

Ultrathin MoS₂ Nanosheets Supported on N-doped Carbon Nanoboxes with Enhanced Lithium Storage and Electrocatalytic Properties

Xin-Yao Yu, Han Hu, Yawen Wang, Hongyu Chen, and Xiong Wen (David) Lou*

Abstract: Molybdenum disulfide (MoS₂) has received considerable interest for electrochemical energy storage and conversion. In this work, we have designed and synthesized a unique hybrid hollow structure by growing ultrathin MoS₂ nanosheets on N-doped carbon shells (denoted as C@MoS₂ nanoboxes). The N-doped carbon shells can greatly improve the conductivity of the hybrid structure and effectively prevent the aggregation of MoS₂ nanosheets. The ultrathin MoS₂ nanosheets could provide more active sites for electrochemical reactions. When evaluated as an anode material for lithium-ion batteries, these C@MoS₂ nanoboxes show high specific capacity of around 1000 mAhg⁻¹, excellent cycling stability up to 200 cycles, and superior rate performance. Moreover, they also show enhanced electrocatalytic activity for the electrochemical hydrogen evolution.

Hollow nanostructured metal oxides/sulfides as an important family of functional materials are of great interest in recent years.^[1–4] In particular, the presence of a well-defined interior void with functional shells endows them with potential applications in energy conversion and storage.^[3,5–8] For example, Wang and co-workers have synthesized several kinds of multishelled metal oxides hollow microspheres and investigated their interesting shell-number-dependent properties in lithium-ion batteries (LIBs) and dye-sensitized solar cells.^[3,5,9] We have recently developed a simple sacrificial template method to synthesize uniform Ni_xCo_{3–x}S₄ hollow nanoprisms with tunable composition which exhibit excellent pseudocapacitive properties.^[8] Despite the great advances, the intrinsic poor electronic/ionic conductivity of metal oxides/sulfides severely limits their practical application in energy conversion and storage devices.

Molybdenum disulfide (MoS₂), a representative layered two-dimensional (2D) material, has received considerable attention in energy conversion and storage.^[10–19] MoS₂ has been suggested as a promising anode material for LIBs because it can deliver very high specific capacities.^[12–14] However, the capacity fading and poor rate performance greatly limit their application. To address these issues, various strategies have been proposed to improve the electrochemical performance of MoS₂ by broadening the interlayer distance of MoS₂, tuning the morphology at nanoscale or using carbonaceous materials as the conductive matrix.^[3,15,20–28] On the other hand, MoS₂-based electrocatalysts have been considered as promising alternatives for platinum for the hydrogen evolution reaction (HER).^[3,11,16] Increasing the number of exposed active sites on the edges and improving the electrical conduction by choosing suitable conductive substrates are two effective methods to enhance the electrocatalytic efficiency of MoS₂.^[11,16,29,30]

Herein, we report the rational design and synthesis of a novel nanosheets-on-box nanostructure composed of ultrathin MoS₂ nanosheets on N-doped carbon nanoboxes designated as C@MoS₂ nanoboxes. As expected, when evaluated as an anode material for LIBs, these C@MoS₂ nanoboxes manifest high specific capacity of around 1000 mAhg⁻¹, excellent cycling stability up to 200 cycles, and superior rate performance. Moreover, they also show enhanced electrocatalytic activity for the electrochemical HER.

The multistep synthesis process for the C@MoS₂ nanoboxes is illustrated in Figure 1. Very uniform α -Fe₂O₃ nanocubes with an average size of about 500 nm (Figure S1 a and b

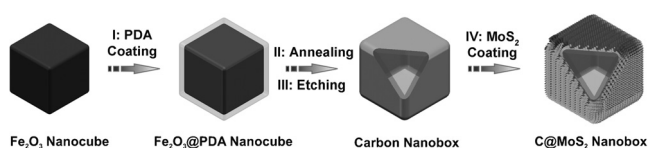


Figure 1. Illustration of the synthesis process of C@MoS₂ nanoboxes.

in the Supporting Information) synthesized by a facile coprecipitation method^[31] are used as templates to synthesize N-doped carbon nanoboxes. In the first step, Fe₂O₃ nanocubes are successfully coated with a uniform and smooth layer of polydopamine (PDA) with a thickness of around 40 nm (Figure S1 c and d). In step II, these core-shell Fe₂O₃@PDA nanocubes are transformed into Fe₃O₄@C nanocubes after carbonization in N₂ (Figure S2).^[32] The Fe₃O₄ core can be easily dissolved by HCl to obtain carbon nanoboxes (step III). Lastly, a layer of ultrathin MoS₂ nanosheets is successfully grown on the surface of carbon nanoboxes through a facile

[*] Dr. X. Y. Yu, Dr. H. Hu, Prof. X. W. Lou
School of Chemical and Biomedical Engineering
Nanyang Technological University
62 Nanyang Drive, Singapore 637459 (Singapore)
E-mail: xwlou@ntu.edu.sg
davidlou88@gmail.com

Homepage: <http://www.ntu.edu.sg/home/xwlou/>

Dr. X. Y. Yu
Nano-materials and Environment Detection Laboratory
Hefei Institutes of Physical Science, Chinese Academy of Sciences
Hefei 230031 (P.R. China)

Y. W. Wang, Prof. H. Y. Chen
Division of Chemistry and Biological Chemistry
Nanyang Technological University
Singapore 637371 (Singapore)

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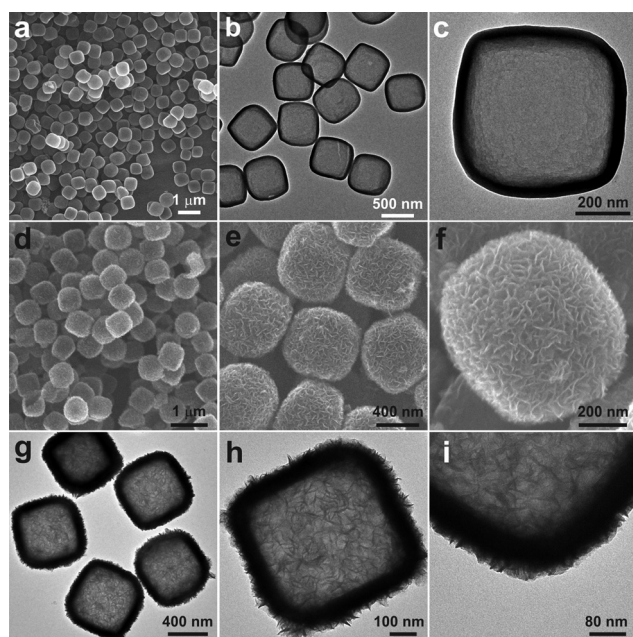


Figure 2. FESEM (a) and TEM (b,c) images of carbon nanoboxes, and FESEM (d–f) and TEM (g–i) images of C@MoS₂ nanoboxes.

solvothermal method, leading to the formation of C@MoS₂ nanoboxes (step IV).

As shown in the low-magnification field-emission scanning electron microscopy (FESEM) image in Figure 2a, the carbon nanoboxes obtained are also very uniform with an average size of about 580 nm. The hollow interior of carbon nanoboxes is further elucidated by transmission electron microscopy (TEM) (Figure 2b,c). The obtained carbon nanoboxes are dispersed in *N,N*-dimethylformamide (DMF) solvent for further growth of MoS₂ nanosheets. The X-ray powder diffraction (XRD) pattern of the obtained product is quasi-amorphous (Figure S3).^[11] After the solvothermal process, the surface of carbon nanoboxes is uniformly covered with MoS₂ nanosheets (Figure 2d,e). The thickness of the MoS₂ shell is about 35 nm. The magnified FESEM image reveals that the MoS₂ layer is randomly assembled by ultrathin nanosheets (Figure 2f). TEM images (Figure 2g–i) confirm the same structural features as shown by the above FESEM observations. It is worth noting that there is no visible interlayer gap observed between the carbon shell and the MoS₂ layer (Figure 2i), indicating that the MoS₂ nanosheets are strongly anchored on the carbon nanoboxes. This can be ascribed to the strong interactions between the functional groups on carbon nanoboxes and the Mo precursor. The uniformly distributed functional groups on carbon nanoboxes could not only provide growing sites for MoS₂ but also prevent the aggregation of formed particles. In the absence of carbon nanoboxes, severely aggregated nanosheets-assembled particles are produced (Figure S4).

The as-obtained C@MoS₂ nanoboxes are further annealed at 700 °C in H₂ for 2 h to obtain highly crystalline MoS₂ nanosheets. All of the diffraction peaks of the annealed product can be perfectly assigned to hexagonal MoS₂ (JCPDS card no. 37-1492; Figure S3). The (002) diffraction peak is

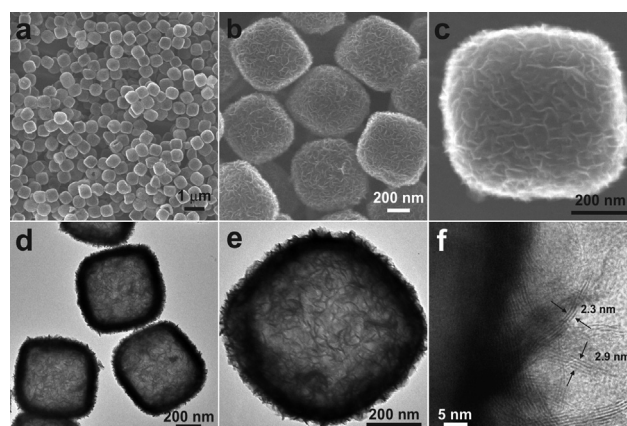


Figure 3. FESEM (a–c) and TEM images (d–f) of C@MoS₂ nanoboxes after annealing in H₂ at 700 °C for 2 h.

shifted to a lower angle of 14.17° compared to the standard angle of 16.71°, indicating an expansion of the interlayer distance.^[23] The FESEM and TEM images in Figure 3a–e show that the nanosheets-on-box nanostructure is perfectly retained. A high-resolution TEM image demonstrates that each MoS₂ nanosheet is composed of three to five layers only (Figure 3f). The interlayer distance (0.66 nm) of MoS₂ on carbon nanoboxes is larger than that of natural MoS₂ (0.62 nm), further verifying the expanded interlayer spacing. This may be attributed to the substrate effect and the ultrathin feature of the MoS₂ nanosheets, leading to formation of an undulated structure.^[23] Raman spectra further demonstrate the few-layered ultrathin nature of MoS₂ nanosheets on carbon nanoboxes (Figure S5).^[33] X-ray photoelectron spectroscopy (XPS) measurements confirm that the annealed C@MoS₂ nanoboxes contain Mo, S, C, N, and O (Figure S6a). The binding energies of Mo 2d_{5/2} and Mo 2d_{3/2} peaks are located at 225.8 and 228.9 eV, respectively, which confirms the Mo⁴⁺ state of Mo in MoS₂ (Figure S6b). The binding energies at 162.6 and 163.8 eV in the S 2p spectrum are attributed to the S^{2–} of MoS₂ (Figure S6c). The high-resolution XPS spectra of C 1s and N 1s verify the successful doping of N in the carbon nanoboxes (Figure S6d,e). The O 1s spectrum confirms the existence of oxygen-containing functional groups (Figure S7). As determined by thermogravimetric analysis, the content of MoS₂ in the nanocomposite is approximately 82 wt% (Figure S8). In virtue of the hollow nanostructure and ultrathin nanosheets, these annealed C@MoS₂ nanoboxes possess a large specific surface area of 123.7 m² g^{–1}, which is higher than that of annealed bare MoS₂ (82.2 m² g^{–1}; Figure S9).

The lithium storage properties of annealed C@MoS₂ nanoboxes are first evaluated by cyclic voltammetry (CV) (Figure S10). In the first cycle, the strong cathodic peak at ca. 1.07 V can be assigned to the insertion of Li⁺ ions into the interlayer MoS₂ lattice to form Li_xMoS₂, whereas the other peak at ca. 0.54 V is due to a further reaction between Li_xMoS₂ and Li⁺, resulting in the formation of metallic Mo nanoparticles and Li₂S.^[12,14,22] In the subsequent anodic scan, a pronounced peak at about 2.34 V can be attributed to the delithiation of Li₂S to sulfur.^[10,23] In the following cycles, two

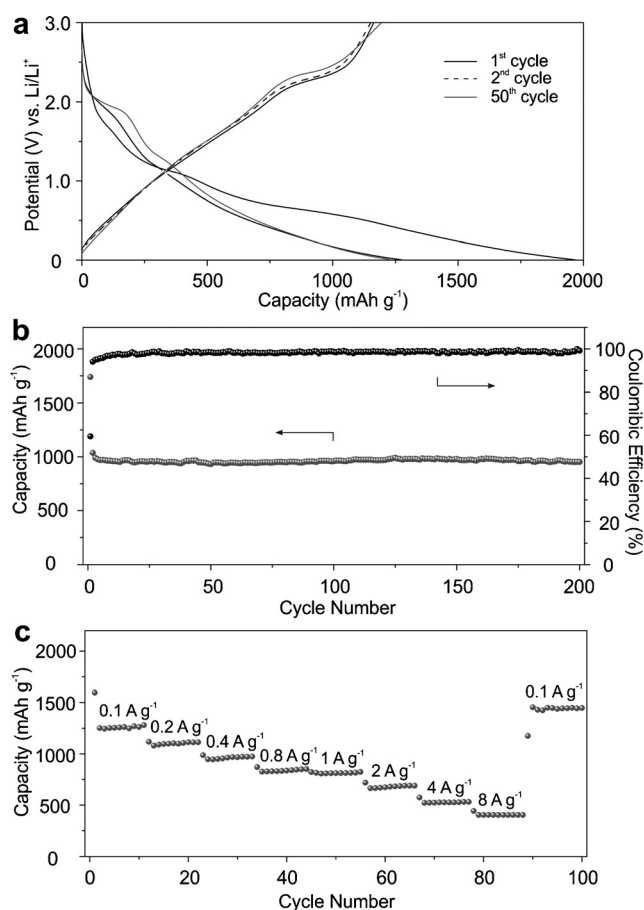


Figure 4. Electrochemical lithium-storage properties of annealed C@MoS₂ nanoboxes: a) discharge-charge voltage profiles for the 1st, 2nd, and 50th cycles at a current density of 0.1 A g⁻¹; b) cycling performance at a current density of 0.4 A g⁻¹ and the corresponding Coulombic efficiency; c) rate performance at various current rates.

cathodic peaks emerge at around 1.88 and 1.17 V, which are related to a multistep lithium insertion mechanism.^[21] Figure 4a shows the representative discharge-charge voltage profiles of the annealed C@MoS₂ nanoboxes at a current density of 0.1 A g⁻¹. The C@MoS₂ electrode delivers high first-cycle discharge and charge capacities of 1966 and 1164 mAh g⁻¹ respectively, corresponding to a Coulombic efficiency (CE) of 59.2%. The initial loss is mainly caused by the decomposition of electrolyte or some irreversible processes such as the formation of a solid-electrolyte interface layer during the first cycle.^[14,21] A discharge capacity of 1274 mAh g⁻¹ is delivered in the second cycle, followed by a charge capacity of 1151 mAh g⁻¹, giving rise to a high CE of about 93%. The discharge capacity remains at about 1233 mAh g⁻¹ after 50 cycles at a current rate of 0.1 A g⁻¹ (Figures 4a and S11). Moreover, the C@MoS₂ nanoboxes can be cycled with high stability at higher current densities of 0.4 and 1.0 A g⁻¹ (Figures 4b and S12). Remarkably, a reversible capacity of 952 mAh g⁻¹ at a current rate of 0.4 A g⁻¹ after 200 cycles can still be retained, with CE of almost 100% throughout the cycling (Figure 4b). The structural integrity of C@MoS₂ can still be maintained after charging/discharging for 200 cycles (Figure S13) although the particles become

significantly larger due to the formation of a gel-like polymeric layer. The rate capability is evaluated at different current densities ranging from 0.1 to 8 A g⁻¹ (Figure 4c). As can be seen, the specific capacities are 1280, 1113, 974, 851, 824, 689, 531, and 403 mAh g⁻¹ at current densities of 0.1, 0.2, 0.4, 0.8, 1, 2, 4, and 8 A g⁻¹, respectively. When the current density is reduced back to 0.1 A g⁻¹, the capacity of the C@MoS₂ electrode quickly recovers to as high as 1448 mAh g⁻¹, probably due to the growth of a gel-like polymeric layer and activation of electrode materials.^[14,21] The cycling stability and rate performance of these C@MoS₂ nanoboxes are superior to annealed bare MoS₂ (Figure S14). Electrochemical impedance spectroscopy measurements show that C@MoS₂ nanoboxes show a smaller diameter of the high-frequency semicircle than bare MoS₂, indicating smaller solid state interface layer resistance (Figure S15).

In addition, the electrocatalytic activity of these C@MoS₂ nanoboxes for HER is also investigated. Previous reports have shown that amorphous MoS₂ materials generally exhibit higher electrocatalytic activity than crystallized samples.^[11,29] As such, another similar nanosheets-on-box architecture is constructed with high-temperature annealed carbon nanoboxes as substrates for amorphous MoS₂ coating (Figure S16). The C@MoS₂ nanoboxes exhibit superior activity over bare MoS₂ in both Tafel slope and cathodic current (Figure S17a,b). A Tafel slope of 55 mV dec⁻¹ is obtained for the C@MoS₂ nanoboxes. The C@MoS₂ nanoboxes electrode only requires overpotentials of 165 and 200 mV to give current densities of 10 and 35 mA cm⁻², respectively. To assess the long-term stability of the C@MoS₂ nanoboxes catalyst, potential sweeps are conducted continuously for 1000 cycles. As can be seen, the polarization curve remains largely unchanged compared to the initial one (Figure S17c).

In summary, a novel hybrid nanostructure of ultrathin MoS₂ nanosheets supported on N-doped carbon nanoboxes has been successfully synthesized. These well-defined C@MoS₂ nanoboxes exhibit enhanced lithium storage and electrocatalytic properties, which could be attributed to their unique structure. Specifically, the N-doped carbon nanoboxes substrate has relatively high conductivity. The hollow structure of carbon nanoboxes and ultrathin building blocks can effectively alleviate the strain caused by the large volume change during cycling. The ultrathin MoS₂ nanosheets possess a high surface area for electrode/electrolyte interface and the diffusion length of electrons and ions can be effectively reduced. All these merits would undoubtedly contribute to the electrochemical performance of the electrode materials, leading to high capacity, long cycle life, and superior rate performance for lithium-ion batteries and low Tafel slope and high cathodic current for hydrogen evolution reaction.

Keywords: lithium-ion batteries · molybdenum disulfide · MoS₂ · water splitting

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[1] Z. Y. Wang, L. Zhou, X. W. Lou, *Adv. Mater.* **2012**, *24*, 1903–1911.

- [2] X. Y. Lai, J. E. Halpert, D. Wang, *Energy Environ. Sci.* **2012**, 5, 5604–5618.
- [3] L. Zhang, H. B. Wu, Y. Yan, X. Wang, X. W. Lou, *Energy Environ. Sci.* **2014**, 7, 3302–3306.
- [4] J. B. Joo, Q. Zhang, I. Lee, M. Dahl, F. Zaera, Y. D. Yin, *Adv. Funct. Mater.* **2012**, 22, 166–174.
- [5] S. M. Xu, C. M. Hessel, H. Ren, R. B. Yu, Q. Jin, M. Yang, H. J. Zhao, D. Wang, *Energy Environ. Sci.* **2014**, 7, 632–637.
- [6] G. Q. Zhang, B. Y. Xia, C. Xiao, L. Yu, X. Wang, Y. Xie, X. W. Lou, *Angew. Chem. Int. Ed.* **2013**, 52, 8643–8647; *Angew. Chem.* **2013**, 125, 8805–8809.
- [7] J. Y. Wang, N. L. Yang, H. J. Tang, Z. H. Dong, Q. Jin, M. Yang, D. Kisailus, H. J. Zhao, Z. Y. Tang, D. Wang, *Angew. Chem. Int. Ed.* **2013**, 52, 6417–6420; *Angew. Chem.* **2013**, 125, 6545–6548.
- [8] L. Yu, L. Zhang, H. B. Wu, X. W. Lou, *Angew. Chem. Int. Ed.* **2014**, 53, 3711–3714; *Angew. Chem.* **2014**, 126, 3785–3788.
- [9] Z. H. Dong, H. Ren, C. M. Hessel, J. Y. Wang, R. B. Yu, Q. Jin, M. Yang, Z. D. Hu, Y. F. Chen, Z. Y. Tang, H. J. Zhao, D. Wang, *Adv. Mater.* **2014**, 26, 905–909.
- [10] X. Xu, Z. Y. Fan, S. J. Ding, D. M. Yu, Y. P. Du, *Nanoscale* **2014**, 6, 5245–5250.
- [11] Y. Yan, X. M. Ge, Z. L. Liu, J. Y. Wang, J. M. Lee, X. Wang, *Nanoscale* **2013**, 5, 7768–7771.
- [12] L. C. Yang, S. N. Wang, J. J. Mao, J. W. Deng, Q. S. Gao, Y. Tang, O. G. Schmidt, *Adv. Mater.* **2013**, 25, 1180–1184.
- [13] K. Chang, W. X. Chen, *Chem. Commun.* **2011**, 47, 4252–4254.
- [14] K. Chang, W. X. Chen, *ACS Nano* **2011**, 5, 4720–4728.
- [15] P. P. Wang, H. Y. Sun, Y. J. Ji, W. H. Li, X. Wang, *Adv. Mater.* **2014**, 26, 964–969.
- [16] Y. G. Li, H. L. Wang, L. M. Xie, Y. Y. Liang, G. S. Hong, H. J. Dai, *J. Am. Chem. Soc.* **2011**, 133, 7296–7299.
- [17] Z. Hu, L. X. Wang, K. Zhang, J. B. Wang, F. Y. Cheng, Z. L. Tao, J. Chen, *Angew. Chem. Int. Ed.* **2014**, 53, 12794–12798; *Angew. Chem.* **2014**, 126, 13008–13012.
- [18] G. Z. Sun, J. Q. Liu, X. Zhang, X. W. Wang, H. Li, Y. Yu, W. Huang, H. Zhang, P. Chen, *Angew. Chem. Int. Ed.* **2014**, 53, 12576–12580; *Angew. Chem.* **2014**, 126, 12784–12788.
- [19] L. N. Ye, C. Z. Wu, W. Guo, Y. Xie, *Chem. Commun.* **2006**, 4738–4740.
- [20] X. H. Cao, Y. M. Shi, W. H. Shi, X. H. Rui, Q. Y. Yan, J. Kong, H. Zhang, *Small* **2013**, 9, 3433–3438.
- [21] X. Xu, Z. Y. Fan, X. Y. Yu, S. J. Ding, D. M. Yu, X. W. Lou, *Adv. Energy Mater.* **2014**, 4, 1400902.
- [22] H. Liu, D. W. Su, R. F. Zhou, B. Sun, G. X. Wang, S. Z. Qiao, *Adv. Energy Mater.* **2012**, 2, 970–975.
- [23] F. Zhou, S. Xin, H. W. Liang, L. T. Song, S. H. Yu, *Angew. Chem. Int. Ed.* **2014**, 53, 11552–11556; *Angew. Chem.* **2014**, 126, 11736–11740.
- [24] J. Wang, J. L. Liu, D. L. Chao, J. X. Yan, J. Y. Lin, Z. X. Shen, *Adv. Mater.* **2014**, 26, 7162–7169.
- [25] C. B. Zhu, X. K. Mu, P. A. van Aken, Y. Yu, J. Maier, *Angew. Chem. Int. Ed.* **2014**, 53, 2152–2156; *Angew. Chem.* **2014**, 126, 2184–2188.
- [26] G. D. Du, Z. P. Guo, S. Q. Wang, R. Zeng, Z. X. Chen, H. K. Liu, *Chem. Commun.* **2010**, 46, 1106–1108.
- [27] K. Chang, D. S. Geng, X. F. Li, J. L. Yang, Y. J. Tang, M. Cai, R. Y. Li, X. L. Sun, *Adv. Energy Mater.* **2013**, 3, 839–844.
- [28] S. K. Das, R. Mallavajula, N. Jayaprakash, L. A. Archer, *J. Mater. Chem.* **2012**, 22, 12988–12992.
- [29] Y. Yan, B. Y. Xia, X. M. Ge, Z. L. Liu, J. Y. Wang, X. Wang, *ACS Appl. Mater. Interfaces* **2013**, 5, 12794–12798.
- [30] J. F. Xie, H. Zhang, S. Li, R. X. Wang, X. Sun, M. Zhou, J. F. Zhou, X. W. Lou, Y. Xie, *Adv. Mater.* **2013**, 25, 5807–5813.
- [31] X. Y. Yu, L. Yu, L. F. Shen, X. H. Song, H. Y. Chen, X. W. Lou, *Adv. Funct. Mater.* **2014**, 24, 7440–7446.
- [32] C. Lei, F. Han, D. Li, W. C. Li, Q. Sun, X. Q. Zhang, A. H. Lu, *Nanoscale* **2013**, 5, 1168–1175.
- [33] M. A. Pimenta, E. Del Corro, B. R. Carvalho, C. Fantini, L. M. Malard, *Acc. Chem. Res.* **2015**, 48, 41–47.

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