HYDROGEN SPILLOVER BOOSTED PLATINUM/CARBON ELECTROCATALYSTS

Cross-Reference to Related Application

[0001] This application claims the benefit of priority of Singapore Patent Application No. 10202250255A, filed 22 June 2022, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The present disclosure relates to an electrocatalyst and devices comprising the electrocatalyst.

Background

[0003] Green hydrogen fuel - one of the spotlights of the fossil fuel transition phase - offers a promising solution to the current pressing energy crisis and climate change. This future fuel may be produced by electrolysis of water driven by an external energy input (e.g. electricity) and is deemed environmentally friendly. Owing to the moderate radical adsorption energy, platinum tends to be recognized as one of the more efficient electrocatalyst in hydrogen evolution reaction (HER), and is traditionally a material of choice for catalyst-coated membrane (CCM) used in commercial water electrolysers.

[0004] However, the scarcity, low annual production, and high cost of platinum metal, significantly limit the industrial scalability of electrolysis to reach terawatt-scale energy production. Notably, the traditional CCM, with a Pt loading as high as 1-2 mg cm^{-2} in water electrolyzer, shares about 36% to 47% of the whole Proton Exchange Membrane (PEM) electrolyzer system costs. As a consequence, the worldwide deployment of hydrogen economy calls for development of practical platinum (Pt) catalysts with low Pt mass loading and maximum Pt atom utilization efficiency.

[0005] There is thus a need to provide for a solution that addresses any of the limitations mentioned above.

Summary

[0006] In a first aspect, there is provided an electrocatalyst comprising:

a carbon support;

a catalyst disposed on the carbon support, wherein the catalyst comprises platinum; and

an interface layer disposed between and in contact with the carbon support and the catalyst,

wherein the interface layer renders hydrogen atom chemisorbed on the catalyst to migrate to the carbon support and have the hydrogen atom released from the carbon support as hydrogen gas.

[0007] In another aspect, there is provided a microcell device comprising the electrocatalyst described in various embodiments of the first aspect.

[0008] In another aspect, there is provided a method of forming the electrocatalyst described in various embodiments of the first aspect, the method comprising:

providing a substrate;

forming the carbon support;

transferring the carbon support onto the substrate;

depositing the interface layer on the carbon support; and

depositing the catalyst on the interface layer.

[0009] In various embodiments of the method, forming the carbon support may include synthesizing the carbon support. In various embodiments of the method, transferring the carbon support onto the substrate may be carried out through polymer assisted-transfer.

Brief Description of the Drawings

[0010] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the present disclosure. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

[0011] FIG. 1A is a diagram illustrating decoupled-HER induced by hydrogen spillover in Pt/C system.

[0012] FIG. 1B shows a fluorescence image of a nanobubble labeled by a single rhodamine 6G (R6G) molecule on graphene during HER (left image), the pixel size is 160 nm×160 nm. The right image shows the center position of the nanobubble is

localized with nanometer accuracy, which is achieved by fitting the emission of the labeling R6G fluorophore to two dimensional (2D) Gaussian functions.

[0013] FIG. 2A shows a schematic illustration (top image) of the total internal reflection fluorescence (TIRF) microscopy setup. Working electrode: catalyst/graphene. Reference electrode: leakless Ag/AgCl. Counter electrode: Pt wire. Electrolyte: 0.5 M H_2SO_4 with 5 nM R6G. The fluorescence images were recorded at 60 frames/s with a 16.7 ms exposure time (unless otherwise noted). FIG. 2A also shows an image (bottom image) of the total TIRF microscope (Nikon Eclipse Ti-U) and the optical path. In the bottom image, the in-situ single-molecule TIRF/electrochemical experiments were conducted on an inverted fluorescence microscope (Nikon Eclipse Ti-U). An adjustable 100 mW, 532 nm laser beam (L6CC Oxxius) with circular polarization was focused onto the material-solution interface via a dichromic mirror (Di02-R635-25x36, Semrock) by a 100× infinity-corrected microscope objective lens (Nikon Plan Apo λ, NA 1.45). Further, to achieve an evanescent field of illumination-tens of nanometers into the solution-the illumination configuration was adjusted to wide-field total internal reflection (TIR). This is achieved by employing a transition stage to shift the laser beam towards the edge of the objective lens, enabling an incidence angle close to the critical angle of the glass-water interface. The emission was filtered by a band-pass filter (ET605/70m, Chroma) and then collected through the oil-immersion objective lens via a quad-edge laser dichroic mirror (Di03-R405/488/532/635-t1-25x36, Semrock). The fluorescence images were captured by an EMCCD camera (Andor iXon3) cooled to -70 °C, at 60 frames per second for a frame size of 256 x 256 pixels. Last but not least, the collected fluorescence signal by the objective was filtered by a Chroma band-pass filter (ET605/70m) and focused onto an EMCCD camera (Andor iXon3) through an achromatic lens with f = 75 mm.

[0014] FIG. 2B shows the fluorescence image sequence of a circular Pt/Ti/graphene device with a Pt thickness of 5 nm and a Ti thickness of 2 nm (the thicknesses of the Pt and Ti layer remain the same unless otherwise noted), which were obtained under a fixed potential of -0.2 V *vs RHE*. Pixel size: 160 nm. Cyan circles are included to guide the eye in identifying the position of the Pt circle. The far-right layer is the corresponding optical image. Scale bar denotes 5 μm.

[0015] FIG. 2C is a plot of intensity-time trace over the 4 pixels × 4 pixels white dotted box shown in FIG. 2A top image. Inset: The distribution of "fluorescence-on" time of nanobubbles on the device in FIG. 2B and its single exponential decay fit.

[0016] FIG. 2D is an optical image of a square-shaped Pt/Ti/Graphene device of the present disclosure.

[0017] FIG. 2E is a plot of synchronized signals of the current density (j) based on the area of Pt and the averaged fluorescence intensity (FL) over the dashed box (demarcated by dotted line) in FIG. 2D. The various insets are images acquired in the TIRF recording at different potentials. Scale bar in each insets denotes 5 μm.

[0018] FIG. 2F shows the results for kinetic analysis of Ha diffusion coefficient, D_{Ha}. The leftmost image is an optical image of the one-dimensional (1D) Pt/Ti nanowire on graphene device with a width of 600 nm for the 1D Pt/Ti nanowire and a width of 55 μm for available graphene receptor. The direction of spillover, *x*, is indicated by the black arrow. The observation region is marked with a dashed box (demarcated by dotted line). The three images in the center are accumulated images of consecutive 10 frames (see FIG. 2G and 2H). The dotted circles are included to guide the eye to identify the location of the nanobubbles. Scale bar denotes 5 μm. The rightmost image is a scatter plot of nanobubble-to-Pt nanowire distance along *x* versus the frame index. The far right nanobubbles are marked using stars.

[0019] FIG. 2G shows bright-field images of the observation area during in-situ TIRF/electrochemical measurement and a series of accumulated fluorescence images for 50 consecutive raw frames. The fluorescence images were recorded at 60 frames per second with a 16.7 ms exposure time.

[0020] FIG. 2H is a plot of the electrochemical current recorded during the experiment in FIG. 2G. The CA test was conducted in 0.5 M H_2SO_4 with 5nM R6G at -0.05 V_{vsRHE} for 150 s.

[0021] FIG. 3A shows three types of microcell on-chip devices of the present disclosure. Type 1: the micro-cell for in situ single molecule total internal reflection fluorescence microscopy (TIRF)/electrochemical test for hydrogen spillover study, which is capable of monitoring the dynamic behavior of hydrogen nanobubbles during the gas-evolving reaction. Images of setup: representative experimental apparatuses (top), home-designed electronic device wire bonded onto a printed circuit board (PCB)

(bottom left), a typical patterned Pt circle device with a defined 60 μm by 60 μm reaction window in a PMMA passivated layer (bottom right). Type 2: the micro-cell for active site study, which explores the possibility of using nanobubbles as activity indicators. Type 3: the micro-cell for quantifying the benefit of hydrogen spillover. The desired area ratio of Pt/C can be determined by comparing the normalized hydrogen evolution reaction (HER) performance of the devices with varied area ratios of exposed Pt and graphene.

[0022] FIG. 3B shows the protocol for the device fabrication of the micro-cells.

[0023] FIG. 4 is a plot of the minimum energy paths (MEPs) of the hydrogen spillover on the Pt/graphene and Pt/Ti/graphene structures, respectively.

[0024] FIG. 5 shows in the left image the laser beam of normal incidence passes through the air-glass interface when the transition stage is at 12.72 mm. The right image shows the laser beam is reflected at 6.35° off the normal when the transition stage is at 12.3 mm.

[0025] FIG. 6 shows a series of frames on MoS_2/graphene device at a constant potential of -0.2 V_{vsRHE}. Reaction condition: 0.5 M H_2SO_4 containing 5 nM R6G molecules. Imaging condition: exposure time of 16.7ms. The scale bar denotes 4 μm.

[0026] FIG. 7 shows an atomic force microscopy (AFM) profile of a spot where stable nanobubbles exist in FIG. 6.

[0027] FIG. 8A shows an optical image of a CVD-grown MoS_2 device.

[0028] FIG. 8B shows the corresponding super-resolved single-molecule image obtained using the device of FIG. 8A at an acquisition time of 150 s at -0.3 V_{vsRHE}.

[0029] FIG. 8C shows the corresponding electrochemical signal of the molecule TIFR/electrochemical microcell measurement for CVD-MoS_2 device of FIG. 8A.

[0030] FIG. 8D shows the consecutive fluorescence frames taken from the device of FIG. 8A. Experiment condition: 0.5 M H_2SO_4 with 5 nM R6G. Imaging condition: an exposure time of 16.7ms. Due to the intrinsic photoluminescence signal, MoS_2 is more identifiable compared to the dark graphene background under laser excitation. As illustrated in FIG. 2B, the generated nanobubbles can be transiently labeled by fluorescent dyes (e.g., R6G), resulting in high contrast compared to the dark background. It is clear that transient nanobubble signals appear and disappear in consecutive frames recorded on CVD-MoS_2 under -0.2V_{vsRHE} in TIRF mode. Further,

the super-resolution image in FIG. 8B clearly resolved the triangular shape of the monolayer MoS_2 in FIG. 8A. Note that random diffused R6G molecules cannot be detected in the experiments due to the fast diffusion ($D=4.0\times10^{-6}cm^2s^{-1}$) of R6G in solution and the strong fluorescence quenching near the electrified surface. Besides, it should be noted that few molecules are present on graphene, which can be attributed to the defects of CVD-graphene.

[0031] FIG. 9A shows the principle of nanobubble labelling.

[0032] FIG. 9B is a plot of intensity decay of evanescent field along the direction perpendicular to the glass surface according to the equation, $I=I_0\exp(-z/d)$. d denotes the penetration depth of the evanescent field. In the present configuration, a green laser beam (λ = 532nm) focuses into the back focal aperture of a *Nikon Plan Apo λ*, 100x, 1.45NA objective. It generates an evanescent field with a penetration depth *d* of 55.086 nm, driving the photon emission of excited single R6G molecules.

[0033] FIG. 10A is a super-resolved single-molecule image of pure graphene under an applied voltage of $0.2V_{vsRHE}$ for 250s.

[0034] FIG. 10B shows the corresponding plot of current density versus time of FIG. 10A. The experiment was conducted in 0.5 M H_2SO_4 with 5 nM R6G and with an exposure time of 16.7 ms. Similar to the phenomena in FIG. 8A to 8D, a few molecules can be observed on graphene, which is attributed to the defects of CVD-graphene.

[0035] FIG. 11 is a plot of the nanobubble nucleation counts signal of the in-situ test in FIG. 2E.

[0036] FIG. 12 is a plot of the nanobubble size distribution on Pt/Ti/graphene device in FIG. 2B under different overpotential during CA tests. Reaction condition: 0.5 M H_2SO_4 containing 5 nM R6G molecules. Imaging condition: exposure time of 16.7 ms for 150 s. The average height of nanobubbles is estimated to be 32.6 nm under -50 mV_{vsRHE}, 35.3 nm under -100 mV_{vsRHE}, 38 nm under -150 mV_{vsRHE}, and 41.3 nm under -200 mV_{vsRHE}.

[0037] FIG. 13A shows an in-situ single-molecule TIRF/micro-cell measurement over a Pt/Ti/graphene device. Left: Optical image of the graphene supported circular Pt/Ti device. The structure of the device is shown schematically in the upper panel. Right: The corresponding super-resolution image at $-0.2V_{vsRHE}$ with an acquisition time of 150 s.

[0038] FIG. 13B shows in-situ single-molecule TIRF/micro-cell measurement over a Pt/graphene device. Top: The schematic structure of the Pt/graphene device. Middle: The optical image. Bottom: The corresponding super-resolution image at -0.2 V_{vsRHE} with an acquisition time of 150 s. Note that the super-resolution analysis of the Pt surface in (A-B) takes into account the transparency (0.5) of 5 nm Pt.

[0039] FIG. 13C shows plots of the nanobubble density profiles for the lines (i-iv) indicated in FIG. 13A.

[0040] FIG. 13D is a plot of the averaged nanobubble density profiles over the dashed rectangles of the same color in FIG. 13A and 13B.

[0041] FIG. 14A is a plot of the kinetic energy barriers of HER path, namely hydrogen desorption on Pt(111), and the spillover-induced D-HER path on different Pt/graphene structures with/without the Ti layer. The free energy change for hydrogen spillover is aligned to zero as it depends on hydrogen coverage. The snapshots display the reaction process on Pt/graphene and Pt/Ti/graphene. The grey, red, wheat, cyan and yellow balls represent C, H, O, Pt and Ti atoms, respectively. The grey dashed line at -0.76 eV marks the hydrogen desorption barrier on Pt through Tafel.

[0042] FIG. 14B is a plot of potential energy profiles of hydrogen spillover on the Pt/Ti/graphene surface with varied θ.

[0043] FIG. 14C is a side view of the Pt/Ti/graphene structure. The arrows indicate the pathway of hydrogen spillover from Pt(111) to graphene.

[0044] FIG. 15 is a plot of the minimum energy paths (MEPs) of the Tafel and Heyrovsky reactions.

[0045] FIG. 16 is a plot of the MEPs of hydrogen migration. Noted that water can assist the hydrogen migration on graphene, resulting in a reduction of barrier from 0.6 to 0.29 eV.

[0046] FIG. 17 is a plot of the MEPs of the Tafel and Heyrovsky reactions on the graphene surface.

[0047] FIG. 18 plots the relationship between temperature (T) and pressure (P) as a function of H_a coverage on the Pt/Ti/graphene surface. At a certain temperature, θ increases as P increases. For the conditions of the hydrogen spillover calculation in FIG. 14A to 14C ($1.27 \leq \theta \leq 1.40$), P is several orders of magnitude lower than the

atmosphere pressure (1 atm), suggesting that the upper limit of θ on the catalyst surface can be extremely high at room temperature.

[0048] FIG. 19A shows optical images Pt/Ti/Graphene micro-cell devices with various P_{Pt}.

[0049] FIG. 19B is a plot of linear sweep voltammetry (LSV) curves of Pt/Ti/graphene devices in FIG. 19A, based on the area of exposed Pt (j_{Pt}).

[0050] FIG. 19C shows scattered plots of j_{Pt} at -50 mV_{vsRHE} and -100 mV_{vsRHE} as a function of P_{Pt} extracted from statistics. Bottom: Scattered plots of Tafel slope versus P_{Pt}.

[0051] FIG. 19D is a plot of LSV curves of Pt/Ti/graphene devices in FIG. 19A, based on the area of exposed reaction window (j_{RW}).

[0052] FIG. 19E is a scattered plot of j_{RW} at -50 mV_{vsRHE} as a function of P_{Pt} extracted from statistics. The plots are fitted by the Lorentz function.

[0053] FIG. 19F is a scattered plot of j_{RW} at -100 mV_{vsRHE} as a function of P_{Pt} extracted from statistics. The plots are fitted by the Lorentz function.

Detailed Description

[0054] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the present disclosure may be practised.

[0055] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0056] The present disclosure describes for an electrocatalyst and devices comprising the electrocatalyst. The present electrocatalyst is advantageous as it affords a synergetic effect of a catalyst (e.g. platinum) and a support (e.g. carbon) to enhance hydrogen spillover, outperforming traditional platinum metal hydrogen evolution activity.

[0057] In the present disclosure, hydrogen spillover is shown to activate carbon support in Pt/C system and provides another dimension to tune the synergetic effects of metals and supports, which might guide electrocatalyst configuration beyond traditional scalability considerations.

[0058] The present electrocatalyst involves an efficient method for enhancing traditional Pt/C catalysts towards higher platinum utilization efficiency and energy conversion efficiency of hydrogen production over 90%.

[0059] For example, one improvement afforded by the present electrocatalyst relates to a 5.66-fold improvement in HER performance at -50 mV_{vsRHE} relative to a pure platinum surface, a 7.47-fold improvement in HER performance at -100 mV_{vsRHE} relative to pure platinum surfaces, and a 26% to 40% higher energy conversion efficiency relative to previously reported commercial 40 wt% Pt/C at a current density of 1000 mA cm^{-2}.

[0060] Another advantage of the present electrocatalyst relates to the remarkably reduced hydrogen spillover barrier from Pt to carbon via interface engineering, i.e. including an interface layer (e.g. a titanium interlayer).

[0061] Another advantage of the present electrocatalyst relates to the enhanced proton reduction rate on platinum. A significant amount of H_a atoms migrate from platinum to the carbon surface, and release the Pt atoms previously occupied by H_a, leading to a higher generation rate of chemisorbed H atoms.

[0062] Another advantage of the present electrocatalyst relates to the support of the electrocatalyst (e.g. activated carbon). The single-molecule imaging directly reveals that the support (e.g. a carbon support) can be activated towards the hydrogen atom combination step of HER by hydrogen spillover. More efficient hydrogen molecule desorption occurs on carbon due to the weaker hydrogen adsorption strength on carbon than that on Pt. Thus, the present electrocatalyst involves the contribution of carbon as active sites, more practically, the area ratio between platinum and carbon.

[0063] Tradtionally, to meet the surged in demand and economic requirements, one approach is to have highly dispersed platinum (Pt) nanoparticles anchored onto mesoporous carbon to be used as catalysts in water electrolyzers. In such approach, the governing empirical criterion for practical platinum carbon (Pt/C) catalyst is to maximize the electrochemical surface area of Pt by increasing the Pt loading and

minimizing the Pt size. Unfortunately, under such approach, in terms of platinum utilization efficiency, only a small portion of surface platinum atoms of the nanoparticles (i.e. platinum atoms at surface of nanoparticles), such as kinks or steps, truly participate in hydrogen evolution reaction. Thus, such traditional approach fails to render platinum-based catalysts with near 100% surface atom utilization efficiency.

[0064] Moreover, in aforesaid traditional approach, the carbon, which is used as a support for the platinum, does not confer any catalytic activity or improvement of the platinum utilization. In fact, the carbon support, e.g. such as the carbon atoms in the carbon support, constitutes a spectator species that is not involved in the electrocatalytic reaction but may merely serve as a skeleton (i.e. structural support) and electron transport.

[0065] However, in the present disclosure, it has been found that atomic hydrogen (H_a) can be electrochemically stored on carbon in Pt/C system, induced by hydrogen spillover at upon potential deposition region (H_{upd}, 0.2-0V versus a reversible hydrogen electrode) of Pt. Besides, it is noted that mild thermal energy input can release the stored hydrogen as H_2 gas from Pt/C. Notably, studies of the present disclosure have shown that the energy barrier of hydrogen spillover from Pt to carbon is as high as 0.8-2 eV which depends sensitively on intimate contact of the interface between Pt nanoparticle and carbon. Therefore**,** the present electrocatalyst is advantageous as it involves significant hydrogen spillover that occurs in the hydrogen evolution potential region, < 0V versus a reversible hydrogen electrode (denotes as $0V_{vsRHE}$), in Pt/C system by engineering the interface between Pt and carbon, and hydrogen can be released from the carbon support with the electrical energy input. In various examples of the present disclosure, carbon is no longer an electrochemically inert spectator but decouples HER by accepting H_a from Pt and undertaking the chemical combination of H_a, which remarkably accelerates the reaction efficiency and the utilization of Pt.

[0066] The present disclosure also relates to method of forming the electrocatalyst.

[0067] Details of various embodiments of the present electrocatalyst, devices comprising the present electrocatalyst, and method of forming the present electrocatalyst, and advantages associated with the various embodiments are described below. Where the embodiments and advantages are already described in the examples section further hereinbelow, they shall not be iterated for brevity.

[0068] The present disclosure relates to an electrocatalyst. The electrocatalyst may comprise a carbon support, a catalyst disposed on the carbon support (the catalyst may comprise platinum), and an interface layer disposed between and in contact with the carbon support and the catalyst, wherein the interface layer renders hydrogen atom chemisorbed on the catalyst to migrate to the carbon support and have the hydrogen atom released from the support as hydrogen gas. The term "chemisorbed" herein refers to involvement of formation of strong chemical bonds between the adsorbate and the adsorbent, resulting in a stable attachment of the adsorbate to the surface. Unlike physisorption, which is characterized by weak van der Waals forces or dipole-dipole interactions, chemisorption involves the sharing or transfer of electrons between the adsorbate and the adsorbent. This may lead to the formation of new chemical bonds or the modification of existing bonds. The term "interface layer", for brevity, can be exchangeably referred to "interface".

[0069] In various embodiments, the interface layer may be disposed on and in contact with a portion of the carbon support. In various embodiments, such a disposition of the interface layer exposes a surface of the carbon support (i) which may be adjacent to the portion and (ii) which the hydrogen atom adsorbed on the catalyst migrates to. Said differently, the interface layer does not cover the entire surface of the carbon support, but covers partially the surface of the carbon support so as to have some surface of the support exposed.

[0070] In various embodiments, the catalyst may be disposed on and in contact with the interface layer which is disposed on and in contact with the portion of the carbon support. In other words, the disposition of the catalyst corresponds in position with where the interface layer is disposed on the carbon support. If the catalyst is not disposed on and in contact with the interface layer, the hydrogen spillover may not be enhanced.

[0071] In various embodiments, wherein the catalyst and the carbon support are not in contact.

[0072] In various embodiments, the carbon support may comprise carbon. The carbon may be any carbon material with a high surface area so as to accommodate higher hydrogen spillover. In various embodiments, the carbon support may comprise carbon nanoparticles, activated carbon, or graphene. The carbon nanoparticles, activated

carbon, and graphene may have a sufficiently high surface area to accommodate the higher hydrogen spillover.

[0073] In various embodiments, the interface layer may comprise or may be a metal interface layer, i.e. a metal layer. In various embodiments, the interface layer may comprise titanium, cobalt, aluminum, and/or nickel. Any suitable metal that renders the same advantages as aforesaid metals may be configured as the interface layer.

[0074] In various embodiments, the interface layer may be crystalline.

[0075] In various embodiments, the surface area ratio of the catalyst to the carbon support which is exposed may be 60:40 to 20:80. The carbon support which is exposed in this instance refers to the surface of the carbon support which the hydrogen atom can migrate to from the catalyst.

[0076] The present disclosure also relates to a microcell device comprising the electrocatalyst described in various embodiments of the first aspect. Embodiments and advantages described for the electrocatalyst of the first aspect can be analogously valid for the present microcell device subsequently described herein, and vice versa. Where the various embodiments and advantages have already been described above and in the examples section further hereinbelow, they shall not be iterated for brevity.

[0077] The present disclosure further relates to a method of forming the electrocatalyst described in various embodiments of the first aspect. Embodiments and advantages described for the electrocatalyst of the first aspect can be analogously valid for the present method subsequently described herein, and vice versa. Where the various embodiments and advantages have already been described above and in the examples section further hereinbelow, they shall not be iterated for brevity.

[0078] In various embodiments, the method may comprise providing a substrate, forming the carbon support, transferring the carbon support onto the substrate, depositing the interface layer on the carbon support, and depositing the catalyst on the interface layer.

[0079] In various embodiments, the interface layer may be a metal interface layer. In various embodiments, the interface layer may comprise titanium, cobalt, aluminum, and/or nickel.

[0080] In various embodiments, forming the carbon support may comprise synthesizing the carbon support in a form of carbon nanoparticles, activated carbon, or

graphene. In other words, carbon nanoparticles, activated carbon, or graphene may be synthesized as the carbon support.

[0081] In various embodiments, transferring the carbon support onto the substrate may comprise transferring the carbon support onto the substrate via polymer assisted-transfer. Polymer assisted-transfer may involve the use of a polymer layer as an “intermediate support” or "handle" to facilitate the transfer process. The process may start by depositing a thin layer of polymer, e.g. polydimethylsiloxane (PDMS) or polymethyl methacrylate (PMMA), onto a “source substrate” that contains the desired material (in this instance the carbon support) to be transferred. The polymer layer adheres to both the “source substrate” and the material to be transferred. The polymer layer may then be carefully peeled or lifted off the “source substrate”, resulting in the detachment of the desired material along with the polymer layer. This combination of the material and the polymer layer may then be placed onto the “target substrate” (in this instance the substrate), and the polymer layer may be gently removed, leaving behind the transferred material on the “target substrate”.

[0082] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the present disclosure.

[0083] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0084] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[0085] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0086] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

Examples

[0087] The present disclosure relates to an electrocatalyst. The present electrocatalyst is capable of unlocking the full potential of surface platinum atoms in carbon-supported platinum systems (Pt/C) for hydrogen production, and more specifically, involves an engineered interface between Pt layer and carbon to significantly reduce a hydrogen spillover barrier, thereby activating catalytically inert carbon for hydrogen production. In one non-limiting example, the area ratio of platinum and carbon in the model Pt/C system has been configured based on hydrogen spillover to be superior to platinum metal, with an electrical-to-chemical energy conversion efficiency of 93.2% at a current density of 1000 mA cm^{-2}.

[0088] The present electrocatalyst, a device (e.g., an electrical cell) comprising the electrocatalyst, and method of forming the electrocatalyst, are described in further details, by way of non-limiting examples, as set forth below.

[0089] Example 1: Introductory discussion

[0090] Hydrogen spillover - in the context of the present disclosure - refers to the migration of activated hydrogen atoms (H_a) from one phase to another, which is crucial in various academic and industrial fields, including mass transport, catalysis, energy storage and conversion and so forth. Particularly, hydrogen spillover, in a broad sense, reveals the dynamic nature of heterogenous hydrogen evolution reaction (HER) catalysis. However, it is difficult to illustrate for hydrogen spillover in HER, as it is rather sketchy and lacks evidence. While it may have been reported that H_a may be stored on carbon by hydrogen spillover from Pt as in the case for a carbon-supported platinum nanoparticles (Pt/C) system specifically in gas phase catalysis, whether hydrogen spillover occurs or how it alters electrocatalytic properties of Pt/C in HER was not described in those reports and/or appears little known.

[0091] Notably, although various approaches may have been developed over the past decades to facilitate H_a storage in Pt/C systems, including the construction of bridge materials, carbon modulation, and doping structures, hydrogen spillover in such traditional approaches suffers from a high energy barrier, typically 0.8-2 eV, giving hydrogen uptake on carbon below demand or even negligible. Reducing the energy barrier is one strategy the present electrocatalyst is capable of so as to achieve significant hydrogen spillover.

[0092] Herein, the present disclosure systematically unveils the role of an interfacial layer (e.g. titanium (Ti) interfacial layer) in facilitating hydrogen spillover in Pt/C system through the combined high-resolution single-molecule imaging, first-principle calculations, and electrochemical verification and implementation, which provides an avenue to remarkably accelerate the reaction efficiency and maximize the utilization of Pt. So far, the governing criterion for practical Pt/C is to maximize the electrochemical surface area of Pt by increasing the Pt loading and minimizing the Pt size, however, this alone cannot render Pt/C catalysts to unlock their full potential of surface platinum atoms in Pt/C systems, e.g. for terawatt-scale energy production by water electrolyzers, because of the coverage of HER-active H_a atoms weakly adsorbed at the atop sites on Pt surface is much smaller than that of HER-inert H_a strongly adsorbed at the 3-fold hollow sites. More importantly, the practical catalysts suffer from severe deactivation due to the constantly generated large-sized bubbles on the Pt surface, especially at high current density. In contrast, the role of carbon in HER has been largely neglected; classically, the carbon support has been only considered as a spectator species, which is not involved in the HER but serves merely as the scaffold and electron transport. However, as shown in FIG. 1A (right image demonstrating for an electrocatalyst of the present disclosure), the Ti interfacial layer can remarkably break the energy barrier of hydrogen spillover and therefore significant H_a spillover occurs during HER in Pt/Ti/C system, carbon is no longer an electrochemically inert spectator but decouples HER by accepting H_a from Pt and undertaking the chemical combination of H_a; hydrogen can be released from the carbon support with the electrical energy input. Noteworthy, this process which an electrocatalyst of the present disclosure is capable of, can refresh Pt active sites previously occupied by strongly adsorbed Ha, and avoid the blockage of the Pt surface by large-sized bubbles. This advantageous mechanism is termed herein “decoupled HER (D-HER)”.

[0093] To validate the above, nanobubbles - the effective nanodetectors for gas-evolving reactions - are used to probe the hydrogen spillover directly. Due to high sensitivity and single-molecule-level resolution, total internal reflection fluorescence microscopy (TIRF) has been demonstrated to be a powerful tool to visualize heterogeneity in space and time at the catalytic interface. Single-molecule TIRF with a homemade on-chip electrocatalytic microcell system were combined, herein termed the

"single-molecule TIRF/micro-cell platform" (see FIG. 2A top and bottom images), for in-situ monitoring of the generated nanobubbles on a single entity in well-defined systems. Due to the high-speed camera recording (60 Hz), sufficient high R6G concentration, and the confined reaction window, the developed platform allowed us to experimentally demonstrate the occurrence of hydrogen spillover and re-examine the function of carbon support during HER with a spatial resolution of 26 nm (FIG. 1B) and temporal resolution of 16.7 ms.

[0094] **Example 2A: Fabrication of microcell devices**

[0095] The microcell devices of the present disclosure are able to address the low surface platinum atom utilization efficiency suffered by traditional Pt/C electrocatalysts in commercial water electrolysers, wherein the present microcell devices involve Pt/C catalysts (as one non-limiting example) and the hydrogen spillover phenomena. Through the examples of the present disclosure, the occurrence of hydrogen spillover has been demonstrated and the function of carbon support during HER over Pt/C with interlayer Ti was investigated, namely well-defined Pt/Ti/graphene micro-devices. To extract as far as possible the effects of a single factor from the complex heterogeneous catalysis, a homemade micro-cell system and a developed in-situ single molecular total internal reflection microscopy (TIRF) fluorescence/electrochemical platform are employed. Specifically, single-molecule TIRF has been combined with a homemade on-chip electrocatalytic microcell system to in-situ monitor electrochemically generated nanobubbles on a single entity, and micro-cell on-chip devices have been fabricated to systematically study the effective spatial extent of activated carbon and the benefit of hydrogen spillover to HER.

[0096] To illustrate the hydrogen spillover phenomena in Pt/Ti/graphene system, three types of microcell on-chip devices are fabricated (FIG. 3A and 3B). Type 1 microcell on the transparent glass substrate (150 μm thickness) is capable of in-situ monitoring the dynamics behavior of hydrogen nanobubbles during the gas-evolving reaction; Type 2 microcell is used to explore the possibility of using nanobubbles as activity indicators; Type 3 microcell is used to configure for a desirable hydrogen spillover induced hydrogen evolution on SiO_2/Si substrates, and the exposed platinum and graphene area accessible to the electrolyte can be well-controlled during fabrication. The desired area ratio of Pt/C can be determined by comparing the area-based HER activity of the devices with the varied

area ratio of exposed Pt and graphene. As shown in FIG. 3A, the fabrication process of type 1 and type 3 consists of five major steps. First, photolithography was adopted to pattern the 32 Au contact pads on 20 × 20 mm glass chips (160 μm) or 20 × 20 mm SiO_2 (275 nm)/Si or glass chips. Second, the chemical vapor deposition prepared monolayer graphene was transferred onto the chips via the standard PMMA assist method. Third, e-beam lithography (EBL) and reactive ion etching (RIE) using O_2 gas (20 W, 40 s) were employed to cut the whole graphene into several electrically separated pieces. Fourth, the Pt patterns were defined by EBL, followed by deposition of transparent Ti (2 nm)/Pt (5 nm) film with a rate of 0.1 Å/s. The 2 nm Ti layer was used as an adhesive layer to enhance the contact between Pt and graphene; otherwise, the interaction between Pt film and graphene is weak, for example, the Pt film was easily peeled off from the graphene film during the reaction. Fifth, the reaction window was exposed by EBL in 1-μm-thick poly (methyl methacrylate) (PMMA) film, allowing the single-entity measurements. For the fabrication of type 2 devices, all the steps are the same as that of type 1 and type 3 except step 4, where exfoliated/CVD-grown MoS_2 was transferred onto the substrates.

[0097] **Example 2B: Characterization - Setup of the in-situ single molecular TIRF fluorescence/electrochemical measurement**

[0098] The in-situ single-molecule TIRF/electrochemical experiments were conducted on an inverted fluorescence microscope (Nikon Eclipse Ti-U) (FIG. 2A bottom image). An adjustable 100 mW, 532 nm laser beam (L6CC Oxxius) with circular polarization was focused onto the material-solution interface via a dichroic mirror ((Di02-R635-25x36, Semrock) by a 100× infinity-corrected microscope objective lens (Nikon Plan Apo λ, NA 1.45). Further, to achieve an evanescent field of illumination, tens of nanometers into the solution, the illumination configuration was adjusted to wide-field total internal reflection (TIR). This was achieved by employing a transition stage to shift the laser beam towards the edge of the objective lens, enabling an incidence angle close to the critical angle of the glass-water interface. The emission was filtered by a band-pass filter (ET605/70m, Chroma) and then collected through the oil-immersion objective lens via a quad-edge laser dichroic mirror (Di03-R405/488/532/635-t1-25x36, Semrock). The fluorescence images were captured by an EMCCD camera (Andor iXon3) cooled to -70°C at 60 frames per second for a frame size of 256 × 256 pixels. Last but not least, the collected fluorescence signal by the objective was filtered

by a Chroma band-pass filter (ET605/70m) and focused onto an EMCCD camera (Andor iXon3) through an achromatic lens with f = 75mm.

[0099] **Example 2C: Characterization - Super-resolved image analysis method**

[00100] As described before, the imaging was recorded by the TIRF microscope at an exposure time of 16.7 ms per frame. The super-resolution analysis method - stochastic optical reconstruction microscopy (STORM) - is based on the photo-switchable nature of the used fluorescence probe, R6G. In general, hundreds or thousands of photons can be emitted from one molecule during one frame (16.7 ms). Therefore, although the raw image has limited lateral resolution (200-300nm) due to the point spread function, the sub-diffraction localization of the excited R6G molecules can be achieved by an Insight3 software through integrated Gaussian-fitting of the position of emitted photons. Then the super-resolution images can be reconstructed from the positions of all single R6G molecules in all recorded frames (around 8000). The R6G molecules labeled nanobubbles can be well-identified due to the high contrast compared to the dark background.

[00101] **Example 2D: Characterization – Computational methods**

[00102] The first-principle calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code, with the revised Perdew-Burke-Ernzerh (RPBE) parametrization of the generalized gradient approximation (GGA) as the exchange-correlation potential and projector-augmented wave (PAW) method for the core region, respectively. The kinetic energy cutoff was chosen to be 350 eV for the plane-wave expansion, and a vacuum region of 20 Å was set to avoid spurious interaction between adjacent slabs. The Pt/graphene and Pt/Ti/graphene structures were modeled in nanoribbon configurations. Three-layer fcc(111) slabs of metal with a width of ~9 Å were placed on graphene along the zigzag direction with the desired lattice mismatch of ~1.6%. The Brillouin zone integration was sampled by a 3 × 1 × 1 k-grid mesh for the large supercell of interfacial structures. Structures were fully relaxed until the force on each atom was less than 0.01 eV/Å. Implicit solvent through Poisson-Boltzmann continuum approximation was used to take solvent effect into account, which was implemented in the VASPsol code. The energy barriers of hydrogen spillover were computed with the climbing image nudged elastic band (NEB) method.

[00103] According to the random walk model for diffusion, the diffusion coefficient, D_{Ha}, of activated hydrogen atoms on graphene can be computed as

$$D_{H_a} = \frac{va^2}{z}, \quad (1)$$

[00104] where a is the traveling distance of Ha in a single hop, v denotes the microscopic jump frequency, and z is the number of neighboring sites to which the hydrogen atoms can hop. According to the transition state theory, the microscopic jump frequency v is related to the activation energy Eact for surface diffusion and can be determined by the following equation

$$v = \frac{kT}{h}\frac{Z^{TS}}{Z^{IS}}\exp\left(\frac{-E_{act}}{kT}\right), \quad (2)$$

[00105] where T is temperature, k is the Boltzmann constant, and h is the Planck constant. The Z^{TS} and Z^{IS} are partition functions of the transition state and the initial state, respectively. The ratio of Z^{TS} and Z^{IS} can be calculated as

$$\frac{Z^{TS}}{Z^{IS}} = \frac{\prod_{i=1}^{3N-1}\frac{\exp\left(\frac{-h\nu_i^*}{2kT}\right)}{1-\exp\left(\frac{-h\nu_i^*}{kT}\right)}}{\prod_{i=1}^{3N}\frac{\exp\left(\frac{-h\nu_i}{2kT}\right)}{1-\exp\left(\frac{-h\nu_i}{kT}\right)}}, \quad (3)$$

[00106] where ν_i^* and ν_i are the real normal modes of vibration on the transition state and the initial state, respectively, and N is the number of vibrating atoms. It should be noted that there is one real normal mode less at the transition state than at the initial state.

[00107] The thermodynamic phase diagram of H on the Pt/Ti/graphene surface is obtained by comparing the difference of the surface free energy ΔG between the pristine and the hydrogenated models as follows,

$$\Delta G = E_{hyd} - E_{pri} - n_H \cdot \mu_H + \Delta F_{vib}, \quad (4)$$

[00108] where E_{hyd} and E_{pri} are the energies of pristine and hydrogenated models, respectively. ΔF_{vib} is the vibrational contribution differences of H on the Pt/Ti/graphene surface. n_H is the number of H atoms, and μ_H is the chemical potential of H that is the functions of hydrogen partial pressure P and temperature T. ΔF_{vib} is calculated as

$$\Delta F_{\text{vib}} = h\nu\left(\frac{1}{2}+\frac{1}{\exp(\frac{h\nu}{kT})-1}\right) + kT\left\{\frac{\frac{h\nu}{kT}}{\exp(\frac{h\nu}{kT})-1} - \ln[1-\exp(-\frac{h\nu}{kT})]\right\}, \quad (5)$$

[00109] where ν is the real normal mode of H vibration. The chemical potential of H as the functions of T and P can be written as

$$2\mu_{\text{H}} = E_{\text{H}_2} - kT\ln(g\cdot Z_{\text{trans}}\cdot Z_{\text{rot}}\cdot Z_{\text{vib}}), \quad (6)$$

[00110] where E_{H_2} is the energy of H_2 at 0 K. $g = 2$ is the degree of degeneracy of the electron energy level. Z_{trans}, Z_{rot} and Z_{vib} are translational, rotational and vibration motions, which are computed by

$$Z_{\text{trans}} = \frac{kT}{P}\cdot\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}, \quad (7)$$

$$Z_{\text{rot}} = \frac{8\pi^2 IkT}{\sigma h^2}, \quad (8)$$

$$Z_{\text{vib}} = \frac{\exp(-\frac{h\nu}{2kT})}{1-\exp(\frac{-h\nu}{kT})}, \quad (9)$$

[00111] where m is the mass of an H_2 molecule, $\sigma = 2$ is the symmetry number for H_2, and I is the moment of inertia I.

[00112] **<u>Example 2E: Characterization – Calculation of the penetration depth of the evanescent field</u>**

[00113] As shown in FIG. 2A bottom image, a transition stage was employed to shift the laser beam to achieve the TIR illumination configuration. Given that the shift of the position of the transition stage is proportional to the shift of the laser beam, the mathematical relationship between the position of the transition stage and the incidence angle of the laser beam was calibrated (FIG. 5). According to Snell's law (see equation below), the shift of incidence is 4.172°.

[00114] $n_1\sin\theta_1 = n_2\sin\theta_2$

[00115] where n_1=1.52, n_2=1 are the incident index of water and air, respectively, and θ_1,θ_2=6.35°are the incident angle and refracted angle, respectively.

[00116] Thus, the incidence angle at 10.2 mm (used in the experiment) can be calculated to be 52.567°.

[00117] Further, the TIR of the laser (λ=532nm) generates an evanescent wave with exponentially decayed intensity, which can excite the R6G fluorophores labeled on nanobubbles. In other words, the effective propagation depth of the evanescent field decides the detection volume in the solution. The penetration depth of the evanescent field can be calculated as follows,

$$d = \frac{\lambda}{4\pi\sqrt{n_1^2 \sin^2(\theta_1) - n_2^2}}$$

[00118] where λ=532 nm, n_1=1.52, n_2=1.012, θ_2=52.567°, and the penetration depth (d) is calculated to be 55.086 nm.

[00119] **Example 2F: Characterization - Calculation of the spatial resolution of in-situ single molecule TIRF/electrochemical measurement**

[00120] FIG. 1B left image shows a raw fluorescence signal of a single R6G molecule on graphene. The fluorescence intensity is distributed over several pixels (pixel size 160 nm) as a point spread function (PSF). The center position of the molecule can be localized by fitting the PSF with 2D Gaussian functions (see equation (i) below, FIG. 1B right plot). Furthermore, the standard deviations of the Gaussian distribution along the x- and y-axes (S_x, S_y) can be used to determine the spatial resolution (σ_x, σ_y), as shown in equation (ii) below.

$$I(x,y) = A + B * \exp\left(-\left(\frac{(x-x_0)^2}{2S_x^2} + \frac{(y-y_0)^2}{2S_y^2}\right)\right), \text{(i)}$$

[00121] where A and B are the background intensity noise and the peak intensity at the center position (x_0,y_0), respectively.

$$\sigma_j = \sqrt{\left(\frac{S_j^2}{N} + \frac{a^2/12}{N} + \frac{8\pi S_j^4 b^2}{a^2 N^2}\right)}, \text{(ii)}$$

[00122] where N denotes the number of photons, a=160nm is the pixel size, and b is the photon/background noise. The index j=x,y refers to the x or y direction.

[00123] Given the pixel size, the spatial resolution depends largely on the number of collected photons (N). In our experiment, the spatial resolution is calculated to be σ_x=27.1nm, σ_y=28.6nm (FIG. 1B right plot). Thus, a nanobubble labeled by a single molecule can be localized with an averaged spatial resolution of $\sigma_{xy}=(\sigma_x+\sigma_y)/2$ =26 nm.

[00124] **Example 2G: Characterization - Lifetime calculation of nanobubbles**

[00125] FIG. 2C presents the intensity trace of a randomly selected spot marked in FIG. 2A top image. It is evident that fluorescent intensity sharply increases and suddenly drops to baseline. In contrast, as shown in FIG. 6, for monolayer MoS_2 devices anchored with MoS_2 nanoparticles (30 nm to 40 nm) (FIG. 7), the fluorescent signal around the nanoparticle fluctuates but is never off. It proves that surface nanoparticles can provide pinning force to stabilize nanobubbles. Additionally, this result indicates that the nanobubbles on an atomically flat surface (FIG. 2B and FIG. 9A to 9D) are indeed transient.

[00126] Next, the lifetime of transient nanobubbles was examined. The insets of FIG. 2C represents histograms of the duration of nanobubble "fluorescence-on" events extracted from nanobubble tracking over devices (40 μm × 40 μm) shown in FIG. 2B. A single exponential decay function (see equation below, dotted line) is used to fit the histograms.

$$y=Aexp(-x/\tau)$$

[00127] where x is the time, y is the number of nanobubbles with "fluorescence-on" at time=x, A is the maximum number of nanobubbles at time=0, and τ is the derived time constant from the fitting.

[00128] The fitted lifetime of nanobubble is $7.50 \pm 5.63 \times 10^{-17}$ ms, which matches well with theoretical calculations, within a factor of 1 order. Therefore, transient nanobubbles frequently nucleate and burst on an atomically flat surface.

[00129] **Example 2H: Characterization - Calculation of the diffusion coefficient of Ha spillover**

[00130] FIG. 2F leftmost image shows the structure of graphene supported 1D Pt/Ti nanowire device, where the width and exposed length of the Pt/Ti nanowire are 600 nm and 50 μm, respectively, and the dimensions of exposed graphene support are 55 μm × 50 μm. Note that the nucleation time of H_2 nanobubble and potentially related changes in H_a concentration were neglected to simplify the calculation. Therefore, the surface diffusion behavior of H_a on the surface of this device can be described by one-dimensional Fick's second law:

$$\frac{\partial C}{\partial t} = D_{H_a} \frac{\partial^2 C}{\partial^2 x}$$

[00131] where D_{Ha} is the surface diffusion coefficient of H_a, and C and t denote the time and the distance from the nanowire along the direction marked by a red arrow in FIG. 2F leftmost image.

[00132] The experiment was carried out under a fixed potential of -0.05 V_{vsRHE}, thus, it is assumed that the H_a concentration at $x = 0$ remained at a constant value of C_0.

[00133] The solution to the equation above is

$$C(x,t) = C_0 erfc(\frac{x}{2\sqrt{D_{Ha}t}})$$

$$erfc\left(\frac{x}{2\sqrt{D_{Ha}t}}\right) = \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{D_{Ha}t}}} e^{-t^2}\,dt$$

[00134] The value of the diffusion length, x, at t can be obtained approximately by

$$x = 2\sqrt{D_{H_a}t}$$

[00135] During the measurement in FIG. 2F center images, the generated H_a atoms on the Pt surface spillover across the Pt-Ti-graphene boundary and subsequently migrate on the graphene surface, followed by desorption and formation of H_2 nanobubbles. Thus, the location and time of the far right nanobubbles was used, namely (0.050 s, 6.2 μm), (0.233 s, 19.6 μm), (0.467 s, 25.5 μm), (0.717 s, 27.4 μm), and (1.050 s, 36.4 μm), as boundary conditions. Thus, the average D_{Ha} is calculated to be 3.06 × 10-6 $cm^2\ s^{-1}$.

[00136] **<u>Example 3A: Results and discussion – Experimental setup and properties of surface nanobubbles</u>**

[00137] In various experiments, catalysts were patterned/transferred onto a transparent monolayer graphene electrode connected to an external potentiostat via Ti/Au electrodes and Au wires (FIG. 3A). Then the reaction window was defined by standard e-beam lithography (EBL) in a poly(methylmethacrylate) (PMMA) passivated film, ensuring that HER occurs in the selected area (FIG. 2D, FIG. 3A) (see FIG. 3B and example 2A). The super-resolution imaging of surface nanobubbles is based on the adsorption of a fluorescence dye under TIRF illumination: upon application of the voltage, the emerging gas-liquid interface can momently trap a Rhodamine 6G (R6G) molecule, resulting in stark contrast within the evanescent field (~55 nm) (FIG. 9A and 9B). Nanobubbles as individual transient fluorescence blinking events on the atomically flat surface can be well recognized in FIG. 2B, where strong contrast spherical objects

are surface nanobubbles. Further, FIG. 2C presents the intensity trace of a randomly selected spot in FIG. 2A under -0.2 V versus a reversible hydrogen electrode (denoted as -0.2 V_{vsRHE}). It is evident that fluorescent intensity suddenly increases and drops sharply to the baseline. In contrast, as shown in FIG. 6, for the monolayer MoS_2 devices anchored with nanoparticles (30 nm to 40 nm) (FIG. 7), the fluorescence signal around the nanoparticle fluctuates but is never off. It proves that surface nanoparticles can provide pinning force to stabilize nanobubbles. Next, the lifetime of transient nanobubbles was examined. As shown in the inset of FIG. 2C, the estimated lifetime of nanobubbles is ~7.5 ms, which matches well with theoretical calculations. Therefore, transient nanobubbles frequently nucleate and burst on the atomically flat Pt/Ti/graphene surface. Additionally, in sharp contrast to the case of the MoS_2/graphene device (FIG. 8A to 8D) and the pure graphene case (FIG. 10A and 10B), a significant amount of nanobubbles present on the graphene surface, in addition to the catalyst (Pt) surface. These results provide unambiguous evidence for the hypothesized D-HER phenomenon in Pt/Ti/graphene system (FIG. 1A).

[00138] **Example 3B: Results and discussion – In-situ test of D-HER**

[00139] To investigate the D-HER, a well-defined hydrogen spillover device (FIG. 2D) was fabricated. FIG. 2E corresponds to the synchronized data over the marked region in FIg. 2D. The insets of FIG. 2E display eight representative fluorescence images, where generated nanobubbles are labeled by R6G with high contrast compared to the dark background, graphene. Strikingly, nanobubbles can be well identified on the observed graphene area with a distance to Pt of at least 5 μm starting at ~0.8 V_{vsRHE}. It is found that the generation of hydrogen nanobubbles is controlled by the applied voltage: the signal of fluorescence intensity (FL) as well as of nanobubble nucleation events (FIG. 12) increase at about 0.8 V_{vsRHE}, reach a plateau at about 0.4 V_{vsRHE}, and decrease at about 0 V_{vsRHE}. The detected response of FL and nucleation events to the applied potential can be attributed to the increase in bubble size; larger nanobubbles have lower, even undetectable FL due to the higher adsorption sites of R6G molecule in the evanescent field (FIG. 9 and 11). In terms of D-HER, this result provides clear evidence of hydrogen spillover from Pt to graphene and H_2 gas formation on graphene. Notably, this device with an exposed area percent of Pt of 0.03% exhibits a current density as high as 5×10^4 mA cm^{-2} at an overpotential of -0.2 V_{vsRHE}, which is nearly 2

orders of magnitude higher than pure platinum. Next, to evaluate the kinetics of H_a spillover, a 1D diffusion device was fabricated to visualize the nanobubble distribution over time (FIG. 2F leftmost image), which was used to estimate the diffusion coefficient of H_a spillover, D_{Ha}, via the classical one-dimensional Fick's second law. FIG. 2F center and rightmost images show that H_a atoms diffuse rapidly after applying voltage, eventually reaching the right edge within 1.17 s (70 frames). Furthermore, the far right nanobubbles marked in red were used to approximately derive the average D_{Ha}, according to Fick's second law, yielding an approximate value of D_{Ha}= 3.06×10^{-6} cm^2 s^{-1}, consistent with previous electrochemical measurement.

[00140] **Example 3C: Results and discussion – Mechanistic understanding of D-HER**

[00141] To visualize the effect of the Ti interfacial layer on Ha spillover, circular Pt/Ti/graphene and Pt/graphene model systems were fabricated and further utilized to explore the effective traveling distance of H_a during HER (FIG. 13A and 13B). As expected, with the Ti interfacial layer, the activated graphene region expands to the whole field of view, as evidenced by the significant amount of nanobubbles nucleated on graphene (FIG. 13A and 13C); in sharp contrast, without the Ti interfacial layer, the density of nanobubbles exhibits a distinct difference: the vast majority of nanobubbles nucleate on Pt surface, while those on graphene surface are negligible (FIG. 13B). FIG. 13D shows the averaged nanobubble density on the graphene or Pt surface for the two devices in FIG. 13A to 13B, respectively. The averaged nanobubble density on graphene of Pt/Ti/graphene device is at least 1 order of magnitude higher than that on Pt for the same device, 2 orders of magnitude higher than that on graphene surface of Pt/graphene, and 4 times higher than that on Pt of Pt/graphene device. These results validate the hypothesis that the Ti interfacial layer can significantly facilitate H_a spillover.

[00142] To gain further insight into the D-HER mechanism, the hydrogen spillover process is carefully studied by the first-principles calculations (FIG. 14A to 14C). On the Pt surface, the protons combine with electrons to form chemisorbed H_a during the reaction (Volmer step). The produced H_a can either be desorbed directly from Pt or spill onto the supported graphene, which is determined by their kinetic barriers and thermodynamic tendencies. The hydrogen desorption from the active Pt(111) surface

via the Tafel and Heyrovsky steps (FIG. 15) was first simulated, whose energy barriers were calculated to be 0.76 and 1.26 eV, respectively. The hydrogen spillover process over two Pt/graphene structures with/without the interfacial Ti layer (insets, FIG. 14A) were examined, corresponding to the experimental devices. For the Pt/graphene structure, the hydrogen spillover barrier from Pt to graphene is 0.85 eV higher than the hydrogen desorption barrier from Pt, confirming the impeded spillover process and matching well with the observed high density of nanobubbles on Pt. In contrast, the interfacial Ti layer can transform the weak physical interaction of Pt/graphene into strong chemical interaction of Pt/Ti/graphene. As a result, the hydrogen spillover barrier is remarkably reduced from 1.61 eV to 0.54 eV (FIG. 4), facilitating the HER transition from the conventional pathway to the decoupled one. The subsequent migration and desorption processes on graphene were then studied. The barrier of hydrogen migration on graphene was calculated to be 0.29 eV with water-mediated cooperative migration (FIG. 16), yielding a D_{Ha} of 3.98×10^{-6} cm^2 s^{-1} at 298 K, in good agreement with experimental results. Besides, the hydrogen desorption on graphene prefers the Heyrovsky route with a low barrier of 0.47 eV (FIG. 17), suggesting that the D-HER path is kinetically more viable than the HER path.

[00143] Given the dependence of H_a coverage and H_a chemical potential on the liquid pressure (FIG. 18) and electrode potential, the free energy change of hydrogen spillover on the Pt/Ti/graphene surface at three moderate values of Ha coverage (FIG. 14B and 14C) was evaluated. The H_a coverage is defined as $\theta = N_H/N_M$, where N_H and N_M denote the number of H_a and metal atoms, respectively. At θ = 1.27, the hydrogen spillover from Pt(111) to graphene is overall endothermic by 1.08 eV. As θ gradually increases from 1.27 to 1.40, the spillover process becomes thermodynamically favorable as final states (e site) have lower energy than initial states (a site). Additionally, when the first hydrogen has been transferred to graphene, the second H_a spillover process becomes easier with the energy reduced from -0.08 to -0.23 eV (red line, FIG. 14B), further driving the spontaneous hydrogen spillover process. Collectively, these results provide solid evidence for the benefits of hydrogen spillover to improve the HER activity in two aspects: i) Hydrogen spillover from Pt to graphene can free the previously occupied active sites on Pt, leading to higher production of chemisorbed H_a, ii) Hydrogen

spillover can activate HER-inert graphene and provide both kinetically and thermodynamically favorable reaction routes for hydrogen desorption

[00144] **Example 3D: Results and discussion – Experimental verification**

[00145] To develop for a desirable utilization efficiency of Pt and quantify the function of spillover, single-entity measurements with micro-cell devices were carried out, in which only a specific region of interest was accessible to the electrolyte, to systematically study the role of graphene support in D-HER (FIG. 19A). Considering the complex morphology of real-world catalysts, the Pt area percentage was chosen ($P_{Pt} = Area_{Pt}/Area_{ReactionWindow}$) as the descriptor to compare the spatial extent of D-HER among catalysts. As shown in FIG. 19A, the reaction window with varied P_{Pt} from 100% to 5% was precisely defined on the devices. FIG. 19B to 19C show the electrochemical results collected from various P_{Pt}, which indicate a nearly linear increase of j_{Pt} (current density based on the area of Pt) at 50 mV_{vsRHE} and 100 mV_{vsRHE} with decreasing the P_{Pt} (FIG. 19C) from 100% to 5%. This stems from the fact, as proved before, that the available graphene can provide an effective area for H_a spillover and combination. Notably, the device with P_{Pt}=5% exhibit a 5.66-fold improvement in j_{Pt} at -50 mV_{vsRHE} relative to a pure platinum surface and a 7.47-fold improvement in j_{Pt} at -100 mV_{vsRHE} relative to pure platinum surfaces, an energy conversion efficiency of 93% at a current density of 1000 mA cm^{-2} which is 26% to 40% higher relative to previously reported commercial 40 wt% Pt/C. Additionally, the slope of j_{Pt} versus P_{Pt} at 100 mV_{vsRHE} is larger than that at 50 mV_{vsRHE}, suggesting that the benefit of hydrogen spillover is more effective under high overpotential. Besides, it can be appreciated to note that the Tafel slope almost levels off as P_{Pt} varies, suggesting the rate-determining step is unchanged.

[00146] However, given a certain electrochemical surface area, reducing P_{Pt} might affect the power density. FIG. 19D to 19F present the corresponding catalytic performance of the devices based on the whole exposed reaction window (j_{RW}), showing a volcanic relationship with an initial increase as decreasing the P_{Pt} from 100% to 70-60%, and then decrease as P_{Pt} decreases further. Therefore, in addition to reducing the Pt loading, the Pt/C catalyst design strategies should emphasize the contribution of carbon as active sites, more practically, the area ratio between platinum and carbon, and

further balance the utilization of Pt atoms and the desired power density, that is P_{Pt}>40%.

[00147] **Example 4: Summary and Applications**

[00148] Hydrogen spillover is well-established in heterogeneous catalysis, yet rarely quantified, or even evidenced in hydrogen evolution reaction (HER). The present disclosure demonstrates that an interfacial titanium layer can effectively drive hydrogen spillover to activate the intrinsic HER-inert carbon of Pt/C and further maximize the platinum utilization efficiency, through the visualization of generated nanobubbles by the developed in-situ single-molecule imaging/micro-cell platform. First-principles calculations confirmed that the interfacial titanium layer can kinetically and thermodynamically facilitate hydrogen spillover from Pt to C, effectively decoupling the two steps of HER occurring at different catalytic sites. Furthermore, the benefits of hydrogen spillover was experimentally demonstrated, revealing that Pt/C catalyst strategies should emphasize the contribution of carbon as active sites and further balance the utilization of Pt atoms and power density.

[00149] The present disclosure illustrated the benefit of hydrogen spillover in HER using interface engineering of Pt/graphene. Various examples of the present disclosure provide direct and solid evidence that HER benefits from hydrogen spillover in 2 aspects. (1) A significant amount of H_a atoms migrate from Pt to the graphene surface, and release the Pt atoms previously occupied by H_a, leading to a higher generation rate of chemisorbed H atoms; (2) Efficient hydrogen molecule desorption on graphene due to the weaker hydrogen adsorption strength on graphene than that on Pt. The present disclosure provides additional guidance for the rational configuration of electrode structures for improved performance. The present disclosure, which provides another dimension to tune the synergetic effect of metal and support, can guide the electrocatalyst configuration beyond scalability.

[00150] In summary, the present disclosure sheds new light on the fundamental understanding of the dynamics of surface nanobubbles, hydrogen spillover phenomena, and the function of carbon support in HER catalysis. The D-HER provides another dimension to tune the synergetic effect of metal and support, guiding the scalability of the electrocatalyst of the present disclosure.

[00151] While the present disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the present disclosure as defined by the appended claims. The scope of the present disclosure is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. An electrocatalyst comprising:

a carbon support;

a catalyst disposed on the carbon support, wherein the catalyst comprises platinum; and

an interface layer disposed between and in contact with the carbon support and the catalyst,

wherein the interface layer renders hydrogen atom chemisorbed on the catalyst to migrate to the carbon support and have the hydrogen atom released from the carbon support as hydrogen gas.

2. The electrocatalyst of claim 1, wherein the interface layer is disposed on and in contact with a portion of the carbon support, exposing a surface of the carbon support (i) which is adjacent to the portion and (ii) which the hydrogen atom adsorbed on the catalyst migrates to.

3. The electrocatalyst of claim 2, wherein the catalyst is disposed on and in contact with the interface layer which is disposed on and in contact with the portion of the carbon support.

4. The electrocatalyst of any one of claims 1 to 3, wherein the catalyst and the carbon support are not in contact.

5. The electrocatalyst of any one of claims 1 to 4, wherein the carbon support comprises carbon nanoparticles, activated carbon, or graphene.

6. The electrocatalyst of any one of claims 1 to 5, wherein the interface layer is a metal interface layer.

7. The electrocatalyst of any one of claims 1 to 6, wherein the interface layer comprises titanium, cobalt, aluminum, and nickel.

8. The electrocatalyst of any one of claims 1 to 7, wherein the interface layer is crystalline.

9. The electrocatalyst of any one of claims 1 to 8, wherein the surface area ratio of the catalyst to the carbon support which is exposed is 60:40 to 20:80.

10. A microcell device comprising the electrocatalyst of any one of claims 1 to 9.

11. A method of forming the electrocatalyst of any one of claims 1 to 9, the method comprising:

providing a substrate;

forming the carbon support;

transferring the carbon support onto the substrate;

depositing the interface layer on the carbon support; and

depositing the catalyst on the interface layer.

12. The method of claim 11, wherein the interface layer is a metal interface layer.

13. The method of claim 11 or 12, wherein the interface layer comprises titanium, cobalt, aluminum, or nickel.

14. The method of any one of claims 11 to 13, wherein forming the carbon support comprises synthesizing the carbon support in a form of carbon nanoparticles, activated carbon, or graphene.

15. The method of any one of claims 11 to 14, wherein transferring the carbon support onto the substrate comprises transferring the carbon support onto the substrate via polymer assisted-transfer.