**ABSTRACT**

The electrocatalyst for hydrogen evolution reaction includes nanosheets of molybdenum disulfide (MoS$_2$) deposited on a carbon fiber substrate. The catalyst is formed in stepwise fashion by chemical vapor deposition of nanosheets of MoO$_3$ onto the substrate, then reducing the MoO$_3$ to nanosheets of MoO$_2$ using sublimed sulfur, then by reaction of sulfur vapor with the MoO$_2$ to form nanosheets of MoS$_2$ on the carbon fiber substrate. The catalyst is multifaceted, having a large density of edges providing catalytically active sites for the hydrogen evolution reaction. The activity of the catalyst is enhanced by coating the catalyst with spherical fullerenes ($nC_{60}$).
Step 1

850 °C

CFP

15 cm

MoO₃

Ar

Step 2

400 °C

MoO₃ on CFP

S

2MoO₃ (s) + S (g) → 2MoO₂ (s) + SO₂ (g)

Step 3

850 °C

MoO₂ on CFP

S

2MoO₂ (s) + S (g) → MoO₂ (s) + SO₂ (g)

FIG. 1
**FIG. 2A**

**FIG. 2B**

**FIG. 2C**

**FIG. 2D**

**FIG. 2E**
**FIG. 4A**

**FIG. 4B**
FIG. 5

FIG. 6
**FIG. 7A**

- Current Density (mA/cm²) vs. Potential (V vs RHE)
- Lines for different concentrations of C₆₀:
  - C₆₀ (0.1 mg/mL)
  - C₆₀ (0.5 mg/mL)
  - C₆₀ (2.0 mg/mL)

**FIG. 7B**

- Current Density (mA/cm²) vs. Potential (V vs RHE)
- Lines for different compositions:
  - MoS₂
  - C₆₀ (0.1 mg/mL)/MoS₂
  - C₆₀ (0.5 mg/mL)/MoS₂
  - C₆₀ (2.0 mg/mL)/MoS₂
0.1 20 mV/s 100 mV/s 60 mV/s 80 mV/s 40 mV/s
Current Density (mA/cm²)

0.1
100 mV/s 40 mV/s 80 mV/s 60 mV/s 20 mV/s
-0.1
0.10 0.15 0.20 0.25 0.30
Potential (V vs RHE)

FIG. 8A

0.1 20 mV/s 100 mV/s 60 mV/s 80 mV/s 40 mV/s
Current Density (mA/cm²)

0.1
100 mV/s 40 mV/s 80 mV/s 60 mV/s 20 mV/s
-0.1
0.10 0.15 0.20 0.25 0.30
Potential (V vs RHE)

FIG. 8B
**FIG. 8C**

Current Density (mA/cm²) vs Potential (V vs RHE)

**FIG. 8D**

ΔJ_{0.20 V} (μA/cm²) vs Scan Rate (mV/s)

- C_{90} (0.1 mg/mL)
- C_{90} (0.5 mg/mL)
- C_{90} (2.0 mg/mL)

Capacitances:
- C_{dl} = 430 μF/cm²
- C_{dl} = 251 μF/cm²
- C_{dl} = 230 μF/cm²
FIG. 9C

FIG. 9D
**FIG. 9E**

- $C_{dl} = 2295 \ \mu \text{F/cm}^2$
- $C_{dl} = 1387 \ \mu \text{F/cm}^2$
- $C_{dl} = 917 \ \mu \text{F/cm}^2$
- $C_{dl} = 707 \ \mu \text{F/cm}^2$

Scan Rate (mV/s) vs. $\Delta J_{0.23} \ \mu \text{A/cm}^2$
Fig. 10A

- \textbf{MoS}_2
- C\textsubscript{60} (0.1 mg/mL)/MoS\textsubscript{2}
- C\textsubscript{60} (0.5 mg/mL)/MoS\textsubscript{2}
- C\textsubscript{60} (2.0 mg/mL)/MoS\textsubscript{2}

\textbf{FIG. 10B}

- C\textsubscript{60} (2.0 mg/mL)
- C\textsubscript{60} (0.5 mg/mL)
- C\textsubscript{60} (0.1 mg/mL)
- MoS\textsubscript{2}
ELECTROCATALYST FOR HYDROGEN EVOLUTION REACTION

TECHNICAL FIELD

[0001] The disclosure of the present patent application relates to an electrocatalyst for hydrogen evolution reaction, and particularly to an electrocatalyst for hydrogen evolution reaction that includes nanosheets of molybdenum disulfide (MoS$_2$) deposited on a carbon fiber substrate.

BACKGROUND ART

[0002] Sunlight shining on earth is intermittent. As such, a fundamental impediment to meaningful utilization of sunlight is the effective storage of solar energy. Water splitting, or the disproportionation of H$_2$O into H$_2$ and O$_2$, represents a promising strategy but is non-trivial because it requires the concerted transfer of four electrons and four protons. In nature, the complex biological machinery for photosynthesis couples multiple pathways wherein the light harvesting, water oxidation, and proton reduction steps are each performed by discrete components. Consequently, there is much interest in hybrid structures wherein discrete components perform each of the individual reactions required for photocatalysis. A viable photocatalytic cycle can be constituted by coupling photocatalytic water oxidation with electrocatalytic hydrogen evolution. The latter hydrogen evolution reaction (HER), however, is beset by a distinctive set of challenges.

[0003] The Pt group metals are excellent catalysts for HER and evolve hydrogen at near-zero overpotentials in acidic media but are cost prohibitive and amongst the least abundant elements available to mankind. There has been a strong push to develop alternatives and some success was achieved with MoS$_2$ as well as transition metal phosphides. In those strategies, however, the electrocatalytic activity of MoS$_2$ was mainly derived from catalytically active edge sites. The basal planes were thought to be catalytically inert with some exceptions. Furthermore, the low charge carrier mobility of MoS$_2$ was an impediment to its use as an electrocatalyst. Also, those materials generally tend to evolve H$_2$ at high overpotentials in comparison to Pt.

[0004] Chemical vapor deposition is ubiquitously used to prepare well-crystallized MoS$_2$ architectures, typically using molybdenum oxide or chloride precursors. A major drawback of this method as applied to the growth of MoS$_2$ is that it necessitates the operation of several concurrent reactions. Consequently, previously obtained MoS$_2$ electrocatalyst samples are often plagued by poor size and shape homogeneity, with sparse substrate coverage.

[0005] Thus, an electrocatalyst for hydrogen evolution reaction solving the aforementioned problems is desired.

DISCLOSURE OF INVENTION

[0006] The electrocatalyst for hydrogen evolution reaction includes homogeneously sized nanosheets of molybdenum disulfide (MoS$_2$) integrated on a carbon fiber paper substrate, with exposed catalytically active edge sites. The nanosheets are well distributed and vertically oriented. The electrocatalyst is prepared by the stepwise reduction and sulfidation of MoO$_3$. The direct integration of edge-exposed MoS$_2$ nanosheets onto CFP yields a 3D architecture with a high surface-to-volume ratio desirable for electrocatalytic applications. The inherent HER activity of the edge-sites of MoS$_2$ can be enhanced significantly by interfacing with nC$_{60}$ nanoclusters, as a result of the enhancement of the conductivity of MoS$_2$ owing to charge transfer.

[0007] These and other features of the present disclosure will become readily apparent upon further review of the following specification and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 is a schematic diagram illustrating the steps for preparing the electrocatalyst for hydrogen evolution reaction.

[0009] FIG. 2A is a FESEM image showing homogeneous distribution of MoS$_2$ nanosheets grown on textured CFP substrate.

[0010] FIG. 2B is a high-magnification SEM image of an individual MoS$_2$ nanosheet.

[0011] FIG. 2C is a low-magnification TEM image of a nanosheet depicting locations of “clean” well-faceted and “collapsed” edges.

[0012] FIG. 2D is an HRTEM image of a “clean” edge.

[0013] FIG. 2E is an HRTEM image of a discontinuous “collapsed” edge.

[0014] FIG. 3A is a FESEM image of MoO$_3$ harvested from a flat Si(100) substrate.

[0015] FIG. 3B is a FESEM image of MoO$_2$ harvested from a flat Si(100) substrate.

[0016] FIG. 3C is a FESEM image of MoS$_2$ harvested from a flat Si(100) substrate.

[0017] FIG. 3D is a FESEM image of MoS$_2$ nanosheets harvested from a flat Si(100) substrate.

[0018] FIG. 3E is a FESEM image of MoS$_2$ nanosheets harvested from a flat Si(100) substrate.

[0019] FIG. 3F is a FESEM image of MoS$_2$ nanosheets harvested from a flat Si(100) substrate, showing additional edge sites created on the basal plane of the nanosheets.

[0020] FIG. 4A shows XRD patterns of MoO$_3$ nanosheets, MoO$_2$ nanodisks, and MoS$_2$ nanosheets prepared on CFP.

[0021] FIG. 4B shows Raman spectra (514.5 nm laser excitation) of MoO$_3$ nanosheets, MoO$_2$ nanodisks, and MoS$_2$ nanosheets prepared on CFP.

[0022] FIG. 4C shows XPS spectra indicating Mo 3d binding energies.

[0023] FIG. 4D shows XPS spectra indicating O 1s binding energies.

[0024] FIG. 4E shows XPS spectra indicating S 2p binding energies.

[0025] FIG. 5 shows Raman spectra of the nC$_{60}$ cluster and hybrid nC$_{60}$/MoS$_2$ architectures.

[0026] FIG. 6 shows the mass spectrum of negatively charged ions emitted from the surface of the clusters deposited on CFP.

[0027] FIG. 7A shows polarization curves of various concentrations of nC$_{60}$ clusters deposited directly onto CFP.

[0028] FIG. 7B shows polarization curves of various concentrations of nC$_{60}$ clusters interfaced with 3D MoS$_2$ nanosheets on CFP.

[0029] FIG. 8A shows a cyclic voltammogram acquired in the range between 0.10-0.30 V vs. RHE for neat nC$_{60}$ clusters deposited on CFP from solutions of C$_{60}$ concentration of 0.1 mg/mL.

[0030] FIG. 8B shows a cyclic voltammogram acquired in the range between 0.10-0.30 V vs. RHE for neat nC$_{60}$ clusters deposited on CFP from solutions of C$_{60}$ concentration of 0.5 mg/mL.
FIG. 8C shows a cyclic voltammogram acquired in the range between 0.10-0.30 V vs. RHE for neat nC₆₀ clusters deposited on CFP from solutions of C₆₀ concentration of 2.0 mg/mL.

FIG. 8D is a graph showing differences in current density ΔIₐ/Iₐ₋ for ΔT=0.20 V versus RHE, plotted as a function of scan rate with each plot fitted to a straight line to determine the C₆₀ values.

FIG. 9A shows a voltammogram acquired in the range of 0.15-0.30 V versus RHE for as-prepared 3D MoS₂.

FIG. 9B shows a voltammogram acquired in the range of 0.15-0.50 V versus RHE for hybrid nC₆₀ (0.1 mg/mL)/MoS₂.

FIG. 9C shows a voltammogram acquired in the range of 0.15-0.50 V versus RHE for hybrid nC₆₀ (0.5 mg/mL)/MoS₂.

FIG. 9D shows a voltammogram acquired in the range of 0.15-0.50 V versus RHE for hybrid nC₆₀ (2.0 mg/mL)/MoS₂.

FIG. 9E is a graph showing differences in current density ΔIₐ/Iₐ₋ for 0.23 V versus RHE are plotted as a function of the scan rate (the C₆₀ values are extrapolated from a linear fit to the plot).

FIG. 10A shows the Nyquist plots of as-prepared 3D MoS₂ nanosheets and hybrid nC₆₀/MoS₂ architectures prepared on CFP measured at ~150 mV vs. RHE.

FIG. 10B shows Rₓ values plotted as a function of potential for nC₆₀, as-prepared 3D MoS₂ nanosheets, and hybrid nC₆₀/MoS₂ architectures prepared on CFP.

Similar reference characters denote corresponding features consistently throughout the attached drawings.

BEST MODE(S) FOR CARRYING OUT THE INVENTION

The electrocatalyst for hydrogen evolution reaction includes high-edge-density MoS₂ nanosheets directly integrated with conductive carbon fiber paper (CFP). The nanosheets can be vertically aligned. The nanosheets can be 3-dimensional, polycrystalline nanosheets. The nanosheets are homogeneously dispersed across centimeter scales and have a high density of exposed edge sites. The nanosheets can include a mixture of faceted as well as discontinuous collapsed edges within the basal planes, induced by volume expansion accompanying topochemical sulfidation, as described herein. The MoS₂ nanosheets on the CFP can exhibit an overpotential 110 value of about 245 mV at 10 mA/cm², a Tafel slope of about 81 mV/dec, and a turnover frequency (TOF) of about 1.28 H₂/sec per active site at ~0.2 V versus RHE in a 0.5 M acidic solution.

The catalyst can further include buckminsterfullerenes or spherical fullerenes (nC₆₀). For example, the 3D MoS₂ nanosheets can be interfaced with nC₆₀ clusters by a facile solution-deposition method. The hybrid structures show greatly enhanced HER activity with an overpotential η₁₀ value of about 172 mV and a Tafel slope of about 60 mV/dec when the deposition concentration of C₆₀ is about 0.5 mg/mL. This condition corresponds to about 2% coverage of the MoS₂ nanosheets by nC₆₀ clusters. The improved activity of the hybrid catalysts is believed to derive from the interfacial charge transfer at nC₆₀/MoS₂ p-n heterojunctions. An optimal coverage of nC₆₀, with a homogeneous distribution can facilitate such interfacial doping.

The catalyst can be formed in stepwise fashion by chemical vapor deposition of nanosheets of MoO₃ onto a carbon fiber substrate, reducing the MoO₃ to nanosheets of MoO₂ using sublimed sulfur, then reacting sulfur vapor with the MoO₂ to form nanosheets of MoS₂ on the carbon fiber substrate. The resulting catalyst is multifaceted, having a large density of edges providing catalytically active sites for hydrogen evolution reaction.

The stepwise vapor transport, reduction, and sublimation steps used to prepare edge-exposed MoS₂ nanosheets on CFP are schematically illustrated in FIG. 1. In the first step, MoO₃ nanosheets that are about 1-2 μm in lateral dimensions are deposited onto CFP by the vapor transport of MoO₃ powder heated to 850°C. In the next step, reaction with sublimed sulfur at 400°C as per:

2MoO₃(s)+S(g)→2MoO₂(s)+SO₂(g) (1)

yields MoO₂ nanosheets with retention of the vertical growth orientation, although the edges are slightly rounded. Finally, the topochemical sulfidation of MoO₂ at 850°C as per:

MoO₂(s)+3S(g)→MoS₂(s)+SO₂(g) (2)

yields faceted MoS₂ nanosheets that are uniformly dispersed and vertically oriented across a large area (about 2 cm²) of the CFP (FIG. 2A). FIGS. 2B-2E illustrate “clean,” well-faceted, and “collapsed” edges of an individual MoS₂ nanosheet.

FIGS. 3A-3F illustrate the morphologies of vapor transported MoO₃ collected on a Si (100) substrate before and after stepwise reduction and sulfidation. These images further enable visualization of the vertical growth direction and high density of edge sites. Notably, the vertical growth orientation is achieved without mediation of a catalyst. Interestingly, the faceted MoO₂ nanosheets are transformed to thicker rounded MoO₂ discs upon reduction and finally converted to faceted MoS₂ nanosheets during sulfidation. The edge geometries in large measure reflect the intrinsic crystal structures of the phases. Orthorhombic α-MoO₃ crystallizes in a layered structure and thus faceted nanosheets are obtained comprising stacked layers. Reduction to monoclinic MoO₂ yields rounded edges, whereas topochemical transformation to 2H—MoS₂ again yields faceted structures reflecting the layered stacking of MoS₂ sheets. The considerable lattice mismatch between MoO₂ and MoS₂ results in a substantial volume change, which creates a distinctive discontinuous motif characterized by faceted “clean” and discontinuous “collapsed” domains along the MoS₂ basal planes. The latter is important as it allows for exposure of an increased density of catalytically active edge-sites.

FIGS. 4A-4E corroborate the phase identification of the prepared materials based on X-ray diffraction (XRD) and Raman microprobe analysis. The XRD patterns acquired on CFP are dominated by the (002) reflections of the graphitic substrate. However, reflections corresponding to the deposited materials are discernible and are indexed to orthorhombic α-MoO₃ (Joint Committee on Powder Diffraction Standards (JCPDS) 76-1003), monoclinic MoO₂ (JCPDS 86-0135), and hexagonal 2H—MoS₂ (JCPDS 87-2416) as shown in FIG. 4A.

Clearer phase assignment is enabled from the Raman spectra shown in FIG. 4B since the graphitic D and G bands from the substrate are only observed above 1300 cm. The Raman bands of the nanosheets formed in the first step are well matched with the Raman active modes of
orthorhombic α-MoO₃ reported in the literature. The detailed Raman band assignments of the prepared α-MoO₃ nanosheets are listed in Table 1.

### TABLE 1

<table>
<thead>
<tr>
<th>Bands (cm⁻¹)</th>
<th>Raman modes</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>995</td>
<td>Ag</td>
<td>vₒ₉ = Mo-O stretch</td>
</tr>
<tr>
<td>819</td>
<td>Ag</td>
<td>v₁ = Mo=O-O stretch</td>
</tr>
<tr>
<td>665 B₃⁺/₂B₂⁺</td>
<td>Ag/B₂⁺/₂A₂⁺</td>
<td>vₒ = Mo-O-Mo stretch and bend</td>
</tr>
<tr>
<td>472</td>
<td></td>
<td>δ = Mo=O-O scissoring</td>
</tr>
<tr>
<td>378</td>
<td>B₃⁺</td>
<td>δ = Mo=O-O scissoring</td>
</tr>
<tr>
<td>364</td>
<td>A₁g</td>
<td>vₒ = Mo-O-Mo bend</td>
</tr>
<tr>
<td>290</td>
<td>B₂⁺</td>
<td>δ = Mo=O-O wagging</td>
</tr>
<tr>
<td>282</td>
<td>B₂⁺</td>
<td>δ = Mo=O-O wagging</td>
</tr>
<tr>
<td>245</td>
<td>B₃⁻</td>
<td>τ = Mo=O-O twist</td>
</tr>
<tr>
<td>216</td>
<td>A₁g</td>
<td>vₒ = Mo-O-Mo twist</td>
</tr>
<tr>
<td>190</td>
<td>B₂⁺</td>
<td>vₐ = Mo-O-Mo twist</td>
</tr>
<tr>
<td>157</td>
<td>A₂g/B₂⁺/₂A₂⁺</td>
<td>τ = Mo-O-Mo twist</td>
</tr>
<tr>
<td>127</td>
<td>A₂g/B₂⁺/₂A₂⁺</td>
<td>vₒ = Mo-O-Mo twist</td>
</tr>
<tr>
<td>114</td>
<td>B₂⁺</td>
<td>vₒ = Mo-O-Mo twist</td>
</tr>
</tbody>
</table>

- **Ag**: Ag B₂g / B₃g, Ag big
- **O = Mo stretch** V O = Mo stretch, V a = Mo — O — Mo stretch
- **vₒ = Mo-O stretch** V a = Mo — O — Mo stretch, vₒ = Mo=O-O stretch and bend
- **δ = Mo=O-O scissoring**
- **τ = Mo-O-Mo twist**
- **vₐ = Mo-O-Mo stretch**
- **vₒ = Mo-O-Mo stretch**

**[0051]** The Raman spectra of the nanodiscs formed by the reduction of the α-MoO₃ nanosheet using sulfur are an excellent match for phonon modes of monoclinic MoO₃ as reported previously in the literature. The sulfide structures on CFP show clear Raman signatures of 2-H MoS₂ including Raman bands at 282, 377, and 404 cm⁻¹, which can be ascribed to modes of E₁g, E₂g, and A₁g symmetry, respectively. X-ray photoelectron spectroscopy (XPS) analysis was performed by acquiring Mo 3d, O 1s, and S 2p core level spectra of each product, to investigate the evolution of the chemical composition (FlG. 4C-4F). The Mo 3d core level spectra are characterized by a distinctive doublet at 233.20 and 236.35 eV ascribed to the binding energies of Mo 3d₅/₂ and 3d₃/₂ states, respectively; these binding energies are characteristic of hexavalent molybdenum, verifying stabilization of the MoO₃ phase. The O is single at 530.95 eV is further in good agreement with the value expected for an inorganic oxide.

**[0052]** Upon reduction with sulfur, the XPS spectra for the nanodiscs show a substantial alteration of the Mo 3d binding energies to 229.80 and 233.05 eV for Mo 3d₃/₂ and 3d₅/₂ states, suggesting the stabilization of a tetravalent oxide of molybdenum. A remarkable shoulder at 236.35 eV attributable to the binding energy of Mo 3d₃/₂ for hexavalent molybdenum indicates incomplete reduction. Corresponding features in the O is core level spectrum at 530.75 and 531.85 eV, can be attributed to MoO₂ and MoO₃, respectively. Furthermore, a distinctive doublet is discernible in S 2p core level spectra at 162.75 and 163.80 eV and can be ascribed to S 2p₁/₂ and S 2p₃/₂ binding energies, respectively, revealing surface sulfidation forms some MoS₂ even at a temperature of 400°C. The nanosheets after sulfidation at 850°C show Mo 3d core level spectra at 229.70 and 232.85 eV attributable to binding energies for Mo 3d₅/₂ and Mo 3d₃/₂, respectively; these values are characteristic of MoS₂. The small shoulder at 226.95 eV is attributed to S 2s. A much more pronounced doublet is observed in S core level spectra at 162.65 and 163.75 eV assigned to S 2p₁/₂ and S 2p₃/₂ binding energies, respectively. These values verify the sulfidation of MoO₂. A broad O is spectrum with a peak at 532.60 eV is attributed to surface-adsorbed oxygen species.

**[0053]** The enthalpy of hydrogen adsorption on MoS₂ edges has been estimated to be endothermic by ca. 0.08 eV and the extent of H-coverage is limited to one in four atoms at the edges of MoS₂. Reducing the overpotential and increasing catalytic efficiency requires a further decrease of the hydrogen adsorption enthalpy and an increase of the extent of H-coverage. One approach involves polarizing Mo—S bonds at the edges via electronic coupling with electron-donating or withdrawing moieties, ideally other semiconductors. Here, the faceted MoS₂ nanosheets were interfaced with nC₆₀ clusters deposited from solution to prepare hybrid architectures. Upon solution deposition from chlorobenzene solution (nC₆₀ of 0.5 mg/mL), nC₆₀ clusters that are ca. 7 μm in diameter are deposited onto the fibers of CFP. Similar morphologies of nC₆₀ were grown on the MoS₂ nanosheets. Energy dispersive X-ray spectroscopy (EDS) maps acquired at C, Mo, and S elemental edges verified the co-localization of the C₆₀ clusters atop the MoS₂ nanosheets. EDS line profiles further verified the co-localization of nC₆₀ clusters on the MoS₂ basal planes. The Raman spectra of the nC₆₀ cluster and hybrid nC₆₀/MoS₂ architectures are shown in FIG. 5. Distinctive Raman modes of C₆₀ are evident in both spectra with bands assigned to phonons of A₁g(1,2) and H₄(1,8) symmetry. Both MoS₂ and C₆₀ modes are discernible in the hybrid architecture. The coverage of nC₆₀ clusters strongly depends on the concentration of the precursor solution. The size of the nC₆₀ clusters increases with increasing concentration from 0.1 to 2.0 mg/mL. Notably, at a concentration of 0.1 mg/mL, the relatively small nC₆₀ clusters are homogeneously distributed throughout the sample; however, upon increasing the concentration to 0.5 mg/mL, the homogeneity is somewhat reduced. Upon increasing the precursor concentration to 2.0 mg/mL, the nC₆₀ clusters are mostly present as large agglomerations that are rather sparsely distributed across the surface. In the concentration range examined, the clusters do not appear to form a continuous percolative network. In order to evaluate quantitatively the coverage of nC₆₀ clusters for a precursor concentration of 0.5 mg/mL, the sample deposited onto CFP has been examined by secondary ion mass spectrometry (SIMS) using 50 keV C₆₀⁺ ions as the source. The mass spectrum of negatively charged ions emitted from the surface of the clusters deposited on CFP is shown in FIG. 6. The ions emitted were carbon, hydrocarbon clusters, and intact molecular cluster ions of C₆₀ with a yield (number of secondary ions detected per single projectile impact) of 0.08%. The C₆₀ clusters are ca. 7 μm in diameter and cover ca. 2% of the total surface area of the carbon fibers of CFP. Indeed, the SEM and SIMS measurements indicate that optimal concentrations of the C₆₀ solution are necessary to maximize interfacial interactions and prevent crystallization into larger nC₆₀ clusters.

**[0054]** The electrocatalytic HER performance of CFP based samples with nC₆₀ clusters alone, as-prepared 3D MoS₂ nanosheets, and hybrid nC₆₀/MoS₂ architectures were investigated in a 0.5 M aqueous solution of H₂SO₄, using a conventional three-electrode setup. Bare CFP was contrasted as a control and was essentially catalytically inert towards HER. In contrast, nC₆₀ (0.5 mg/mL) clusters on CFP exhibited a finite cathodic current density with an overpotential of 355 mV, reaching a current density of 10 mA/cm² (iₐ₀) and a Tafel slope of 169 mV/dec. The 3D
faceted MoS2 nanosheets on CFP showed HER activity with a η10 value of 245 mV and a Tafel slope of 81 mV/dec. Remarkably, interfac ing the MoS2 nanosheets with nC60 resulted in a much lower overpotential. Hybrid nC60 (0.5 mg/mL)/MoS2 structures had a η10 value of 172 mV and a Tafel slope of 60 mV/dec. These results clearly indicate the synergistic enhancement of HER activity as a result of coupling between nC60 and MoS2.

A high Tafel slope value of pristine nC60 on CFP (>120 mV/dec) indicated that HER proceeds through the Volmer mechanism, wherein proton reduction yielding hydrogen ad-atoms bound to the active sites represents the rate determining step. In contrast, low Tafel slope values measured for as-prepared 3D MoS2 and hybrid nC60/MoS2 (60 and 80 mV/dec) suggest the operation of the Volmer-Heyrovsky mechanism wherein the rate-determining steps involve both proton reduction and hydrogen desorption. It is noteworthy that the HER performance of the 3D array of MoS2 nanosheets with a high density of exposed edge-sites and their hybrid structures interfaced with nC60 are either higher or comparable to previously reported values for bulk or nanostructured MoS2. In addition, the hybrid materials reported here possess the advantages of well-defined architectures, conductive substrates, and scalability to centimeter-sized dimensions.

Fig. 7A-7B contrast the polarization curves of various concentrations of nC60 clusters either deposited directly onto CFP or interfaced with 3D MoS2 nanosheets on CFP. The cathodic current density of the neat nC60 cluster formed on CFP measured at ~0.4 V versus RHE is gradually decreased from 22.6 to 18.5 to 14.6 mA/cm2 as the concentration of C60 deposition solution is increased from 0.1 to 0.5 to 2.0 mg/mL. With increasing concentration of C60 solution, the overpotential η10 is also increased from 331 to 353 to 363 mV. As noted above, the hybrid nC60/MoS2 electrocatalyst prepared using 0.5 mg/mL C60 deposition solution shows the best HER performance with the highest current density (J0.25r=18.0 mA/cm2 at 0.2 V vs. RHE), lowest η10 value (172 mV), and the lowest Tafel slope (60 mV/dec). The nC60 (0.1 mg/mL)/MoS2 sample (J0.25r=5.2 mA/cm2, η10=-245 mV, and Tafel slope=74 mV/dec) exhibits substantially lower performance that is analogous to the 3D MoS2 nanosheets without t-C60 hybridization. J0.25r=5.0 mA/cm2, η10=-245 mV, and Tafel slope=81 mV/dec. At such low concentrations, the limited nC60 coverage likely limits the extent to which the edge reactivity is modulated. At substantially higher solution concentrations of C60, the HER performance is diminished as well. The nC60 (2.0 mg/mL)/MoS2 sample is characterized by values of J0.25r=3.9 mA/cm2, η10=273 mV, and a Tafel slope=80 mV/dec. The lack of synergistic enhancement in the latter case can be attributed to the sparse and heterogeneous distribution of nC60 (2.0 mg/mL). The large agglomerations observed suggest that the buckminsterfullerene clusters are not effectively interfaced with MoS2, which likely perturbs the electronic coupling necessary for improved HER performance as described below.

In order to examine the mechanistic basis for the observed modulation of electrocatalytic properties upon interfac ing with nC60, electrochemically active surface areas (ECSA) of all the samples were estimated by measuring the double-layer capacitance (Cdl) from cyclic voltammetry (CV) data across a potential range with no Faradic current. The voltammograms were collected at various scan rates (20-100 mV/s) in the potential range of 0.10-0.30 V versus RHE, where the current is preponderantly due to the charging of the double layer (and not due to proton reduction). Figs. 8A-8D and 9A-9E depict CV curves acquired for nC60, 3D nanosheets of MoS2, and hybrid nC60/MoS2 architectures with various C60 concentrations. The differences (Δη) of anodic and cathodic current densities at 0.20 and 0.23 V versus RHE for each CV plot is shown as a function of the scan rate in Fig. 8D and Fig. 9E. The slope of each Δη versus scan rate plot is equal to a value of 2Cdl/Δη. The ECSA were obtained from the ratio of the measured Cdl with respect to the specific capacitance of flat crystalline MoS2 (ca. 66.7 μF/cm2). The resulting Cdl and ECSA values are displayed as a function of C60 concentration in Fig. 8C. Significantly, the Cdl and ECSA of nC60 on CFP (9A) and hybrid nC60/MoS2 on CFP (9B and 9C) are respectively lower and higher than those of 3D MoS2 nanosheets on CFP (9D), and are decreased with increasing C60 concentration. From these results, it can be inferred that the nC60 clusters formed on CFP or MoS2/CFP are increasingly agglomerated and crystallized with increasing C60 concentration in solution, which is consistent with the morphologies observed by SEM. Furthermore, the Cdl and ECSA of hybrid nC60/MoS2 appear to be the sum of those of nC60 and 3D MoS2 nanosheets on CFP. However, an increased concentration of electrochemically active sites does not necessarily translate to increased HER activity since the nC60 clusters alone are much less active as compared to the 3D MoS2 architectures. The decrease of Cdl and ECSA with increasing C60 concentration of the precursor solution leads only to a slight deterioration of the cathodic current density for nC60/CFP and the Tafel slope is mostly preserved, indicating that the changes in Cdl, ECSA, and the resulting number of active sites do not fundamentally alter the HER mechanism (i.e., Volmer reaction in the neat C60) and rate (Fig. 9E). These two sets of observations suggest that the improved HER performance observed for the hybrid nC60, (0.5 mg/mL)/MoS2 electrocatalyst is derived from an intrinsic enhancement of the inherent catalytic activity of MoS2 for HER rather than an increase in the number of active sites upon C60 deposition.

The turnover frequency (TOF), defined as the number of H2 molecules evolved per active site per unit time, is an essential parameter to contrast the inherent catalytic activity of different systems. The TOF can be calculated using the expression TOF=JnF/2F(εCSA), where J is the current density, nF is Avogadro’s number, 2 is the stoichiometric number of electrons consumed at the electrode during HER, F is Faraday’s constant, n is the number of active sites (1.64×1015 cm2) on a flat surface of crystalline MoS2, and ECSA is the electrochemically active surface area of the electrode. Fig. 7D plots the TOF (per active site) of the 3D MoS2/CFP and hybrid nC60 (0.5 mg/mL)/MoS2 structure prepared on CFP in the applied potential range of -0.1 to -0.3 V versus RHE; in this regime, the HER is controlled by electrode kinetics with minimal influence from other effects. The measured TOF of the hybrid nC60 (0.5 mg/mL)/MoS2 structure at -0.2 V (2.35 H2/s per active site) is nearly twice as high as that of 3D MoS2 nanosheets (1.28 H2/s per active site) on CFP. These results highlight the synergistic enhancement of the inherent catalytic activity of the edge sites of the MoS2 nanosheets.
upon nC60 hybridization. The 3D hybrid architectures constructed on mesoporous CFP clearly represent viable electrocatalysts.

[0059] In order to further investigate a possible origin of the enhanced HER performance observed for the hybrid nC60 (0.5 mg/mL)/MoS2 structure, electrochemical impedance measurements were performed at various potentials between 10 and -250 mV by sweeping the frequency from 200 kHz to 100 mHz with an AC amplitude of 10 mV. FIG. 10A shows the Nyquist plots of as-prepared 3D MoS2 nanosheets and hybrid nC60/MoS2 architectures prepared on CFP measured at -150 mV vs. RHE. The Nyquist plots are fitted to an equivalent circuit model (inset of FIG. 10A) comprising the following elements: an ohmic resistance (R_o), a charge-transfer resistance (R_t), constant phase element (Q), and a Warburg constant (W). The obtained R_o values are plotted as a function of potential in FIG. 10B for nC60, as-prepared 3D MoS2 nanosheets, and hybrid nC60/ MoS2 architectures prepared on CFP. The kinetics of electrocatalytic HER on the different electrode samples can be evaluated based on their respective R_o values with a lower R_o value corresponding to a faster reaction rate. The resulting R_o values reveal a similar trend as the η_{10} and Tafel slope values deduced from the cathodic current density in polarization curves (FIGS. 7A-7B and 8A-8B); specifically, the R_o values of 3D MoS2/CFP and hybrid nC60/MoS2 prepared on CFP are nearly two orders of magnitude lower than those of nC60/CFP. Furthermore, the lowest R_o values are obtained for the hybrid nC60 (0.5 mg/mL)/MoS2 structure. Taken together, these results suggest that the enhanced HER performance observed upon interfacing with nC60 derive from the increased conductance of the hybrid constructs when C60 is appropriately interfaced with MoS2.

[0060] Indeed, recent ab initio density functional theory calculations of C60/MoS2 constructs are particularly instructive in understanding the nature of the interface formed between these two semiconductors. Prior studies have determined that the lowest energy configuration for these heterostructures corresponds to the hexagonal rings of C60 situating directly above S sites on the basal planes of MoS2, resulting in buckminsterfullerene molecules being able to rotate freely on the surface. This configuration yields a Type-II interface with charge depletion from C60 and charge accumulation on MoS2 estimated to be ca. 0.055 e- per C60 unit. This directionally charge transfer is thought to be key to the reduced resistance of the hybrid constructs. Indeed, the Type-II alignment has been further verified by recent theoretical and experimental studies of C60/MoS2 hybrids. Studies have predicted that the valence band edge of MoS2 (~4.5 eV) resides lower than that of C60 (~3.8 eV), resulting in charge transfer and electron accumulation on MoS2 when the two semiconductors are interfaced. Upon application of an electric field, the steadily increasing electron density in MoS2 reduces the junction-barrier height, further allowing facile electron tunneling and transport and giving rise to conductive pathways along the interfaces of the resulting C60/MoS2 p-n heterojunctions. Therefore, based on the measured TOF, deduced resistance values, and charge transfer resistance values extrapolated from EIS data, the enhanced HER performance of the hybrid nC60 (0.5 mg/mL)/MoS2 structure likely derives from a charge transfer mechanism. The nC60 clusters donate electron density to MoS2 and give rise to a conductive interfacial layer that is much more effective at charge transport as compared to the relatively insulating basal planes of MoS2. Such charge transfer may also polarize the Mo=S bonds reducing the enthalpy of hydrogen adsorption. Notably, this mechanism, essentially invoking interfacial doping of MoS2, is quite distinct from the hybrid MoS2/carbon nanotube and MoS2/graphene heterostructures wherein the latter components actually form conductive pathways for electron transport between the CFP electrodes and the catalytically active edge sites, thereby mitigating the poor transport characteristics of the basal planes of 2H—MoS2.

[0061] The role of interfacial doping is further underscored by the dependence of HER performance on the concentration of the C60 precursor solution and the morphology of the nC60 clusters. Agglomerated C60 clusters that are homogeneously dispersed across the MoS2 basal planes will be ineffective at modulating the electronic structure of MoS2 through electron transfer. To assess the long-term stability of nC60 (0.5 mg/mL)/CFP, 3D MoS2/CFP, and hybrid nC60 (0.5 mg/mL)/MoS2 on CFP as electrocatalysts for HER, CV sweeps have been performed for 1000 cycles in a 0.5 M aqueous solution of H2SO4 in the range between -0.2 and 0.2 V versus RHE at a scan rate of 100 mV/s. The polarization curve for the 3D MoS2 on CFP is almost exactly superimposable upon the initial data suggesting no degradation in performance (FIG. 7B). In contrast, after 1000 cycles, the hybrid nC60/MoS2 catalysts show a slight increase of the overpotential η_{10} to 181 mV and the Tafel slope is changed to 65 mV/dec. The observed changes are suggestive of the partial loss of C60 clusters upon prolonged electrocatalytic cycling, which likely disrupts some of the interfacial charge transfer and thereby disrupts charge transport between the CFP substrate and active catalytic edges.

[0062] The electrocatalyst for hydrogen evolution reaction will now be illustrated by the following examples, which do not limit the scope defined by the appended claims.

Example 1

Preparation of MoS2 Nanosheets, C60 Clusters, and their Hybrid Structures

[0063] The CVD processes were performed using a 1-inch-diameter horizontal cold-wall quartz tube furnace equipped with gas flow controls. In the first step to prepare MoO3 nanosheets, 15.0 mg of MoO3 powder (Sigma-Aldrich, purity >99.5%) was placed within an alumina boat, which was placed at the center of tube. A bare CFP substrate (Toray Paper 120) with dimensions of 7 cm x 1 cm size was placed downstream from the MoO3 source at a distance of 15 cm from the alumina boat. After an initial Ar purge for 30 min, the MoO3 powder was heated to 850°C at a ramp rate of 20°C/min and transported under a 68.3 scm Ar flow at 1 atm. After holding at 850°C for 10 min, the furnace was allowed to cool naturally to room temperature. Subsequently, MoO3 nanosheets integrated onto ca. 2 cm² areas of the CFP were recovered. Such nanosheets were reproducibly formed at a distance of ca. 18-20 cm from the alumina boat. The MoO3-deposited CFP was cut to dimensions of 4 cm x 1 cm thereby preserving margins on all sides. This substrate was then placed at the center of the tube furnace but downstream at a distance of 20 cm from an alumina boat containing 100 mg of elemental sulfur powder (Alfa Aesar, 99.5% purity). Next, after purging with Ar, the reactor was heated to a temperature of 400°C at a ramp rate of 20°
C./min under an Ar flow of 100 sccm at 1 atm to facilitate the reaction of sublimed sulfur with the MoO₃ nanosheets. After holding at 400°C for 20 min, the furnace was then naturally cooled to room temperature. Subsequently, a final CVD step was performed by replacing the spent sulfur in the alumina boat with an additional 100 mg of fresh elemental sulfur. The reactor was heated to 850°C at a ramp rate of 20°C/min under a 100 sccm flow of Ar at 1 atm for 20 min after which the furnace was allowed to naturally cool to room temperature. The CFP paper was then removed from the center of the furnace for characterization and electrocatalytic evaluation.

Example 2

Structural Characterization

The morphology of the prepared materials was examined by field-emission scanning electron microscopy using a JEOL JSM-7500F instrument. The edge sites of MoS₂ flakes harvested from the MoS₂-CFP sample by ultrasonication for 1 h in toluene were examined by high-resolution transmission electron microscopy using a JEOL JEM-2100 instrument operated at an accelerating voltage of 200 keV. Phase assignment was performed with the help of X-ray diffraction using a Bruker D8-Advance instrument equipped with a Cu Kα source (λ=1.5418 Å) as well as by Raman microprobe analysis using a Jobin-Yvon HORIBA LabRAM HR800 instrument coupled to an Olympus BX41 microscope. Raman spectra were collected with excitation from the 514.5 nm line of an Ar-ion laser; the laser power was kept below 10 mW to minimize photooxidation. The chemical composition and oxidation states of MoO₃, MoO₂, and Mo₂S prepared on CFP were investigated by X-ray photoelectron spectroscopy (XPS, Omicron XPS) with Mg Kα radiation (1253.6 eV). Energy calibration was achieved by setting the C1s line from adventitious hydrocarbons to 284.8 eV. The elemental composition of the C₆₀ clusters deposited on CFP and Mo₂S₂-deposited CFP was examined by energy-dispersive X-ray spectroscopy (EDS) coupled to the FE-SEM system. The coverage of C₆₀ (0.5 mg/mL) clusters deposited on CFP was measured on a custom-made secondary ion mass spectrometer (SIMS) using C₆₀²⁺ projectiles with an energy of 50 keV as the source.

Example 3

Electrochemical Characterization

The HER performance of the prepared materials was evaluated using a three-electrode configuration with the help of a Bio-Logic potentiostat (SP-200). All of the measurements were performed in a 0.5 M aqueous solution of H₂SO₄ purged with N₂ gas. MoS₂-CFP, C₆₀/CFP, and the hybrid structures prepared on CFP were individually used as the working electrodes. A saturated calomel electrode (SCE) and a Pt plate were used as reference and counter electrodes, respectively. The potential versus SCE (Eₘₚₜ) was converted to the potential versus the reversible hydrogen electrode (RHE) (Eₜₚₜ) using the relation Eₜₚₜ=Eₘₚₜ+0.279 V. Polarization curves for HER were measured using linear sweep voltammetry (LSV) in the range between 0.1 and -0.4 V versus RHE at a scan rate of 8 mV/s. The polarization curves were corrected for the ohmic potential drop (IR) losses, where R is the series resistance of the electrochemical cell as determined by electrochemical impedance spectroscopy (EIS) measurements. EIS measurements were performed in the range between 200 kHz and 50 mHz using an AC amplitude of 25 mV. The EIS measurements for obtaining the charge-transfer resistance (Rct) values were performed at various potentials between 10 and -250 mV by sweeping the frequency from 200 kHz to 100 mHz using an AC amplitude of 10 mV. In order to estimate the electrochemically active surface area (ECSA) of the samples, the double-layer capacitance (Cdl) of the samples was determined by cyclic voltammetry (CV) in the potential range of 0.10-0.30 V versus RHE at scan rates between 20-100 mV/s.

It is to be understood that the electrocatalyst for hydrogen evolution reaction is not limited to the specific embodiments described above, but encompasses any and all embodiments within the scope of the generic language of the following claims enabled by the embodiments described herein, or otherwise shown in the drawings or described above in terms sufficient to enable one of ordinary skill in the art to make and use the claimed electrocatalyst for hydrogen evolution reaction.

We claim:

1. An electrocatalyst for hydrogen evolution reaction, comprising:
   - a carbon fiber paper substrate; and
   - a plurality of nanosheets of MoS₂ on the carbon fiber substrate, the nanosheets having a plurality of catalytically active edge sites along basal planes thereof.

2. The electrocatalyst for hydrogen evolution reaction according to claim 1, wherein the basal planes comprise faceted edges.

3. The electrocatalyst for hydrogen evolution reaction according to claim 2, wherein the basal planes comprise collapsed edges.

4. The electrocatalyst for hydrogen evolution reaction according to claim 1, wherein the nanosheets further comprise spherical fullerene nanoclusters.

5. The electrocatalyst for hydrogen evolution reaction according to claim 1, wherein the spherical fullerene nanoclusters are about 7 μm in diameter.

6. The electrocatalyst for hydrogen evolution reaction according to claim 5, wherein the spherical fullerene nanoclusters cover about 2% of the total surface area of carbon fibers of the carbon fiber paper substrate.

7. The electrocatalyst for hydrogen evolution reaction according to claim 1, wherein the nanosheets are dispersed across an area of about 2 cm² of the carbon fiber paper substrate.

8. A method of making an electrocatalyst for hydrogen evolution reaction, comprising the steps of:
   - depositing nanosheets of MoO₃ onto a carbon fiber paper by chemical vapor deposition;
   - reducing the nanosheets of MoO₃ to nanosheets of MoO₂ by reaction with sublimed sulfur; and
   - sulfiding the nanosheets of MoO₂ to form nanosheets of MoS₂ integrated with the carbon fiber paper substrate,
the nanosheets of MoS₂ integrated with the carbon fiber paper substrate providing the electrocatalyst for hydrogen evolution reaction.

9. The method of making an electrocatalyst for hydrogen evolution reaction according to claim 8, wherein the nanosheets of MoO₃ deposited onto the carbon fiber paper are about 1-2 μm in lateral dimensions.

10. The method of making an electrocatalyst for hydrogen evolution reaction according to claim 8, wherein the reaction with sublimed sulfur occurs at a temperature of about 400°C.

11. The method of making an electrocatalyst for hydrogen evolution reaction according to claim 8, wherein the sulfiding of the nanosheets of MoO₂ occurs at a temperature of about 850°C.

12. The method of making an electrocatalyst for hydrogen evolution reaction according to claim 8, wherein the nanosheets of MoS₂ comprise a plurality of catalytically active edge sites along basal planes thereof.

13. The method of making an electrocatalyst for hydrogen evolution reaction according to claim 8, further comprising: immersing the nanosheets of MoS₂ integrated with the carbon fiber paper substrate in a solution of spherical fullerenes (nC₆₀); and annealing the nanosheets of MoS₂ integrated with the carbon fiber paper substrate after immersion in the fullerenes.

14. An electrocatalyst for hydrogen evolution reaction prepared according to the method of claim 8.

15. A method of making an electrocatalyst for hydrogen evolution reaction, comprising the steps of: depositing nanosheets of MoO₃ onto carbon fiber paper by chemical vapor deposition; reducing the nanosheets of MoO₃ to nanosheets of MoO₂ by reaction with sublimed sulfur; sulfiding the nanosheets of MoO₂ to form nanosheets of MoS₂ integrated with the carbon fiber paper substrate; the nanosheets of MoS₂ integrated with the carbon fiber paper substrate providing the electrocatalyst for hydrogen evolution reaction; immersing the nanosheets of MoS₂ integrated with the carbon fiber paper substrate in a solution of spherical fullerenes (nC₆₀); and annealing the nanosheets of MoS₂ integrated with the carbon fiber paper substrate after immersion in the fullerenes.

16. The method of making an electrocatalyst for hydrogen evolution reaction, according to claim 15, wherein the nanosheets of MoO₂ deposited onto the carbon fiber paper are about 1-2 μm in lateral dimensions.

17. The method of making an electrocatalyst for hydrogen evolution reaction, according to claim 15, wherein the reaction with sublimed sulfur occurs at a temperature of about 400°C.

18. The method of making an electrocatalyst for hydrogen evolution reaction according to claim 15, wherein the sulfiding of the nanosheets of MoO₂ occurs at a temperature of about 850°C.

19. The method of making an electrocatalyst for hydrogen evolution reaction according to claim 15, wherein the nanosheets of MoS₂ comprise a plurality of catalytically active edge sites along basal planes thereof.

20. An electrocatalyst for hydrogen evolution reaction prepared according to the method of claim 15.

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