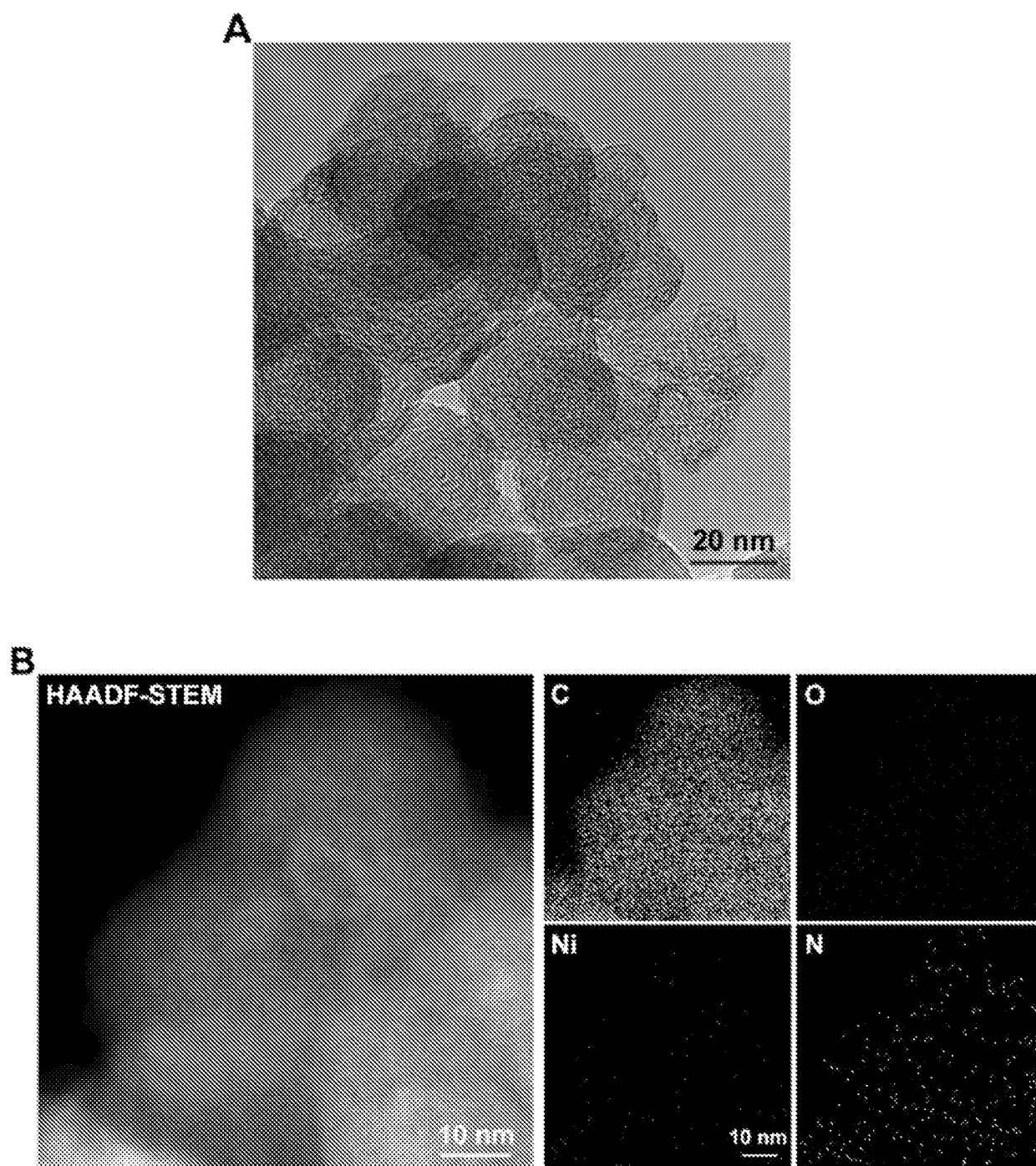
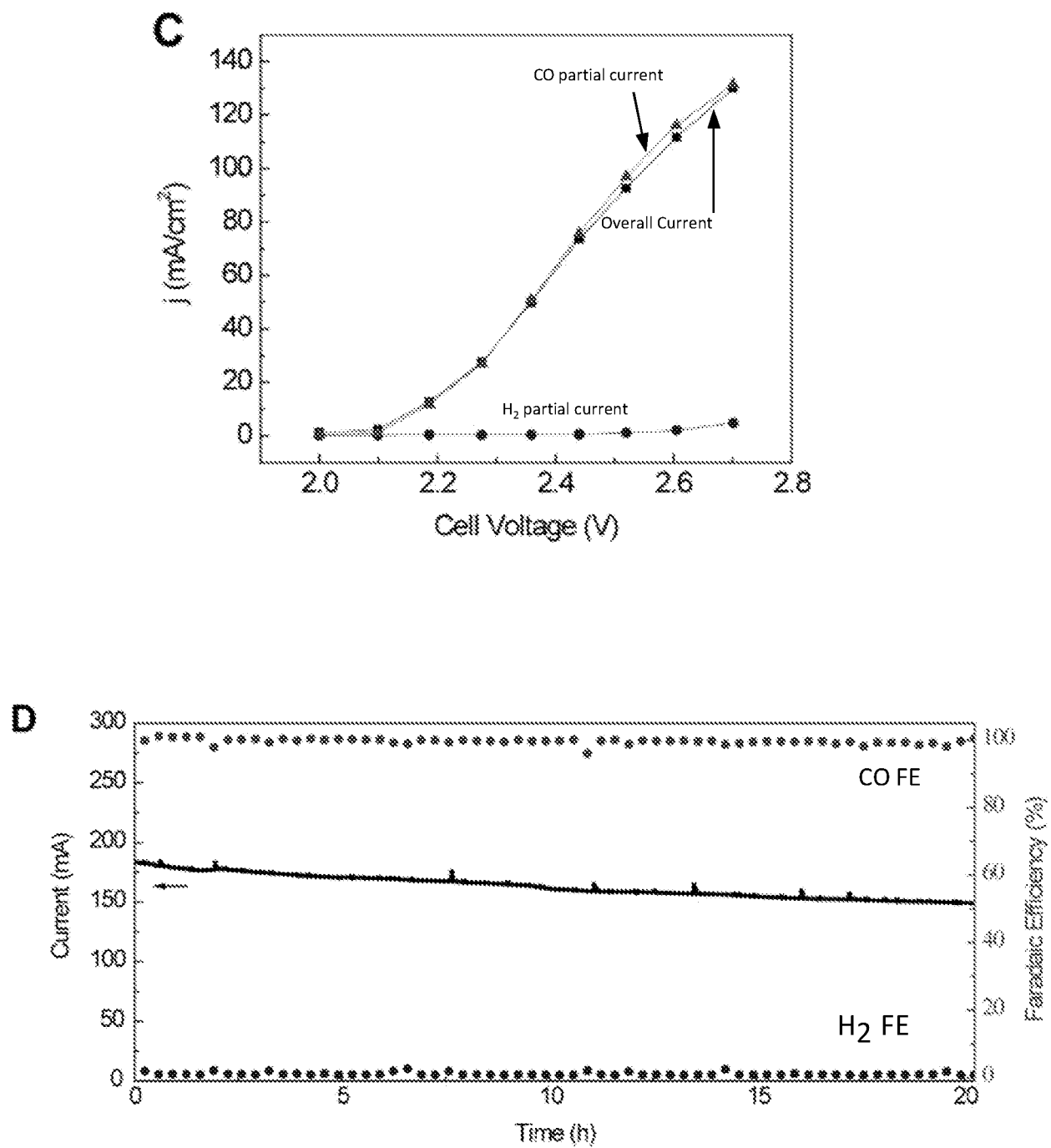
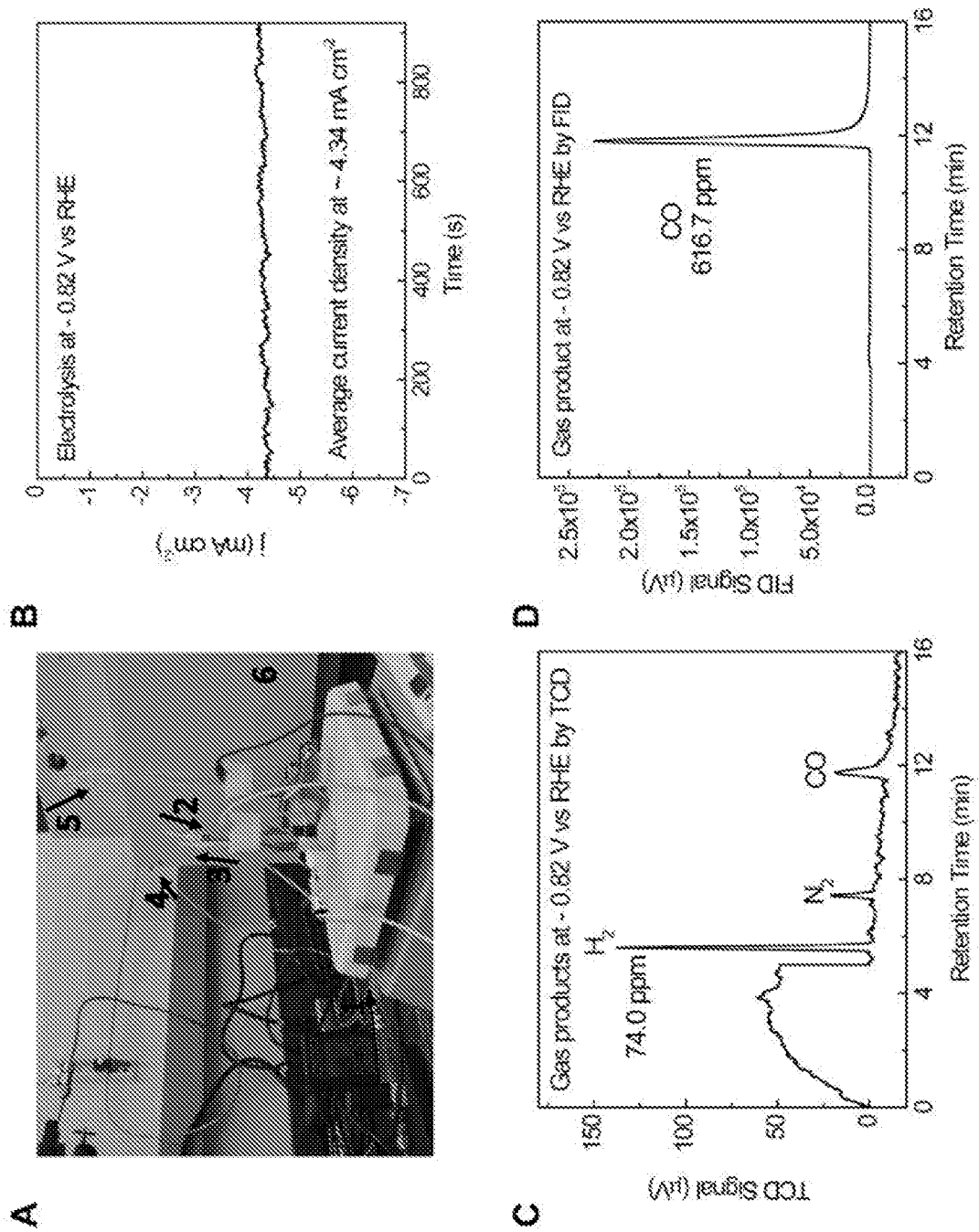


Figure 20C-20D



Figures 21A-21D



Figures 21E-21F

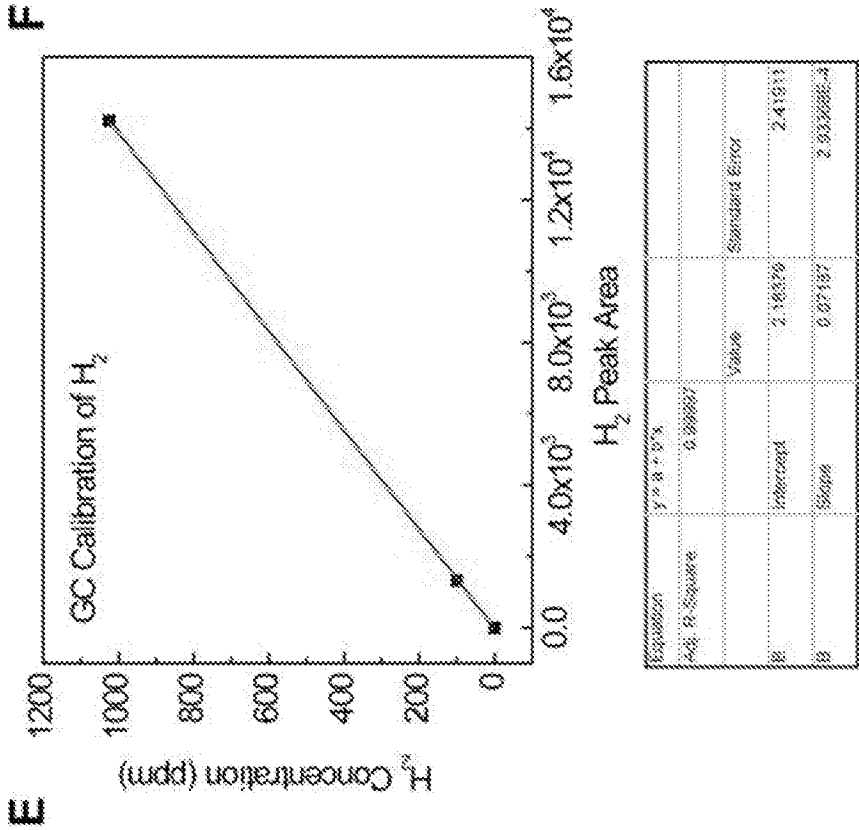


Figure 22

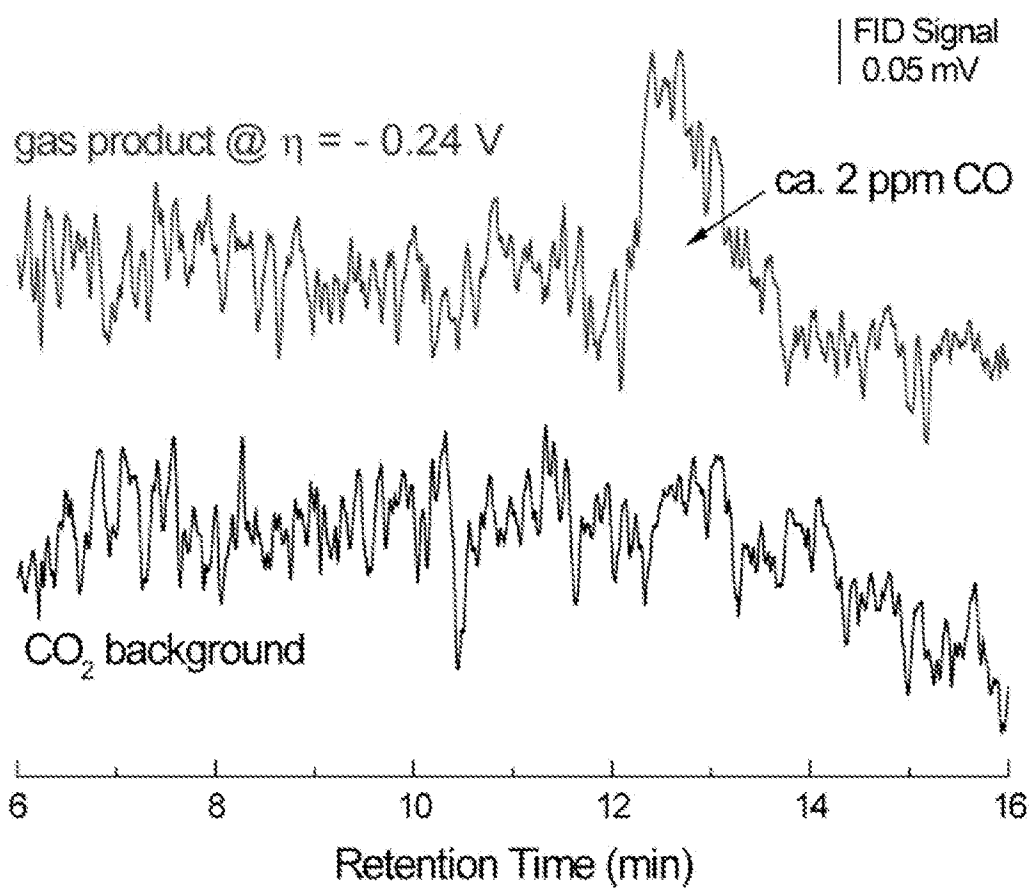


Figure 23

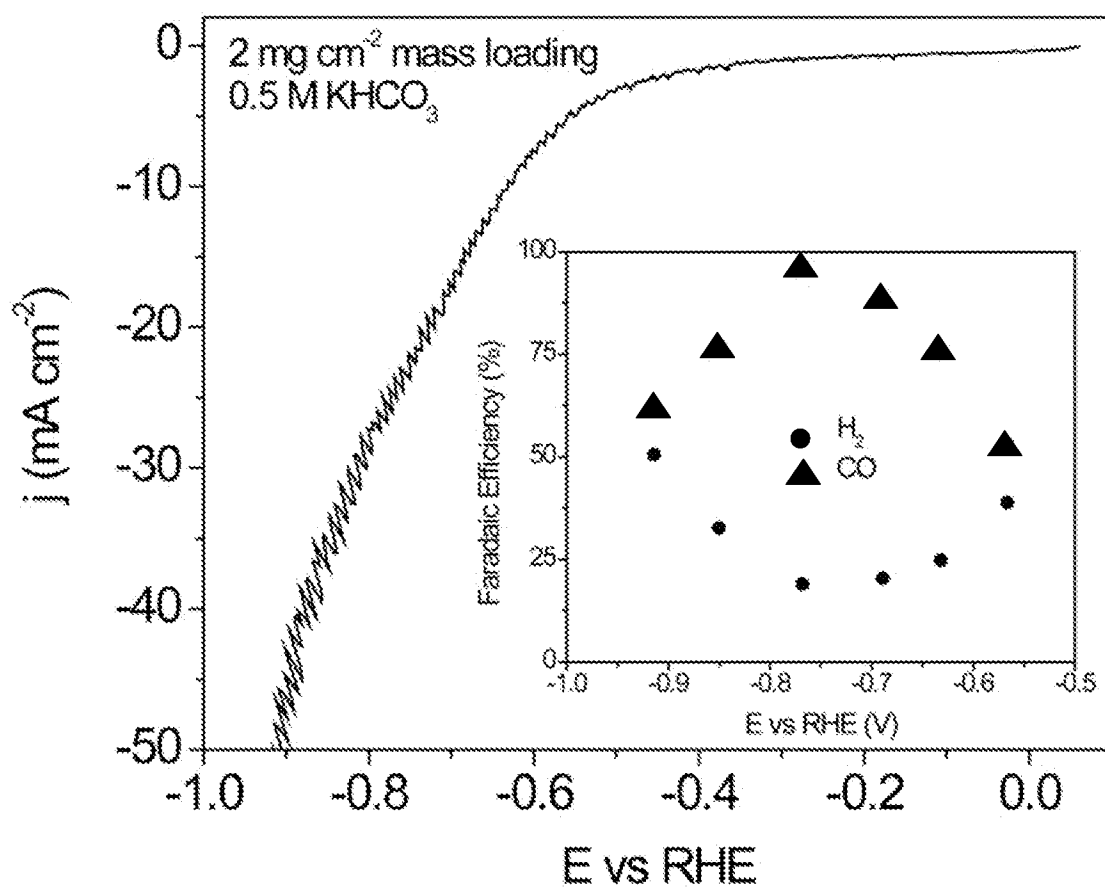


Figure 24

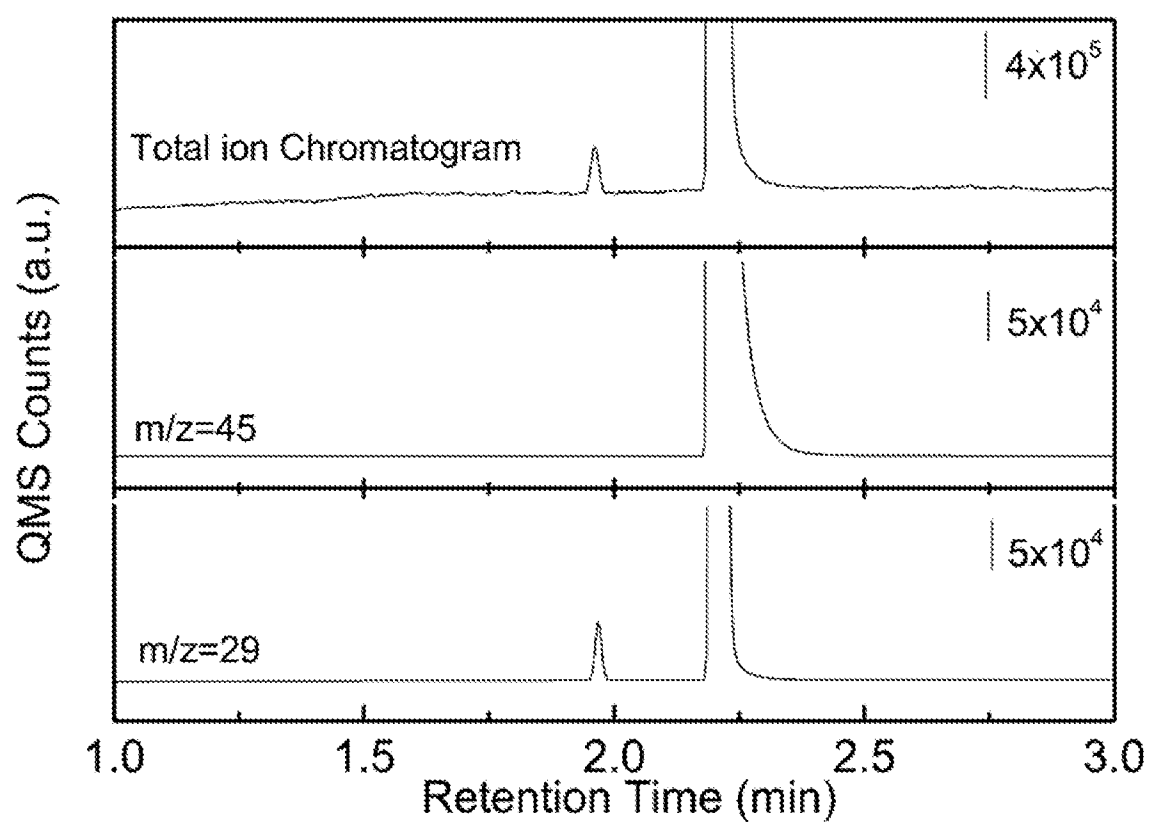
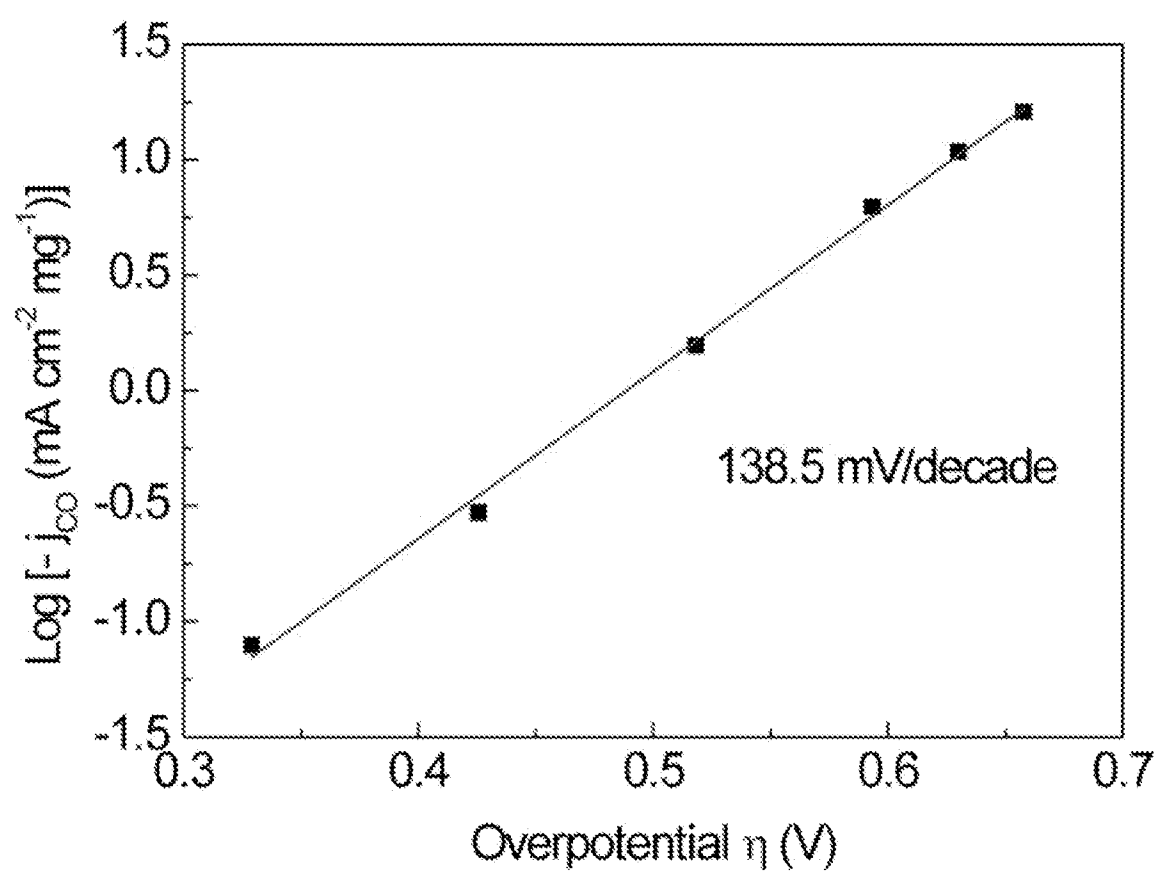
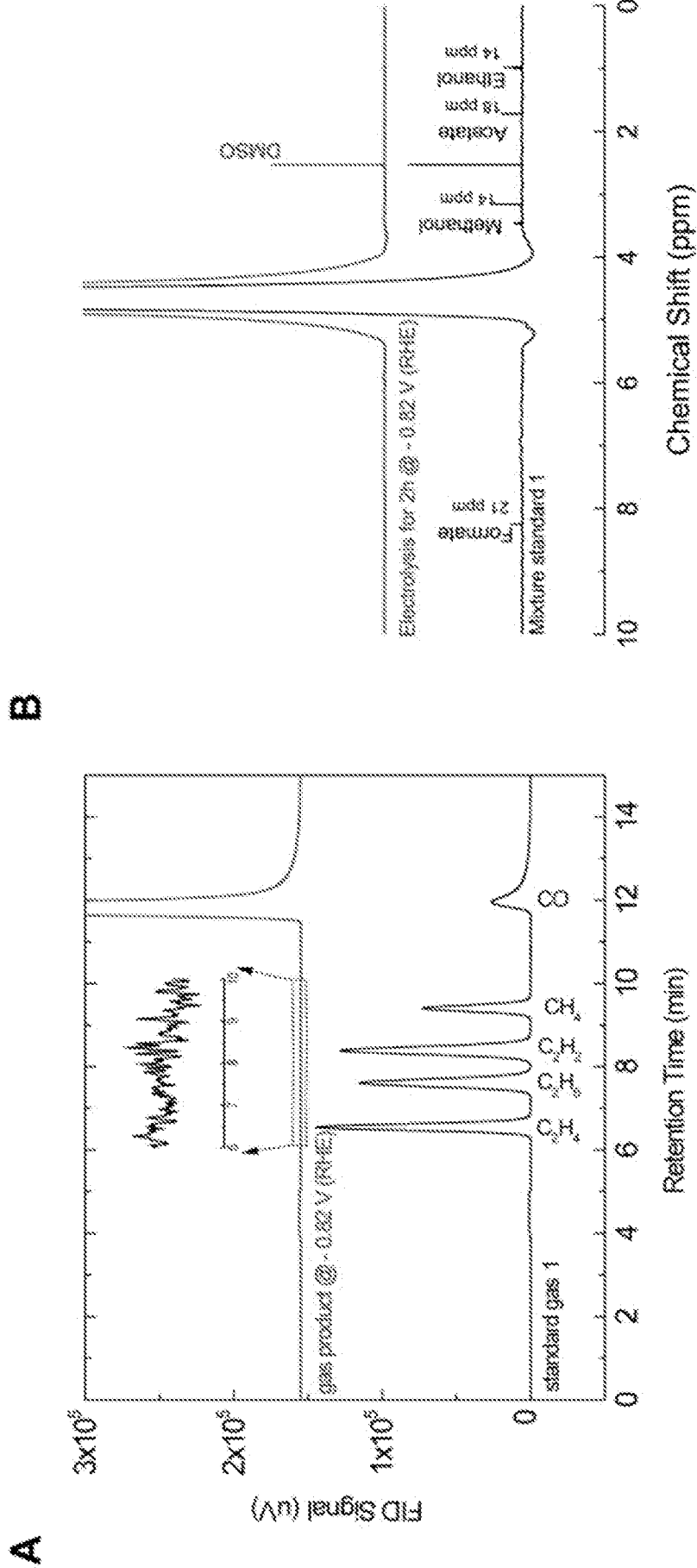


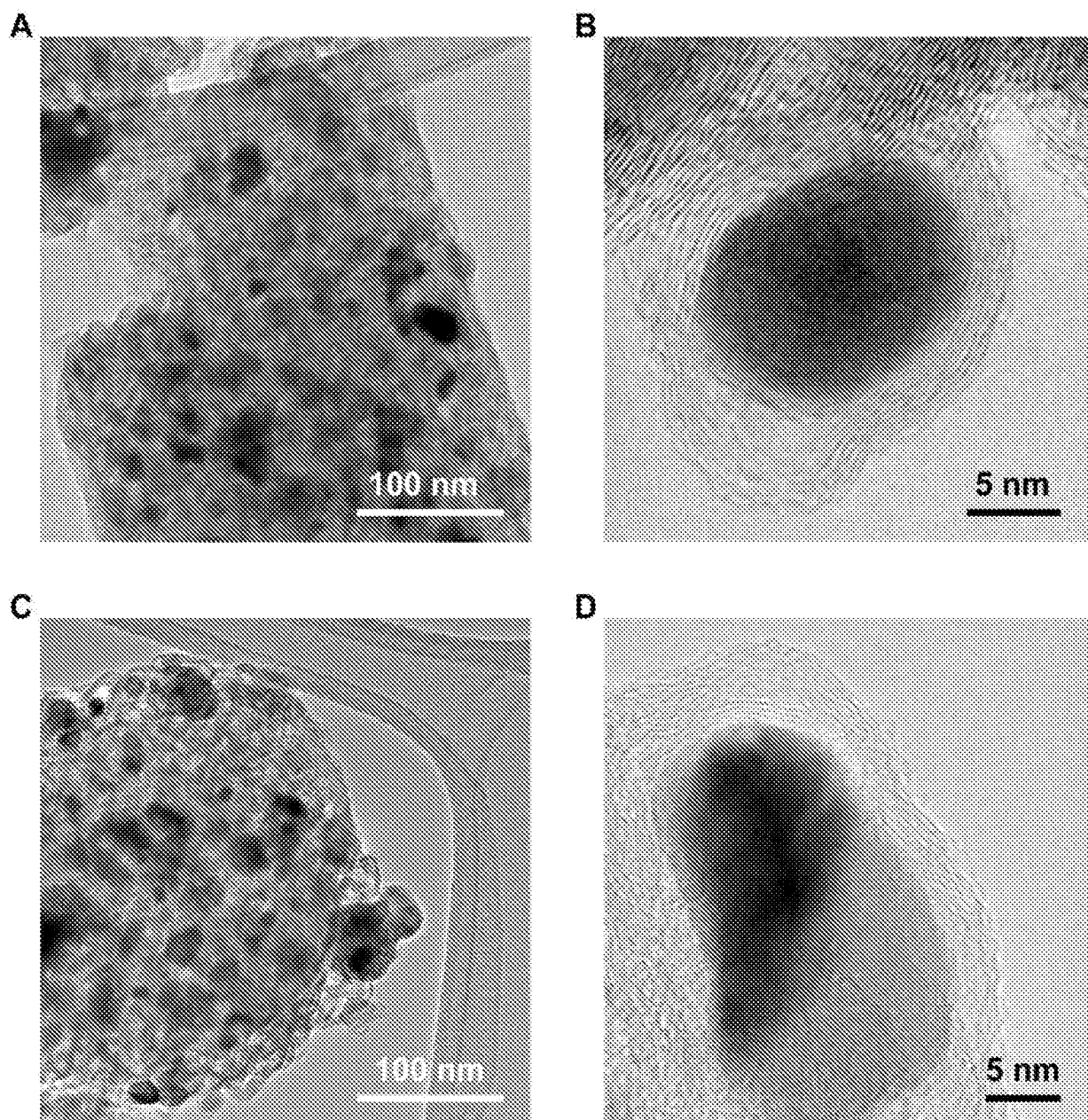
Figure 25



Figures 26A-26B



Figures 27A-27D



Figures 28A-28C

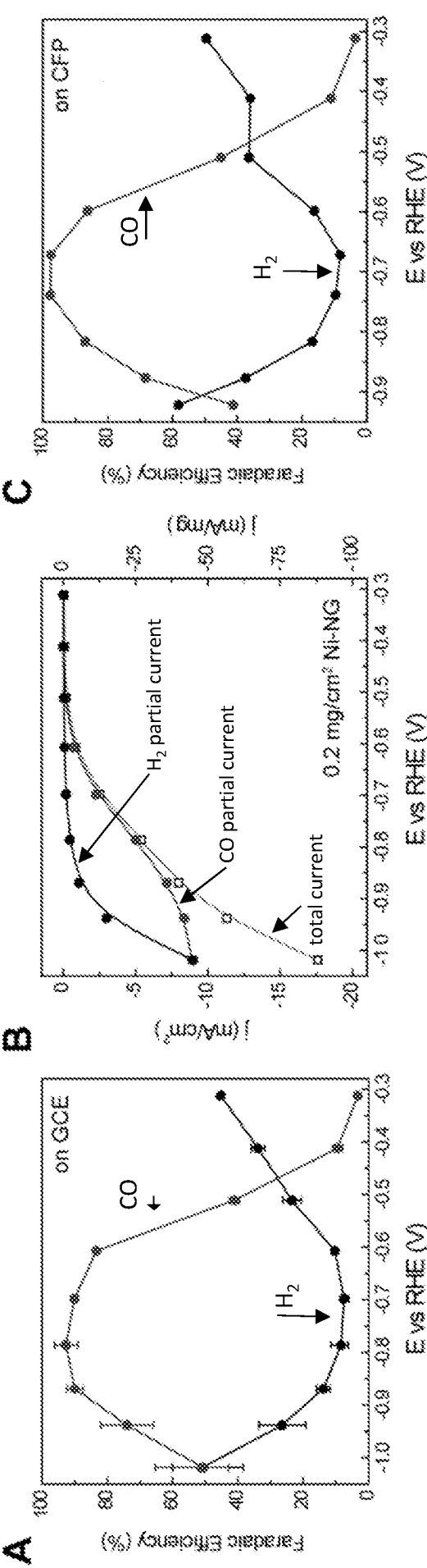
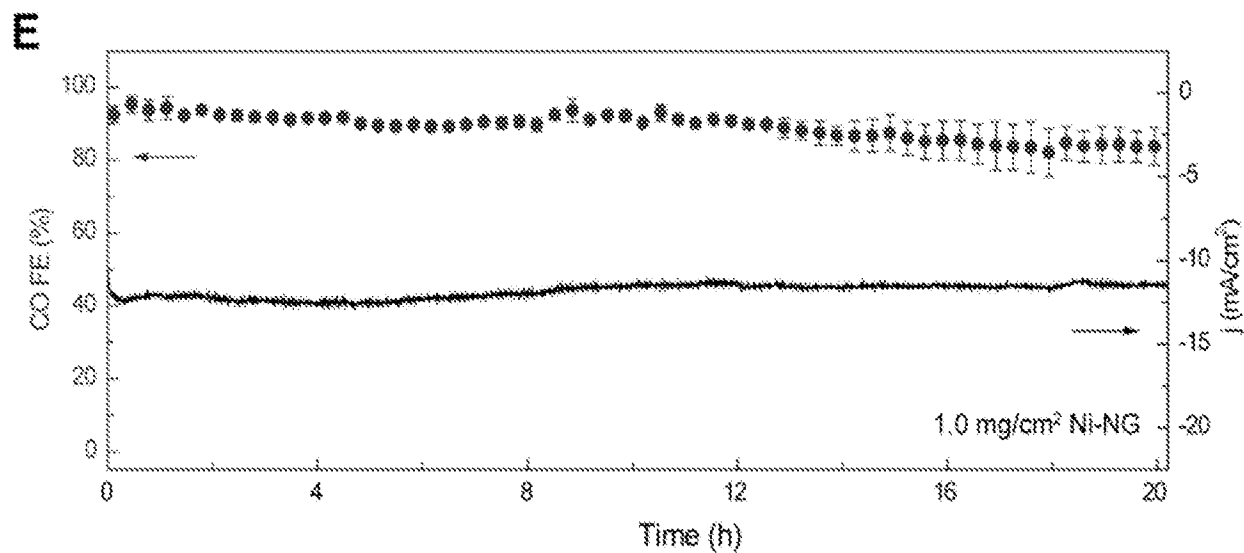
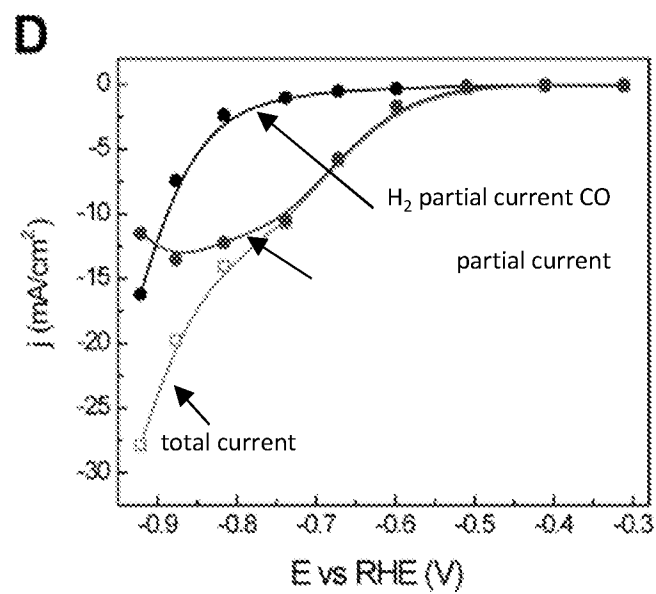


Figure 28D-28E



Figures 29A-29B

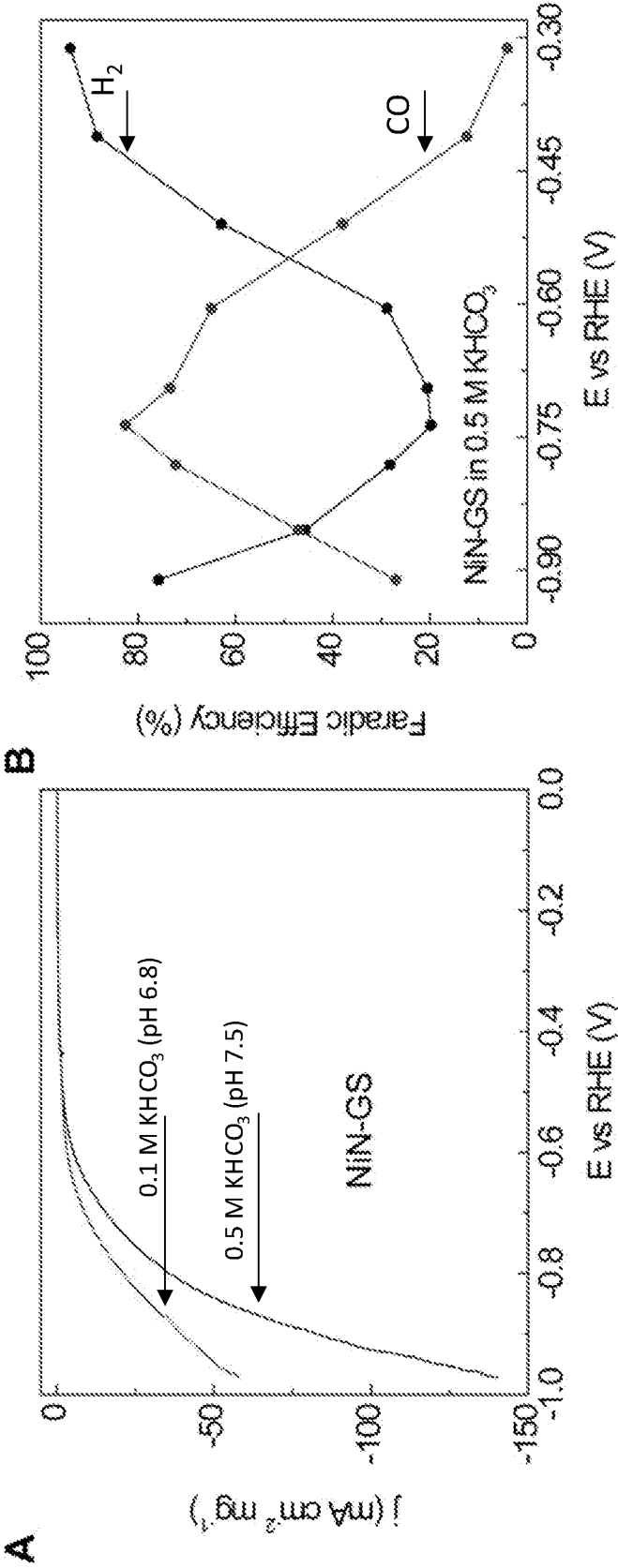
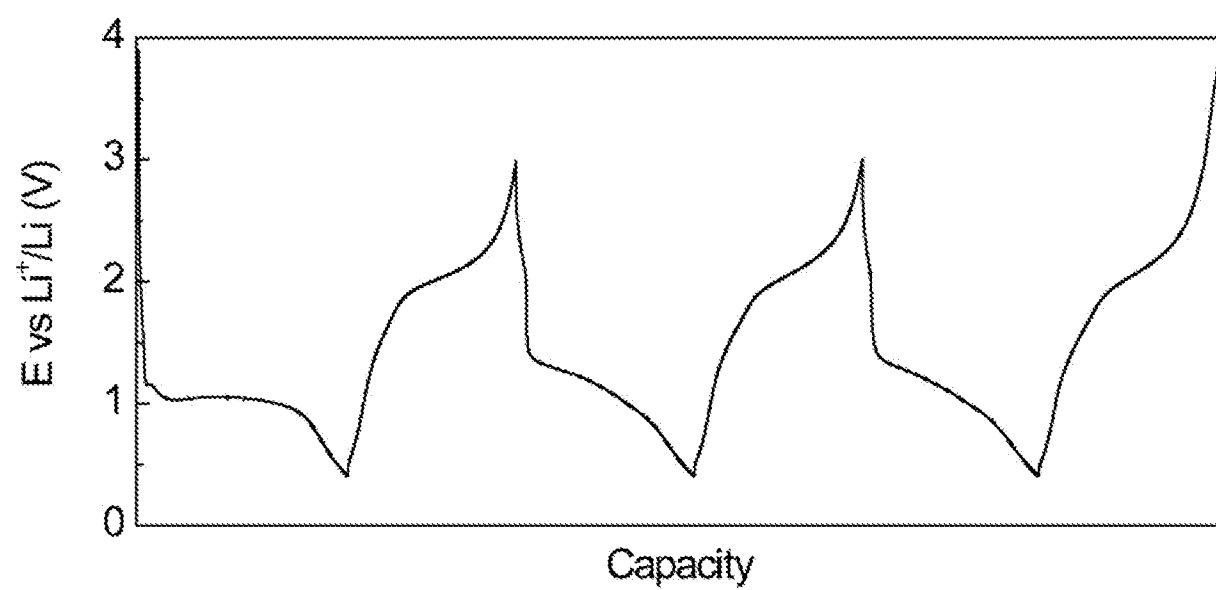


Figure 30



Figures 31A-31D

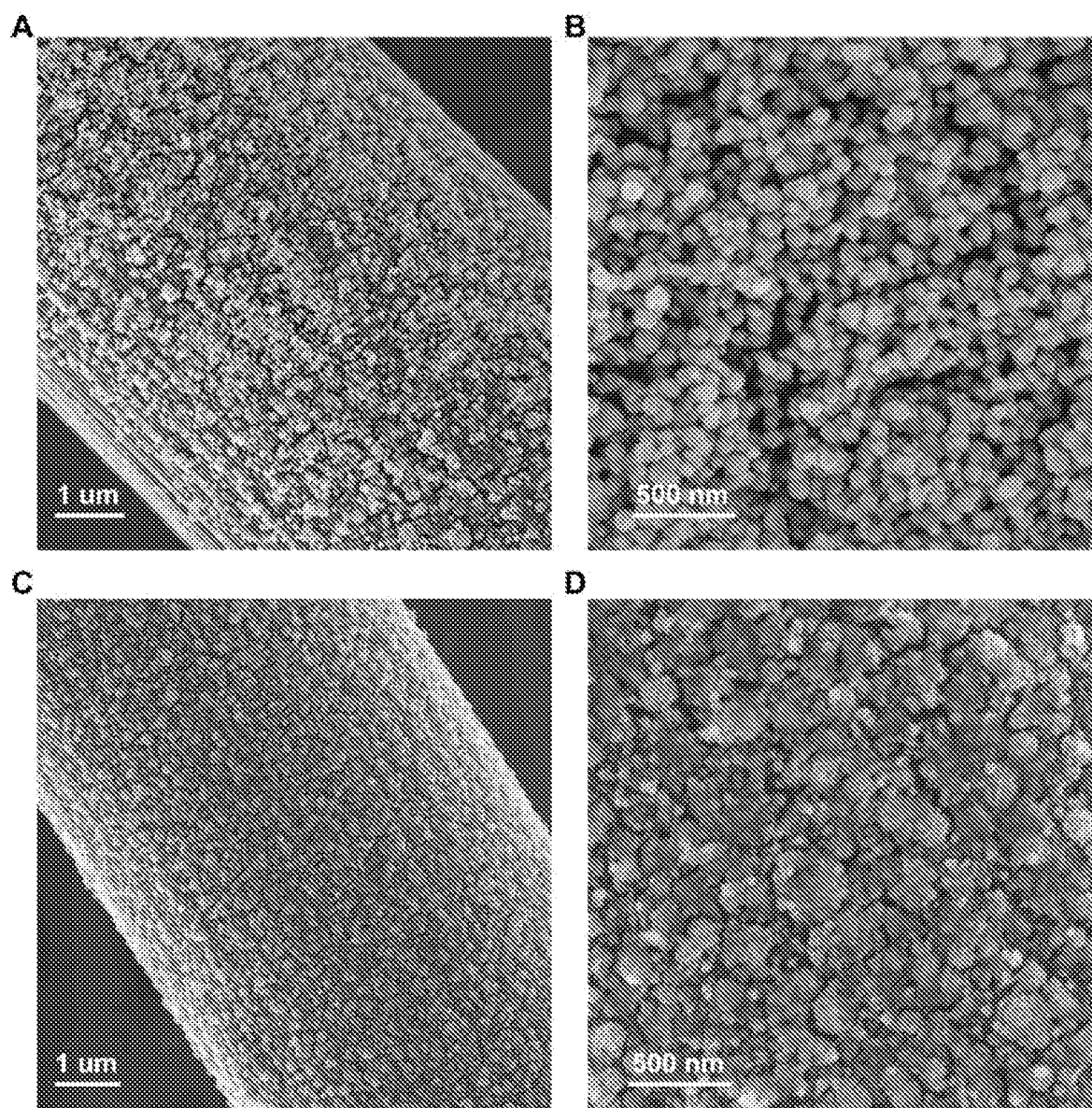
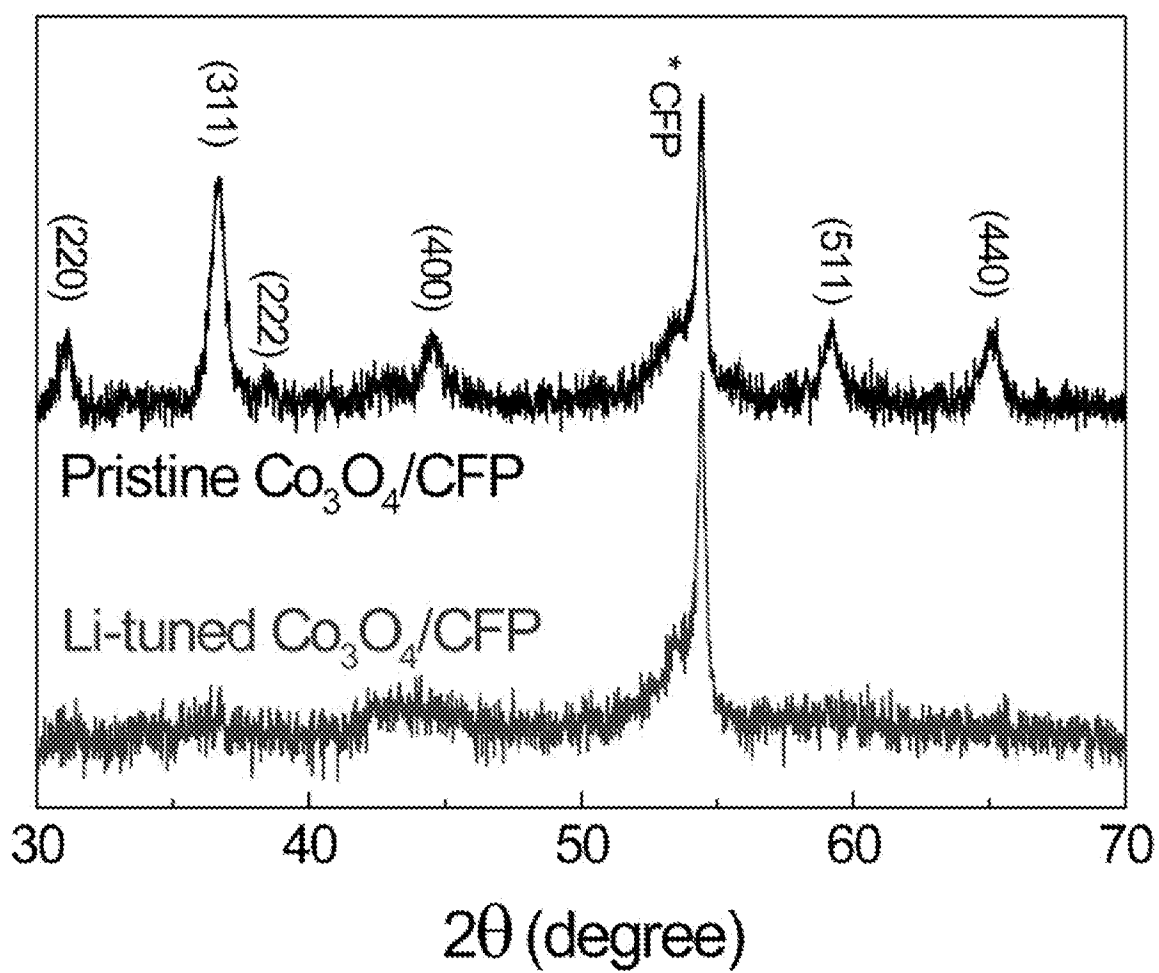
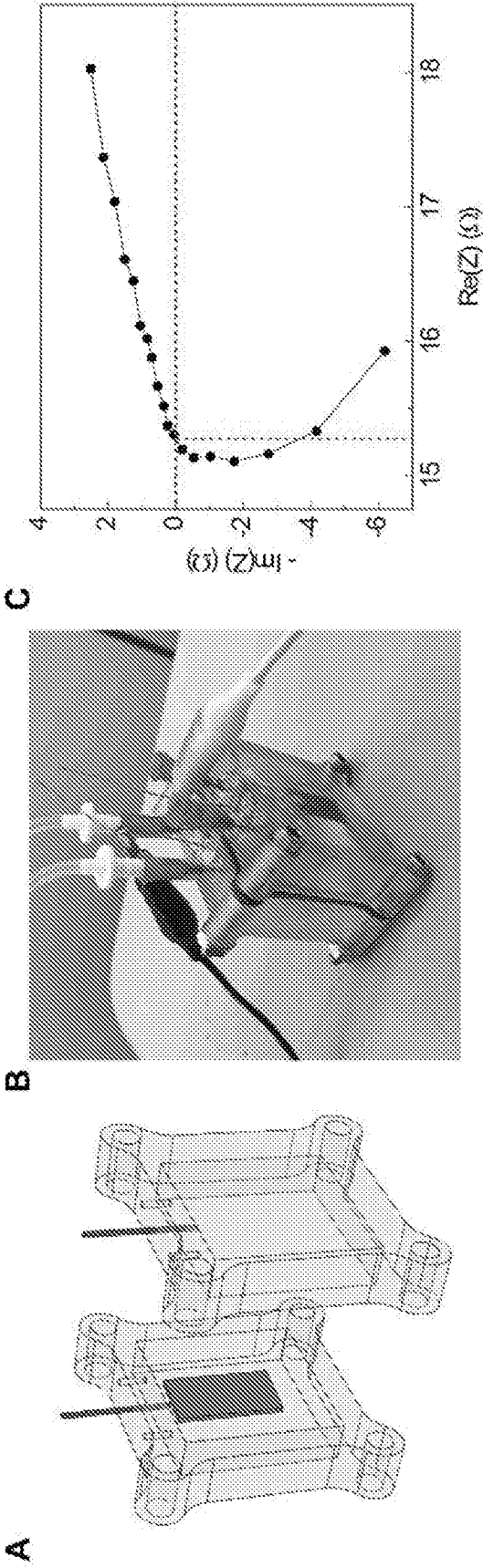


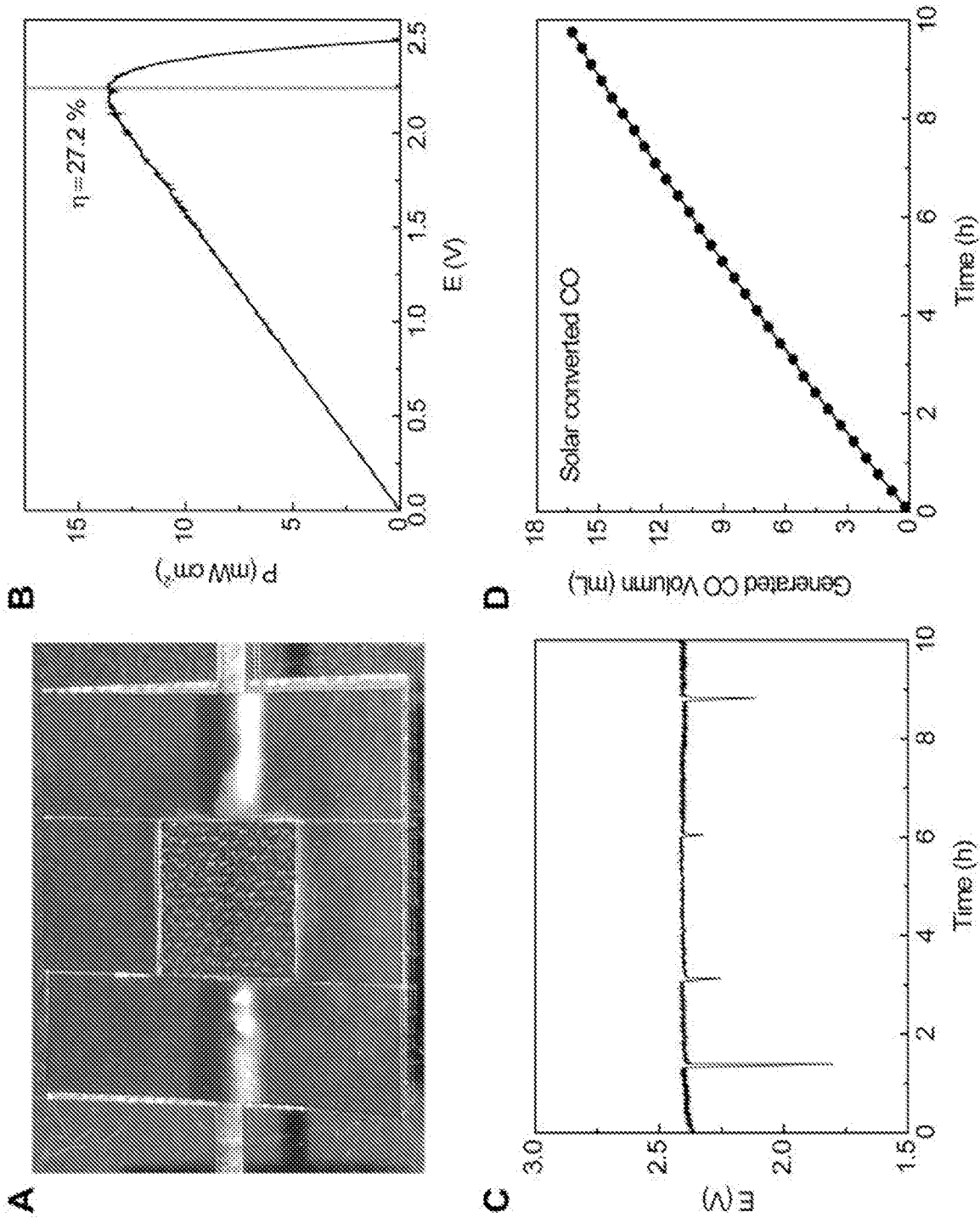
Figure 32



Figures 33A-33C



Figures 34A-34D



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/27919

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-12 directed to a composition comprising a transition metal atom or cluster incorporated within an electrically conductive support material.

Group II: Claims 13-19, directed to a method of fabricating a catalyst.

Group III: Claims 20-37, directed to methods of electrochemically reducing CO₂.

***** Continued in the Supplemental Sheet below *****

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-12

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/27919

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 23/70, B01J 23/40, B01J 32/00, B01J 37/08, C25B 11/04, H01M 4/86 (2018.01)

CPC - B01J 35/006, B01J 37/088, B01J 2231/625, B01J 2531/0211, H01M 4/885, H01M 4/926

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YOO et al, 'Enhanced Electrocatalytic Activity of Pt Subnanoclusters on Graphene Nanosheet Surface', Nano Letters, volume 9, issue 6, 30 April 2009 (30.04.2009), pg 2255-2259.	1-3
X - Y	JP 2010-129385 A (NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY et al), para [0007]-[0008].	1-2, 4 ----- 11
X	QIU et al, 'Nanoporous Graphene with Single-Atom Nickel Dopants: An Efficient and Stable Catalyst for Electrochemical Hydrogen Production' Angewandte Chemie International Edition, volume 54, 16 October 2015 (16.10.2015), pg 14031-14035.	1, 5-6, 12
X	JIA et al, 'Pt nanoclusters stabilized by N-doped carbon nanofibers for hydrogen production from formic acid', Journal of Catalysis, volume 307, 10 August 2013 (10.08.2013), pg 94-102.	1, 7-10
Y	JANG et al, 'Rational syntheses of core-shell Fe _x @Pt nanoparticles for the study of electrocatalytic oxygen reduction reaction', Scientific Reports, volume 3, article 2872, 7 October 2013 (07.10.2013), pg 1-8.	11

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14.06.2018

Date of mailing of the international search report

23 AUG 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

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Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/27919

Continuation of: Box III - Observations where unity of invention is lacking:

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Special Technical Features

Group II includes the special technical features of special technical features of a catalyst, formed by mixing a transition metal salt and a carbon source, and heating the mixture; not required by Groups I or III.

Group III includes the special technical features of a method of reducing CO₂ in a liquid medium and/or reducing CO₂ to CO, comprising contacting CO₂ with a composition and applying a voltage potential to the composition sufficient to reduce CO₂; not required by Groups I-II.

Shared Technical Features

Groups I-III share the common technical features of the composition of claim 1. However, these shared technical features do not represent a contribution over prior art as being anticipated by JP 2010-129385 A to National Institute of Advanced Industrial Science and Technology et al (hereinafter 'AIST') which teaches a composition (para [0007], 'a novel electrode material in which a platinum cluster of a subnanometer was supported in the form of a graphene sheet') comprising an electrically conductive support material (para [0007], 'graphene'; note that the 'graphene' described by AIST is reduced graphene oxide, per the synthetic procedure of para [0008], 'monolayer oxidized graphene sheet is prepared. A pale yellow solution is formed. Next, reduction treatment is carried out with hydrazine') and a transition metal atom or cluster (para [0007], 'a platinum cluster of a subnanometer'), wherein the transition metal atom or cluster is incorporated within the electrically conductive support material (para [0007], platinum atoms are covalently bonded to graphene and strongly bonded to such an extent that they do not diffuse').

Therefore, Groups I-III lack unity under PCT Rule 13 because no two of them share a same or corresponding technical feature.