Fabrication of graphene-based electrode in less than a minute through hybrid microwave annealing

Duck Hyun Youn1, Ji-Wook Jang1,*, Jae Young Kim1, Jum Suk Jang2, Sun Hee Choi3 & Jae Sung Lee1

1School of Nano-Bioscience and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798 Korea, 2Division of Biotechnology, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan 570-752, Korea, 3Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea.

Highly efficient and stable MoS2 nanocrystals on graphene sheets (MoS2/GR) are synthesized via a hybrid microwave annealing process. Through only 45 second-irradiation using a household microwave oven equipped with a graphite susceptor, crystallization of MoS2 and thermal reduction of graphene oxide into graphene are achieved, indicating that our synthetic method is ultrafast and energy-economic. Graphene plays a crucial role as an excellent microwave absorber as well as an ideal support material that mediates the growth of MoS2 nanocrystals. The formed MoS2/GR electrocatalyst exhibits high activity of hydrogen evolution reaction with small onset overpotential of 0.1 V and Tafel slope of 50 mV per decade together with an excellent stability in acid media. Thus our hybrid microwave annealing could be an efficient generic method to fabricate various graphene-based hybrid electric materials for broad applications.

Graphene, two-dimensional carbon material, possesses unique properties such as excellent electrical and thermal conductivities, good mechanical strength, and high specific surface area1,2. Owing to its excellent properties, graphene has been regarded as an ideal component to fabricate electrode materials in the field of energy conversion and storage. In particular, various combinations of graphene and inorganic metal compounds, graphene-metal hybrid electrodes, have attracted tremendous attention in a broad range of applications including fuel cells3, batteries4, supercapacitors5, photocatalysts6, and solar cells7 because graphene can enhance the electrocatalytic activities of immobilized metal compounds.

Fabrication methods of graphene-based hybrid electrodes are critical for their performance as emphasized in several recent reviews8-10. For graphene-based hybrid electrodes for energy related systems, graphene oxide (GO) derived from graphite is the preferred starting material due to low cost and high yield compared to higher quality but expensive pure graphene produced from epitaxial growth or chemical vapor deposition. In general, graphene-metal hybrid electrodes can be prepared by the reduction of metal precursors using a reducing agent like NaBH4 or via electrochemical reduction. On the other hand, graphene-metal oxide, sulfide, phosphate hybrid electrodes can be synthesized by various methods in the presence of GO. For example, TiO2 nanoparticles on reduced graphene oxide (TiO2/RGO) hybrid was synthesized by hydrothermal method at 120 °C for 3 h and Cds/RGO by solvothermal method 180 °C for 12 h in DMSO as a solvent11,12. In addition, Co(OH)2/RGO was prepared via reflux at 83 °C for 4 h using isopropyl alcohol and Na2S as a solvent and reducing agent respectively13. A precipitation followed by calcination method was used to synthesize Fe3O4/RGO14, SnO2/RGO15, and LiFePO4/RGO hybrid electrodes16. However, these general synthetic routes including hydrothermal, solvothermal, reflux, and calcination techniques are rather complex or time- and energy-consuming, and require high temperatures, hour-scale reaction times, and various reaction steps. Therefore, we need to develop a more facile approach for the synthesis of graphene–based hybrid electrodes.

Microwave heating is an alternative method to fabricate the graphene-based hybrid electrodes. Compared to other synthetic routes, it is a more rapid heating process generating smaller and more uniform nanoparticles onto graphene with decreased reaction time. The microwave heating in general involves direct interactions of microwave with the atoms, ions and molecules of the material, thus the temperature of entire sample can be raised dramatically in a very short time17. Mn3O4/graphene and NiCo2O4/graphene hybrid electrodes were prepared by microwave assisted hydrothermal method at 200 °C for 5 h18. Various graphene–metal sulfides such as ZnS, CdS,
Ag₂S, and Cu₂S electrodes were synthesized by microwave heating for ~15 min using ethylene glycol as a solvent, microwave absorbent, and reducing agent of GO.

Although the solvent-based microwave reaction has an advantage of a shorter reaction time than the usual thermal methods, it has drawbacks of non-uniform heating and presence of an upper limit in the reaction temperature since most of irradiated microwave is absorbed by solvent. In addition, most of non-conducting materials cannot efficiently absorb the low frequency (2.45 GHz) household microwave at room temperature due to their low dielectric properties and high attenuation distance. Thus, further shortening of the reaction time down to minute- or second-scale is difficult in solvent-based microwave reaction. Here we report for the first time an extremely simple, ultrafast (less than 1 min), and energy-economic "hybrid microwave annealing (HMA)" synthesis of the graphene-based hybrid electrodes.

The HMA (Figure 1) combines this microwave heating with an additional heating from an effective microwave absorber (susceptor) in our case) increased dramatically first and the susceptor transfers the heat to the target material via the conventional heating mechanisms. Then, the target materials could absorb microwave effectively due to the changed dielectric properties and attenuation distance at the elevated temperature. This combined action of microwaves and microwave-coupled external heating source in HMA system has been mainly used for sintering ceramics. Surprisingly, however, it is rarely used for the chemical synthesis process to the best of our knowledge.

Molybdenum disulfide (MoS₂) of a two-dimensional layered structure exhibits unique electronic, optical, mechanical, and chemical properties, which have attracted a wide range of interest encompassing catalysis, batteries, electronics, photocatalysis, and solar cells. In recent years, MoS₂ has been proven to be an active electrocatalyst for hydrogen evolution reaction (HER), which is traditionally catalyzed by expensive and scarce platinum. Hence, we selected MoS₂/GR hybrid electrode as a target system to apply the HMA fabrication process.

In this report, we used the HMA process to fabricate MoS₂/GR (75 wt% MoS₂) as an efficient HER electrocatalyst. Here, the graphite susceptor initiates the reaction including thermal reduction of GO to GR, and as a good microwave absorber GR further facilitates the reaction by effectively absorbing the microwave. Hence, GR in the MoS₂/GR becomes an additional susceptor imbedded in the sample, which becomes more effective because of close contact with MoS₂. In HER, the obtained MoS₂/GR hybrid showed a good onset potential of ca. 0.1 V and Tafel slope value of 50 mVdec⁻¹. The performance represents one of the best values in HER by MoS₂-based catalysts. In the HMA process, crystallization of MoS₂ and reduction of GO occur at the same time in extremely short treatment time of only 45 seconds in a household microwave oven. Thus, our MoS₂/GR hybrid synthesized by the novel method proposed here could be a promising electrocatalyst for HER, and the process could be applied to synthesis of various other graphene-based hybrid electrical materials for many applications.

**Results**

Physicochemical properties of MoS₂/GR hybrid. Figure 1 illustrates schematically the synthetic method for MoS₂/GR hybrid electrocatalysts. By simply mixing MoCl₅, GO, thiourea, and ethanol in one pot, it is possible to generate a precursor state of metal-thiourea complex. The metal precursor reacts with ethanol vigorously, releasing major part of the chlorine as HCl and generating molybdenum orthoester. By adding thiourea, a viscous metal-thiourea complex is formed on GO. After the evaporation of ethanol, the glass reactor is purged with argon gas to drive out a small amount of remaining oxygen. The reactor is moved onto graphite susceptor and the microwave reaction proceeds just for 45 seconds. The temperature of the system increases up to ~700°C during the reaction occurring under dry inert gas conditions. Thus, the graphite susceptor absorbs the microwave (2.45 GHz) and generated heat that is transferred to the precursors by the conventional heat transfer mechanisms (Heat I). Then the heated precursor effectively absorbs the microwave energy by its modified dielectric properties and attenuation distance (Heat II). Besides, GO is reduced thermally to GR by releasing the oxygen functional groups of GO in the form of CO or CO₂. In turn, GR acts as a good absorber for microwave and facilitates further the MoS₂ crystallization (Heat III). During the 45 seconds of HMA, these three kinds of heat (I-III) contribute to crystallization of MoS₂ and reduction of GO. In comparison, crystallization of MoS₂ was observed in a minute even without GO. However, without applying graphite susceptor, crystalline MoS₂ was not formed even after 1 hour, indicating the decisive role of graphite susceptor in the HMA process.

Figure 2 compares the XRD patterns of MoS₂/GR hybrid with those of bare MoS₂ synthesized without GO. The inset denotes the XRD patterns of the pristine GO and synthesized GR via HMA method without metal precursor. As indicated, the XRD patterns of the synthesized catalysts are generally consistent with the reference XRD pattern of hexagonal MoS₂ (JCPDS 01-075-1539). No other phases were detected and hence MoS₂ is the dominant phase. The MoS₂ in MoS₂/GR has better crystallinity than that of bare MoS₂, showing the beneficial effect of GR as an imbedded secondary

---

### Figure 1

Schematic illustration of the hybrid microwave annealing (HMA) system to prepare MoS₂/GR composite catalyst. Magnified images (right) represent the three different heats involved in crystallization of MoS₂ and reduction of graphene oxide.
susceptor during the HMA process for crystallization of MoS$_2$. The (002) peak at 14° originates from stacking layers confirming the layered structure of MoS$_2$. The absence of the peak around 11° in MoS$_2$ samples indicates that the reduction of GO to GR by microwave irradiation, which will be further demonstrated by Raman and XPS measurements later.

Structural details of MoS$_2$/GR were investigated by TEM analyses. MoS$_2$ nanocrystals consisting of 4 – 10 layers are dispersed on GR in Figure 3a and Figure S1a. The free-standing MoS$_2$ nanocrystals staying away from the GR sheets are not seen. HR-TEM image (inset of Figure 3a) shows that MoS$_2$ has a layered structure with an interlayer distance of 0.624 nm, which corresponds to (002) plane of hexagonal MoS$_2$. In stark contrast to MoS$_2$/GR hybrid, bare MoS$_2$ exhibits highly aggregated nanocrystals of MoS$_2$ (Figure 3b and Figure S1b). The dark parts of the TEM image originate from the aggregation of MoS$_2$ nanocrystals. Electron energy loss spectroscopy (EELS) of TEM provides further morphological information of MoS$_2$/GR hybrid. Figure 3e and 3f show the elemental mapping images of MoS$_2$/GR are displayed in Figure S2, which demonstrate the existence of Mo, S, and C in the sample.

Similar results were obtained from SEM analyses in Figure S3. The SEM images of MoS$_2$/GR hybrid exhibit a wrinkled paper-like morphology of GR. Although MoS$_2$ nanoparticles are not seen in this image, energy dispersive spectroscopy (EDS) measurements in Figure S3b reveal the presence of MoS$_2$ on the surface of GR with ca. 1 : 2 molar ratio of Mo and S. Furthermore, EDS mapping images in Figure S4 strongly support that GR layers are uniformly covered with MoS$_2$ nanocrystals. The corresponding EELS spectra of MoS$_2$/GR are displayed in Figure S2, which demonstrate the existence of Mo, S, and C in the sample.

Conductivities of the synthesized catalysts were measured by the four point probe method and the results are summarized in Table 1.

Figure 2 | XRD patterns of synthesized MoS$_2$/GR and bare MoS$_2$. Vertical lines indicate reference pattern of MoS$_2$ (ICPDS 01-075-1539). The inset shows XRD patterns of the pristine GO and synthesized GR by HMA.

Figure 3 | TEM images and the corresponding high-resolution TEM images of (a) MoS$_2$/GR and (b) bare MoS$_2$. Element mapping images of MoS$_2$/GR using electron energy loss spectroscopy (EELS) for (c) raw image, (d) carbon, (e) sulfur, and (f) molybdenum.

Bare MoS$_2$ itself is a very poor electrical conductor with its sheet resistance exceeding the measurement limit (500 × 10$^6$ Ω. The commercial MoS$_2$ (Aldrich) shows a measurable, but very large sheet resistance of 2.6 × 10$^7$ Ω. The MoS$_2$/GR hybrid exhibits a dramatically reduced (by a factor of ∼10$^5$) sheet resistance of 4 Ω. Thus the conductivity of MoS$_2$/GR was ∼10$^3$ times higher than that of commercial MoS$_2$. During the microwave heating, GO is converted to GR and it is further reduced as GR itself absorbs the microwave effectively. The high conductivity of graphene is responsible for the good conductivity of MoS$_2$/GR. The good conductivity is an essential requirement for a high activity in electrocatalysis, which was easily achieved here by adopting GO to MoS$_2$ with a brief microwave heating to convert GO to GR.

The reactions between Mo and thiourea were followed by infrared (IR) spectroscopy in Figure 4a. As Mo precursor (MoCl$_5$) was mixed with thiourea under ambient conditions, blue shift (from 730.9 to 715.5 cm$^{-1}$) of the C=S stretching peak and red shift (from 1473.3 to 1514.3 cm$^{-1}$) of the C-N stretching peak are observed. The results indicate the reduced and increased double bond characteristics of C=S and C-N bonds, respectively, indicating the bond formation between Mo (V) and S of thiourea$^{41,44}$ to yield a Mo-thiourea complex. In the presence of GO with the Mo-thiourea complex (GO-Mothiourea), the shape and position of NH$_3$ stretching peaks at 2800 ~ 3700 cm$^{-1}$ are different from those of Mo-thiourea. Also, the C=O stretching peak is shifted from 1623.8 to 1608.3 cm$^{-1}$ compared to
pristine GO. The changes in NH$_2$ and C=O stretching peaks denote the strong interaction between GO with the Mo-thiourea complex. During the synthesis process of MoS$_2$/GR hybrid, sulfur in thiourea and Mo precursor are combined into a Mo-thiourea complex as evidenced in IR results. In the presence of GO, the Mo precursor is attracted through oxygen functional groups of GO, generating the GO-Mo-thiourea complex. Thus, essentially the same chemical transformation takes place on the GO layers.

In Raman spectra of Figure 4b, the $I_D/I_G$ peak ratio (1.29) of GO-Mo-thiourea complex is higher than that of GO (0.9), indicating the increased disorders$^{45}$. At the ambient temperature, the GO-Mo-thiourea complex is formed, but GO is yet to be reduced to GR. Thus, the increased $I_D/I_G$ peak ratio could be attributable mainly to the strong interaction between GO and Mo-thiourea complex, which results in the increased disorders$^{46}$. These Raman results are generally consistent with the IR results as well as the results of TEM and SEM analyses. Upon HMA treatment, the Mo-thiourea complex turns into MoS$_2$ as indicated by two prominent peaks of MoS$_2$, an in-plane mode (E$^{2g}$, 382.0 cm$^{-1}$) and an out-of-plane mode (A$^{1g}$, 408.5 cm$^{-1}$)$^{35}$. In addition, the $I_D/I_G$ ratio of 1.15 for MoS$_2$/GR is higher than 0.9 for GO. The increased $I_D/I_G$ ratio indicates the formation of GR by reduction of GO$^{47–49}$.

Chemical states of MoS$_2$/GR composite were further investigated by XPS. In Mo 3d spectra, two dominant peaks at 233 and 229 eV are assigned to Mo$^{4+}$ 3d$_{3/2}$ and 3d$_{5/2}$, respectively$^{33–35}$, which originate from MoS$_2$ in Figure 4c. The shoulder peaks around 236 eV originating from Mo$^{5+}$ 3d$_{3/2}$ reveal the existence of amorphous MoO$_3$.$^{50}$ The amorphous trace of MoO$_3$ species, which should have been derived from exposure of the sample to air, hardly affects the local structure of MoS$_2$ as discussed below. The C1s spectrum of MoS$_2$/GR is presented in Figure 4d. Various peaks are observed at 284.8, 286.2, 287.8, and 289.0 eV, corresponding to C-C, C=O, C=O, and C(O)O, respectively$^{50}$. Typical GO has several oxygen-containing functional groups including hydroxyl, carboxyl, and epoxy groups, and thus it exhibits broad peaks in 280–290 eV range as shown in Figure S5a. However, in Figure 4d, intensity of the peaks related with oxygen-containing functional groups decreases significantly to the level of pure GR (Figure S5b), suggesting the reduction of GO to GR. Thus, considering these results of XRD (absence of the peak around 11°), Raman (the increased $I_D/I_G$ ratio compared to GO), and XPS (the decreased intensity of the peaks for oxygen-containing functional groups), we could confirm that GO is effectively reduced to GR by HMA for 45 seconds.

The Fourier-transformed EXAFS spectra of MoS$_2$ catalysts in Figure 5 show two distinct peaks; one (A) at 1.0–2.3 Å and the other (B) at 2.3–3.3 Å. The peak A denotes the interaction of the nearest neighboring sulfur atoms with a central molybdenum atom and the peak B is attributed to Mo-Mo scattering, as revealed by FEFF cal-

---

**Table 1 | Electrical properties of MoS$_2$ and MoS$_2$/GR composite**

| Catalyst           | Sheet Resistance$^a$ (Ω$^{-1}$) | Conductivity$^a$ (Sm$^{-1}$) | $R_{ct}$ (Ω) | Capacitance$^b$ (µF) |
|--------------------|---------------------------------|------------------------------|-------------|---------------------|
| MoS$_2$/GR         | 4.09 ($\pm$0.07)                | 6.11 $\times$ 10$^2$        | 35          | 1246                |
| MoS$_2$            | >500 $\times$ 10$^6$            |                              | 1130        | 56.64               |
| MoS$_2$ (Ald)      | 2.60 ($\pm$0.06) $\times$ 10$^4$ | 1.92 $\times$ 10$^{-3}$      | 3600        | 16.81               |

$^a$From 4-point probe method, $^b$ Extracted from fitting electrochemical impedance spectra to an equivalent circuit.

---

**Figure 4** | (a) IR spectra of thiourea, GO, Mo-thiourea, and Go-Mo-thiourea complex. (b) Raman spectra of GO, Go-Mo-thiourea complex, and MoS$_2$/GR. XPS spectra of MoS$_2$/GR for (c) Mo 3d, (d) C 1s.
The MoS$_2$/GR hybrid catalyst showed relatively small $\eta$ of 0.12 V. Since recently-developed best MoS$_2$-based electrocatalysts exhibit $\eta$ of 0.1–0.2 V$^{2,3}$–$^{39}$, we can state that our HMA method can produce one of the best-performing MoS$_2$-based electrocatalysts. In the absence of GR, bare MoS$_2$ exhibits significantly lower activity in terms of $\eta$ (ca. 0.2 V) and current density. Commercial MoS$_2$ shows even lower HER activity than bare MoS$_2$. For further investigation of HER activity, polarization results were fitted to Tafel equation ($\eta = \alpha + b \log(j)$), where $j$ is the current density and $b$ is the Tafel slope. In Figure 6b, Pt shows 30 mV/dec of Tafel slope, which is consistent with the reported values. The Tafel slope of MoS$_2$/GR hybrid was 50 mV/dec, far outperforming bare MoS$_2$ (180 mV/dec). Our Tafel slope is somewhat higher than the value reported by Dai et al. for MoS$_2$/RGO hybrid (40 mV/dec)$^{35}$, but comparable to or less than the values obtained using MoS$_2$/Au(111) catalyst$^{35}$, core (MoO$_3$)-shell (MoS$_2$) catalyst$^{34}$, and double-gyroid MoS$_2$ catalyst (55–60 mV/dec)$^{39}$. This indicates that the surface state of our MoS$_2$/GR is similar to those of other active MoS$_2$-based catalysts with maximum exposed edges of MoS$_2$ nanocrystals, which have been identified as active sites for HER$^{35}$. By combining MoS$_2$ and GR, aggregation of MoS$_2$ is markedly reduced compared to bare MoS$_2$, exposing more MoS$_2$ sites available to HER. At the same time, GR provides highly conducting electron pathway to the loaded MoS$_2$ nanocrystals and thus increases the activity of active sites with aid of a strong MoS$_2$-GR interaction. Besides the high activity, synthesized MoS$_2$/GR hybrid exhibits very good electrochemical stability. After a thousand potential-cycling tests between -0.3 and 0.2 V, activity loss of MoS$_2$/GR is negligible as shown in Figure 6c. Furthermore, the crystalline structure and morphology of the MoS$_2$/GR were generally conserved after electrochemical stability test (Figure S8). Such a good stability and activity of our MoS$_2$/GR electrocatalyst as well as the exceptional speed and energy economy of the fabrication method make the HMA process a viable candidate to manufacture the practical MoS$_2$-based electrocatalysts for HER in a large scale.

To investigate electrochemical characteristics of MoS$_2$/GR, electrochemical impedance spectroscopy (EIS) measurements were conducted. Figure 6d displays the obtained Nyquist plots. The data were fitted with an equivalent circuit shown in the inset of Figure 6d, and the resultant fitting parameters are summarized in Table 1. A semicircle consisting of charge transfer resistance ($R_{ct}$) and corresponding capacitance describes the charge-transfer process at the interface between electrocatalyst and electrolyte. In general, $R_{ct}$ value is inversely proportional to electrocatalytic activity. The obtained $R_{ct}$ value of MoS$_2$/GR (35 $\Omega$) is much lower than those of bare MoS$_2$ (1130 $\Omega$) and commercial MoS$_2$ (3600 $\Omega$). Thus, such a lower $R_{ct}$ value of MoS$_2$/GR indicates that its high electrocatalytic activity for HER is ascribed to the highly conductive GR layers that improve the charge transfer characteristics of MoS$_2$. In addition to the low $R_{ct}$ value, MoS$_2$/GR exhibits a much higher capacitance value of 1246 $\mu$F compared to 56.64 and 16.81 $\mu$F for bare MoS$_2$ and commercial MoS$_2$, respectively. By combining GR and MoS$_2$, the aggregation of MoS$_2$ is significantly reduced as confirmed by TEM/SEM analyses.

Table 2: Structural parameters calculated from Mo K-edge EXAFS fits for MoS$_2$ catalysts

| Catalysts | Mo-S | Mo-Mo |
|-----------|------|-------|
| MoS$_2$ (Ald) | 6.0 $\pm$ 0.24(1) | 0.003(1) |
| MoS$_2$ | 6.4 $\pm$ 0.08(2) | 2.1(5) | 2.75(2) | 0.012(5) | 0.02(1) | 0.006(1) |
| MoS$_2$/GR | 6.0 $\pm$ 0.04(1) | 2.2(6) | 2.82(2) | 0.014(5) | 1.6(5) | 3.16(2) |

*coordination number, $b$ bond distance, $c$ Debye-Waller factor, $d$ a sum-of-squares measure of the fractional misfit. $e$ fixed parameter, $f$ very small value due to weak correlation with the small coordination number. The number in parentheses denotes an uncertainty of the calculated parameter at the last digit place.
MoS2 nanocrystals could be in contact with electrolyte and thus could participate in HER. The EIS results confirm that the enhanced activity of MoS2/GR originates from two main factors: i) increased activity of each active site by improved charge transfer characteristics and ii) increased number of active sites accessible by electrolyte by dispersing MoS2 particles on graphene layers. In both cases, GR plays crucial roles by revealing its excellent electron conductivity and minimizing the aggregation of MoS2 nanocrystals. In addition, it is a good microwave absorber and assists the HMA process in formation of MoS2 crystals.

Discussion
In this report, we have synthesized MoS2/GR hybrid catalyst for HER by a new method of hybrid microwave annealing. Herein, the graphite susceptor initiates the formation of MoS2 nanocrystals and reduction of graphene oxide by transferring heat to the reaction system. The thermally reduced graphene further facilitates the reaction by effectively absorbing the microwave and transmitting the heat to MoS2 crystals. The process produces the highly crystalline MoS2 in the second-scale (only 45 seconds in the present case) by irradiation using a 1000 W household microwave oven. Thus our synthetic method is ultrafast and energy-economic. Note that the general synthetic methods of MoS2 involve various steps including sulfurization using H2S gas, hydrothermal or solvothermal treatment requiring high temperatures and more than hour-scale heat treatment. Thus, we could conclude that our synthetic method of MoS2/GR hybrid electrocatalyst has the following advantages: i) Reduction of GO to GR occurs simultaneously with the crystallization of MoS2. ii) Thermal treatment step of MoS2 on GR is not required. iii) Scale up is very easy. Furthermore the MoS2/GR composite synthesized by our method exhibits high HER activity with small η of 0.12 V and Tafel slope of 50 mV/dec. This performance represents one of the best among reported MoS2-based electrocatalysts for HER. In addition, it exhibits an excellent stability under repeated potential cycling tests. The enhanced electrochemical properties of MoS2/GR are attributed to the increased activity of active MoS2 sites and increased number of the sites by excellent conducting and textural properties of graphene.

Methods
Catalysts preparation. Graphene oxide (GO) prepared by Hummer’s method was ultrasonically dispersed in 20 ml ethanol. 1 g MoCl5 was dissolved in 2.53 ml of ethanol, which was added to GO-containing solution. Stoichiometric amount of thiourea (560 mg), as a sulfur source, was added to the solution under vigorous stirring. After 1 h stirring, the solution was dried in an oven to evaporate excess amount of ethanol and irradiated using a 1000 W household microwave oven for 45 seconds. Followed by washing with excess amount of water and ethanol, we could obtain MoS2/GR powder. The final yield of MoS2 was ca. 85–90%. The nominal contents of MoS2 in MoS2/GR composite was 75 wt%. As a control experiment, bare MoS2 was synthesized by carrying out the procedure without GO.

Catalysts characterization. Crystalline structures of synthesized catalysts were revealed by X-ray diffraction (XRD, PANalytical PW 3040/60 X’pert), and structural details were investigated by scanning electron microscopy (SEM, JEOL JSM-7410F)/ energy dispersive spectroscopy (EDS) and transmission electron microscopy (Cs-corrected HR-STEM, JEOL JEM-2200FS)/electron energy loss microscopy (EELS) at National Center of Nanomaterials Technology (NCNT). Conductivity of the catalysts was measured by the four point probe method (Keithley 2400) using pelletized samples. Reaction mechanism was elucidated using infra-red spectroscopy (IR,
Electrochemical Tests. Electrochemical measurements including linear sweep voltammetry (LSV) and durability tests were carried out in a conventional three electrode cell with N2 purged aqueous solution of 0.5 M H2SO4 using a potentiostat (Ivium technologies) equipped with a rotating disk electrode setup (RDE, PAR Model 636 RDE). The Ag/AgCl (3 M NaCl) electrode and a Pt wire were used as reference and counter electrodes, respectively. In this paper, all the potentials were referred to the reversible hydrogen electrode (RHE) without specification. The working electrodes were prepared by dispersing 20 mg of catalyst in 2 ml of deionized water and 40 μl of 9% Nafion solution and pipetting out 15 μl of slurry onto a glassy carbon electrode (0.19365 cm²). 9 μl of Nafion solution was added on top to fix the electrocatalyst. The LSV tests were performed at a scan rate of 5 mV s⁻¹ with 900 rpm. The durability tests were carried out by repeating the potential scan from 0.4 V to −0.3 V with 1000 cycles. In the identical cell setup, electrochemical impedance spectroscopy (EIS) was carried out. The frequency range was from 100 kHz to 1 mHz with a modulation amplitude of 10 mV at −0.2 V bias voltage. The EIS spectra were fitted by the Z-view software.

1. Balandin, A. A. Thermal properties of graphene and nanostructured carbon materials. J. Mater. Sci. 10, 569–581 (2011).
2. Chen, L., Hernandez, Y., Feng, X. & Muller, K. From nanographene and graphene nanoribbons to graphene sheets: chemical synthesis. Angew. Chem. Int. Ed. 51, 7640–7654 (2012).
3. Youn, D. H. et al. A highly efficient transition metal nitride-based electrocatalyst for oxygen reduction reaction: TiN on a CNT-graphene hybrid support. J. Mater. Chem. A 1, 8007–8015 (2013).
4. Yang, J. et al. LiFePO4-graphene as a superior cathode material for rechargeable lithium batteries: impact of stacked graphene and unfolded graphene. Energy Environ. Sci. 6, 1521–1528 (2013).
5. Chen, S., Zhu, J. & Wang, X. One-step synthesis of graphene—cobalt hydroxide nanocomposites and their electrochemical properties. J. Phys. Chem. C 114, 11829–11834 (2010).
6. Zhang, H., Lv, X., Li, Y., Wang, Y. & Li, J. P25-graphene composite as a high performance photocatalyst. ACS Nano 4, 380–386 (2009).
7. Youn, D. H. et al. Hybridized graphene nanoribbons on CNT-graphene hybrid support as noble-metal-free counter electrode for quantum dot-sensitized solar cells. ChemSusChem 6, 261–267 (2013).
8. Bai, H., Li, C. & Shi, G. Functional composites based on chemically reduced graphene oxide. Adv. Funct. Mater. 23, 1089–1115 (2011).
9. Huang, X., Zeng, Z., Fan, Z., Liu, J. & Zhang, H. Graphene-based electrodes. Adv. Mater. 24, 5979–6004 (2012).
10. Sun, Y., Wu, Q. & Shi, G. Graphene based new energy materials. Energy Environ. Sci. 4, 1113–1132 (2011).
11. Cao, A. et al. A facile one-step method to produce graphene–CdS quantum dot nanocomposites as promising optoelectronic materials. Adv. Mater. 22, 103–106 (2010).
12. Bashkova, S. & Bando, T. J. Adsorption/reduction of NO2 on graphite oxide/iron composites. Ind. Eng. Chem. Res. 48, 10884–10891 (2009).
13. Zhang, L. et al. Mono dispersed SnO2 nanoparticles on both sides of single layer graphene sheets as anode materials in Li-ion batteries. J. Mater. Chem. 20, 5463–5467 (2010).
14. Menezes, R. R., Souto, P. M. & Kiminami, R. H. G. A. Microwave fast sintering of ceramic materials: Sintering of Ceramics - New Emerging Techniques [Lakshmanan A. (ed.)] 3–26 (Intech, Rijeka, 2012).
15. Chang, K.-H. et al. A unique strategy for preparing single-phase unitary/binary oxides–graphene composites. Chem. Commun. 46, 7957–7959 (2010).
16. Bai, S. et al. Optical properties and a simple and general route for the rapid synthesis of reduced graphene oxide–metal sulfide nanocomposites. Eur. J. Inorg. Chem. 2013, 256–262 (2013).
17. Brosnan, K. H., Messing, G. L. & Agrawal, D. K. Microwave sintering of alumina at 2.45 GHz. J. Am. Ceram. Soc. 86, 1507–1512 (2003).
18. Chakraborty, M. & Arora, O. Microwave versus conventional sintering: A review of fundamentals, advantages and applications. J. Alloys Compd. 494, 175–189 (2010).
19. Prabhu, G., Chakraborty, A. & Sarma, B. Microwave sintering of tungsten. Int. J. Refract. Met. Hard Mater. 27, 545–548 (2009).
55. Rehr, J. J., Kas, J. J., Vila, F. D., Prange, M. P. & Jorissen, K. Parameter-free calculations of X-ray spectra with FEFF9. *Phys. Chem. Chem. Phys.* **12**, 5503–5513 (2010).

**Acknowledgments**

This work has been supported by BK Plus Program, Basic Science Research Program (No. 2012-007247), and Korea Center for Artificial Photosynthesis (KCAP) located in Sogang University funded by the Ministry of Science, ICT and Future Planning (MSIP) through the National Research Foundation of Korea (No. 2009-0093880).

**Author contributions**

D.H.Y. and J.-W.J. designed and performed the experiments. J.Y.K. helped to measure and analyze the EIS data. J.S.J. and S.H.C. helped to perform the XAS measurements and analyzed the EXAFS data. J.S.L. supervised the project.

**Additional information**

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/  
Supplementary information accompanies this paper at http://www.nature.com/scientificreports  
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Youn, D.H. et al. Fabrication of graphene-based electrode in less than a minute through hybrid microwave annealing. *Sci. Rep.* 4, 5492; DOI:10.1038/srep05492 (2014).