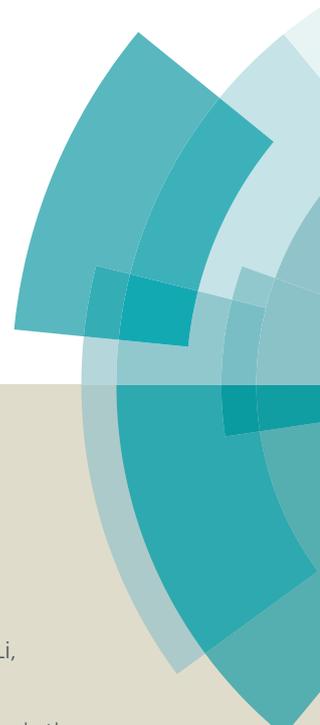
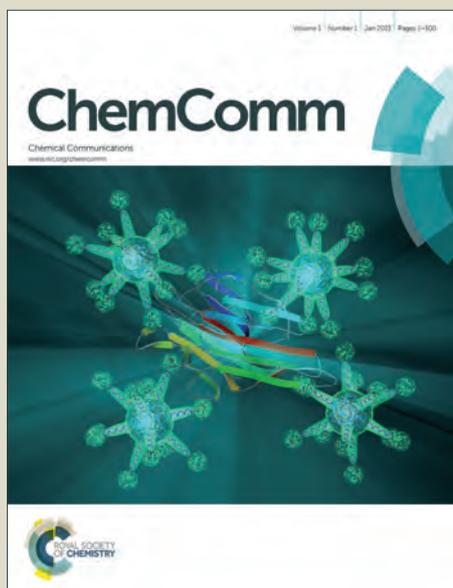


ChemComm

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: L. F. Pan, Y. H. Li, S. Yang, P. F. Liu, M. Q. Yu and H. Yang, *Chem. Commun.*, 2014, DOI: 10.1039/C4CC05698A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Molybdenum Carbide Stabilized on Graphene with High Electrocatalytic Activity for Hydrogen Evolution Reaction †

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Lin Feng Pan,^a Yu Hang Li,^a Shuang Yang,^a Peng Fei Liu,^a Ming Quan Yu^a
and Hua Gui Yang^{*a, b}

In this work, we developed a general two-step method to prepare molybdenum carbide (Mo₂C) nanoparticles stabilized by carbon layer on reduced graphene oxide (RGO) sheets. The Mo₂C/RGO hybrid shows excellent performance which is attributed to the intimate interactions between Mo₂C and the graphene as well as the outer protection of carbon layer.

Increasing energy demand caused by rapid development with environmental crisis has led to the exploitation of hydrogen.^{1, 2, 3} Recent works have shown that transition metal carbides,⁴⁻⁷ nitrides,^{8, 9} sulfides^{10, 11} and phosphides^{12, 13} exhibit promising properties making them potential substitutes for scarce Pt-group metals for hydrogen evolution reaction (HER). Among these, transition metal carbides display remarkable catalytic activities due to the unique d-band electronic structures.¹⁴ Some strategies for designing catalysts with improved efficiency and reliability are developed, including nanostructuring,¹⁵ optimizing hydrogen binding energy,¹⁶ interaction with the supporting material,¹⁷ and exploiting hybrid structures.¹¹

Graphene is an excellent substrate to host active nanomaterials for energy applications due to its high conductivity, large surface area, flexibility, and chemical stability. In recent years, although decoration of nanoparticles on graphene oxide (GO) has been shown, rational design and controllable synthesis of strongly coupled inorganic/graphene hybrids remains a long-standing challenge for developing advanced catalysts and energy-storage materials.¹⁸ One of the biggest problems hindering the integration of nanoparticles with graphene sheets is the stability of the interaction between them in addition to regulating the reduction of GO.¹⁹

Here we report a general two-step method for growing carbide nanocrystals on reduced graphene oxide (RGO) sheets. Glucose is used as stabilizing agent and carbon precursor as well as the reducing agent of GO. The resulting Mo₂C/RGO hybrid demonstrates high HER electrocatalytic activity with overpotential (η) of ~70 mV and small Tafel slope of 54 mV dec⁻¹ (at a mass loading of 0.285 mg cm⁻²). It is assumed that the encapsulation phase caused a unique host-guest electronic interaction change.²⁰ As a result, catalytic functionality can be achieved on the outside surface.

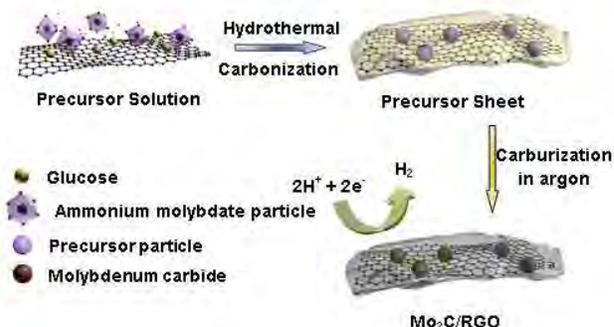


Fig. 1 Synthetic procedure of Mo₂C with graphene sheets.

As illustrated in Fig. 1 the Mo₂C/RGO hybrid was synthesized firstly by hydrothermal carbonization (HTC) reaction of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) and glucose in a GO suspension at 180 °C. Under hydrothermal conditions, amorphous Mo₂C coalesces into 3D-like particles around 50 nm in the absence of GO sheets (Fig. 2a). The presence of GO results in the reduction of particle size (around 10 nm) and significantly accelerates the carbonization reaction (Fig. 2b).²¹ The stark morphological difference (Fig. S1) revealed by scanning electron microscopy (SEM) highlights the important role of GO as an effective supporting material for growing nanostructured materials. Glucose realized its value by stabilizing the Mo₂C seeds and helping to reduce GO.²² A thermal treatment of the hydrothermal product in argon at 750 °C gave rise to the final hybrid materials. During the process, amorphous Mo₂C was carburized and GO was finally reduced to RGO. Transmission electron microscopy (TEM) images further disclose the stabilizing function of glucose (Fig. 2c). A thickness increment can be observed by the comparison of naked GO sheets (Fig. 2d and Fig. S2), which is caused by the carbonization of glucose.²¹

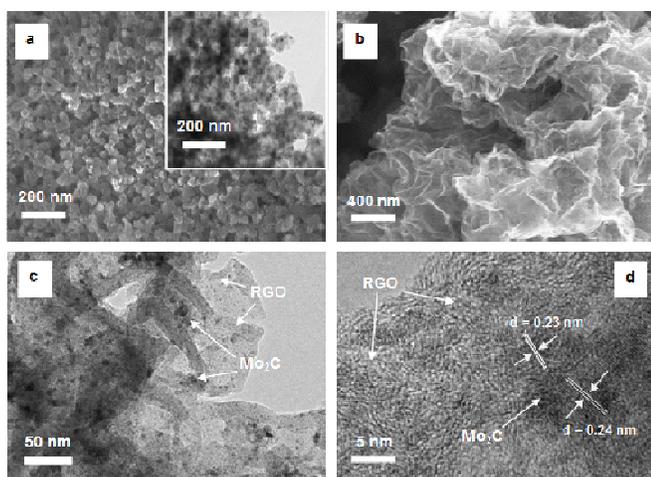


Fig. 2 a,b) SEM images of the bare Mo₂C nanoparticles and the Mo₂C/RGO hybrid. The inset in (a) shows the TEM image of the annealed bare Mo₂C nanoparticles. c) TEM image of the Mo₂C/RGO hybrid. d) HRTEM image of the Mo₂C stabilized on graphene support.

The Mo₂C/RGO hybrid was characterized by X-ray diffraction (XRD), and the patterns of hydrothermal and carburized Mo₂C/RGO are shown in Fig. 3a. Comparing to the GO pattern (Fig. S3), the disappearance of the 10.89° peak confirms the reduction of the GO sheets.²³ The broad diffraction peak (down) located at $2\theta \approx 23^\circ$ is assigned to amorphous carbon and the (002) plane of stacked graphene sheets,^{24,25} while the sharp peak of the carburized product is consistent with the reference XRD patterns of hexagonal Mo₂C (JCPDS No. 00-035-0787). No peak of byproducts can be observed, indicating effectiveness of the synthetic method to fabricate pure

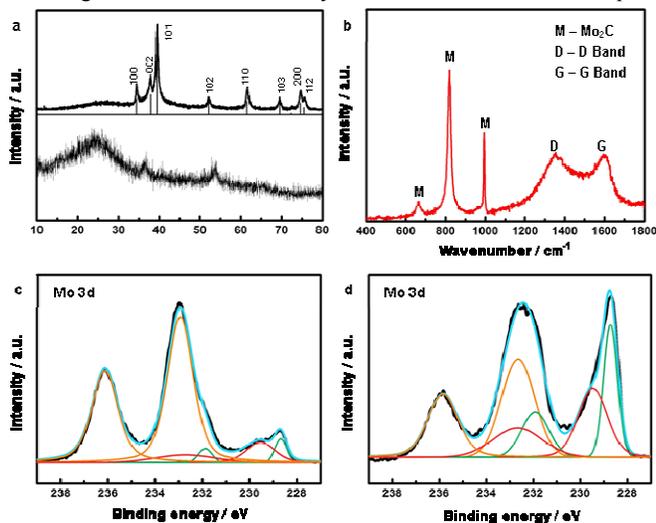


Fig. 3 a) XRD patterns of the hydrothermal product (down) and the carburized (up) Mo₂C/RGO hybrid. b) Raman spectrum of the Mo₂C/RGO hybrid. c,d) XPS Mo 3d spectra (without background, black) and the fitting peaks (cyan) of bare Mo₂C (c) and Mo₂C/RGO (d). MoO₃: orange, MoO₂: red, Mo₂C: green.

phase of Mo₂C on graphene support. The Raman spectrum (Fig. 3b) of the Mo₂C/RGO shows characteristic bands of molybdenum carbide,²⁶ as the main product, and the conclusion is in agreement with XRD patterns. Also D band at 1350 cm⁻¹ and G band at 1580 cm⁻¹, corresponding to the disordered graphitic carbon and the Eg vibration of the sp²-bonded carbon atoms, respectively, are observed. The D/G intensity ratio (1.024) indicates more graphene domains formed on RGO sheets through annealing, which enhances

the electrical conductivity of RGO sheets and thus facilitates the charge transfer.²⁷

To probe the electronic structures on the surface of the catalysts, Mo₂C and Mo₂C/RGO were analyzed by X-ray photoelectron spectroscopy (XPS) (Fig. 3c and Fig. 3d).²⁸ In accordance with previous studies, the surfaces of the catalysts can be contaminated with molybdenum oxides (MoO₂ and MoO₃) when exposed to air.⁴ The abundance of Mo in the form of Mo₂C is more than 20% higher in Mo₂C/RGO than in Mo₂C. Considering the same preparing and storage condition, the quantitative analysis of XPS intensities reveals different degrees of surface contamination, indicating a better stability in our hybrid materials.⁶ The reduction of GO to RGO is also confirmed by C 1s spectrum in the XPS measurement (Fig. S4).

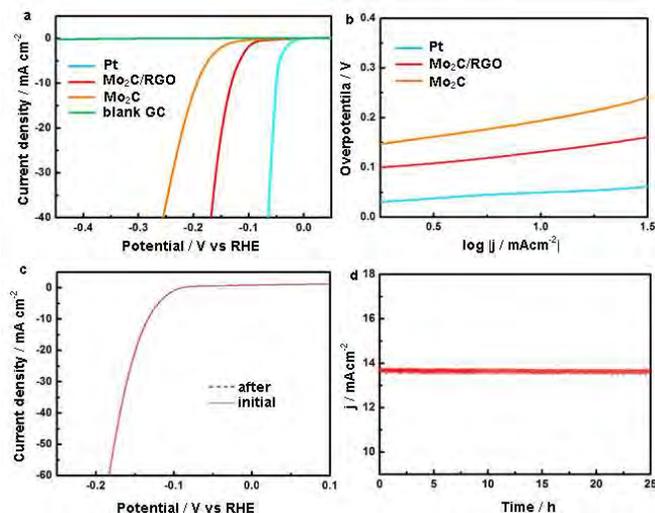


Fig. 4 a) Polarization curves of various samples as indicated. b) Corresponding Tafel plots. c) Durability test showing negligible current loss after 1000 CV cycles. Inset: time dependence of current density under static overpotential of 140 mV.

We investigated the electrocatalytic HER activities of the Mo₂C/RGO hybrid material deposited on a glassy carbon electrode in 0.5 M H₂SO₄ solution using a typical three-electrode setup, as described in the experimental section. As a control experiment, we also performed measurements using a commercial Pt catalyst (5 wt% Pt on Vulcan carbon black) exhibiting high HER catalytic activity with nearly zero onset overpotential and high current density. The polarization curve (*i*-*V* plot, not *i*R corrected) demonstrating the HER activity of Mo₂C/RGO hybrid on a glassy carbon electrode (Fig. 4a) is compared with a bare glassy carbon control. A low overpotential voltage ~70 mV can be observed and the cathodic current rose rapidly under more negative potentials. Notably, bare Mo₂C without graphene support exhibited lower HER performance and relatively high Tafel slope, although the curve trend is similar to the supported material. The overpotential for driving a current of 10 mA cm⁻² (η_{10}) which is useful metric for comparing catalysts for solar hydrogen production was determined to be 130 mV. To compare with other representative nonprecious metal catalysts, the mass activity at 150 mV was further measured to be ~77 mA mg⁻¹, making the hybrid one of the best HER catalysts among recently reported Mo-based electrocatalysts.^{5,7,15,29} The linear portions of the Tafel plots (Fig. 4b) were fit to the Tafel equation ($\eta = b \log j + a$, where *j* is the current density and *b* is the Tafel slope), yielding Tafel slopes of ~30, ~57.3 and ~76.7 mV decade⁻¹ for Pt, the Mo₂C/RGO hybrid and free Mo₂C, respectively. The slope (b) of 76.7 mV dec⁻¹ and 57.3 mV dec⁻¹ have ruled out the possibility that the discharge reaction is the rate-determining step, but without powerful

mechanistic analysis technique only speculation can be raised, because the measured Tafel slopes are different from the limiting slopes of 29, 38 and 116 mV dec⁻¹.^{3, 30} These results demonstrate dramatic effects of RGO hybrid in enhancing the activity of the loaded materials. It is suggested that the graphene support and the graphitized carbon can substantially increase the conductivity of the synthesized catalysts, providing high surface area to contact with electrolyte.

Stability in acid media is another important criterion for a good electrocatalyst. To assess this, we cycled the Mo₂C/RGO hybrid catalyst continuously for 1000 cycles. Only negligible difference is afforded in the curves as shown in Fig. 4c. Fig. 4d shows the long-term stability tested by electrolysis at a fixed potential. The catalytic currents remain at around 13.7 mA cm⁻² over 24 h demonstrating that Mo₂C/RGO hybrid is stable under experimental conditions employed for this system.

Conclusions

In conclusion, a carbon layer stabilized Mo₂C/RGO composites was successfully prepared by in a universal two-step method. Glucose functions as stabilizing agent, carbon precursor and reducing agent for GO. Mo₂C nanocrystals are dispersed on graphene sheets and stabilized by outer graphitic layers. With excellent electrical coupling and large surface area for facile contact with electrolyte, the Mo₂C/RGO hybrid exhibits excellent HER activity and stability revealing the effectiveness of our synthetic method. We believe that the present synthetic route can be further extended to produce other in situ growing metal carbide/carbon hybrid materials with promising applications for electrocatalytic water splitting, supercapacitors and fuel cells.

This work was financially supported by National Natural Science Foundation of China (21373083), SRF for ROCS, SEM, SRFDP, Programme for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

Notes and references

^a Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.

^b Centre for Clean Environment and Energy, Gold Coast Campus, Griffith University, Queensland 4222, Australia.

Correspondence and requests for materials should be addressed to H.G.Y. (hgyang@ecust.edu.cn).

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

- N. S. Lewis and D. G. Nocera, *Proceedings of the National Academy of Sciences*, 2006, **103**, 15729-15735.
- J. O. M. Bockris, *International Journal of Hydrogen Energy*, 2002, **27**, 731-740.
- T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets and D. G. Nocera, *Chemical Reviews*, 2010, **110**, 6474-6502.
- H. Vrubel and X. Hu, *Angewandte Chemie International Edition*, 2012, **51**, 12703-12706.
- W.-F. Chen, S. Iyer, S. Iyer, K. Sasaki, C.-H. Wang, Y. Zhu, J. T. Muckerman and E. Fujita, *Energy & Environmental Science*, 2013, **6**, 1818.
- C. Wan, Y. N. Regmi and B. M. Leonard, *Angewandte Chemie*, 2014, **126**, 6525-6528.
- D. H. Youn, S. Han, J. Y. Kim, J. Y. Kim, H. Park, S. H. Choi and J. S. Lee, *ACS Nano*, 2014, **8**, 5164-5173.
- W.-F. Chen, K. Sasaki, C. Ma, A. I. Frenkel, N. Marinkovic, J. T. Muckerman, Y. Zhu and R. R. Adzic, *Angewandte Chemie International Edition*, 2012, **51**, 6131-6135.
- B. Cao, G. M. Veith, J. C. Neufeld, R. R. Adzic and P. G. Khalifah, *Journal of the American Chemical Society*, 2013, **135**, 19186-19192.
- T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch and I. Chorkendorff, *Science*, 2007, **317**, 100-102.
- Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, *Journal of the American Chemical Society*, 2011, **133**, 7296-7299.
- E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, *Journal of the American Chemical Society*, 2013.
- E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, *Angewandte Chemie International Edition*, 2014, **53**, 5427-5430.
- R. B. Levy and M. Boudart, *Science*, 1973, **181**, 547-549.
- L. Liao, S. Wang, J. Xiao, X. Bian, Y. Zhang, M. D. Scanlon, X. Hu, Y. Tang, B. Liu and H. H. Girault, *Energy & Environmental Science*, 2014.
- R. Subbaraman, D. Tripkovic, K.-C. Chang, D. Strmcnik, A. P. Paulikas, P. Hirunsit, M. Chan, J. Greeley, V. Stamenkovic and N. M. Markovic, *Nat Mater*, 2012, **11**, 550-557.
- C. Tsai, F. Abild-Pedersen and J. K. Nørskov, *Nano Letters*, 2014.
- C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, *Angewandte Chemie International Edition*, 2009, **48**, 7752-7777.
- S. Yang, X. Feng, S. Ivanovici and K. Müllen, *Angewandte Chemie International Edition*, 2010, **49**, 8408-8411.
- Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing, N. J. Bjerrum and Q. Li, *Angewandte Chemie*, 2014, **126**, 3823-3823.
- D. Krishnan, K. Raidongia, J. Shao and J. Huang, *ACS Nano*, 2013.
- C. Zhu, S. Guo, Y. Fang and S. Dong, *ACS Nano*, 2010, **4**, 2429-2437.
- H. M. A. Hassan, V. Abdelsayed, A. E. R. S. Khder, K. M. AbouZeid, J. Turner, M. S. El-Shall, S. I. Al-Resayes and A. A. El-Azhary, *Journal of Materials Chemistry*, 2009, **19**, 3832-3837.
- C. Hu, H. Cheng, Y. Zhao, Y. Hu, Y. Liu, L. Dai and L. Qu, *Advanced Materials*, 2012, **24**, 5493-5498.
- H. Wang, A. Wang, X. Wang and T. Zhang, *Chemical Communications*, 2008, 2565-2567.
- T.-C. Xiao, A. P. E. York, H. Al-Megren, C. V. Williams, H.-T. Wang and M. L. H. Green, *Journal of Catalysis*, 2001, **202**, 100-109.
- Y. Hou, T. Huang, Z. Wen, S. Mao, S. Cui and J. Chen, *Advanced Energy Materials*, 2014, DOI: 10.1002/aenm.201400337.
- J. A. Schaidle, A. C. Lausche and L. T. Thompson, *Journal of Catalysis*, 2010, **272**, 235-245.
- W.-F. Chen, J. T. Muckerman and E. Fujita, *Chem Commun (Camb)*, 2013, **49**, 8896-8909.
- J. O. M. Bockris and E. C. Potter, *Journal of The Electrochemical Society*, 1952, **99**, 169-186.