



Growth of graphene from solid amorphous carbon: A new geometry for control carbon diffusion barrier

Anfeng Zhang^{a,b}, Li Wang^a, Zhenyu Wang^{a,*}, Rende Chen^a, Xiaoping Li^c, Yuanbing Wang^c, Aiyang Wang^{a,b,**}

^a Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, China

^b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China

^c Wuhan Jouleyacht Co., Ltd, Wuhan, 430206, China

ARTICLE INFO

Handling Editor: Mr. Paul Mayrhofer

Keywords:

Amorphous carbon
Annealing
Graphene
Carbon materials
Diffusion

ABSTRACT

As an alternative strategy to fabricate high-quality graphene over a large area, metal catalysis has been attempted at elevated temperatures with solid carbon sources. However, graphene was generally fabricated on the surface of metal catalysis layer using amorphous carbon as solid carbon sources. In this study, a thin Al₂O₃ barrier (1 nm) deposited on an amorphous-C/Ni bilayer stack is demonstrated to enable direct growth of few layer graphene (FLG) identified as 3–4 layers on substrate surface at 700 °C and 800 °C. Moreover, the obtained graphene shows a good transmittance (93%) under the light source of 550 nm. The findings provide a way to directly synthesis FLG on the required substrate at low temperature, which may dramatically broaden the applications range of graphene.

Graphene, a single layer of carbon atoms in a honeycomb crystal structure, offers several special properties including excellent electrical conductivity, thermal conductivity and light transmittance, which make it a promising material for a wide range of applications, particularly in electronic devices [1]. Various approaches, such as mechanical exfoliation, epitaxial growth, chemical vapor deposition (CVD), etc., have been developed to prepare graphene. Recently, solid amorphous carbon could directly transform to the graphene with high-quality and controllable thickness by metal catalysts, which has been receiving considerable attention [2]. Ivan et al. [3], for instance reported the growth of large-area (1 × 1 cm²) and monolayer graphene by different solid carbon sources.

In previous work [4,5], we successfully prepared graphene via Ni-catalyzed crystallization of amorphous carbon (ta-C), and proposed the growth mechanism of graphene. However, graphene was separated from the substrate with the Ni layer, and the additional complex transfer process would bring a large number of defects, which dramatically restricted its applications. Direct preparation of high-quality graphene on substrates still pose an enormous challenge. It was surprise to found

that Tiwari et al. obtained graphene flakes having large surface area with greater homogeneity, by applying pressure on the substrate/Ni/PMMA film during annealing [6]. Hofmann et al. demonstrated that introducing a diffusion barrier of nanometer-thick Al₂O₃ between solid carbon source and catalyst enabled the growth of uniform monolayer graphene at 600 °C [7]. Therefore, controlling the carbon supply during the catalytic transformation of solid carbon sources played a vital role in improving the quality and homogeneity of graphene.

In this study, we fabricated a new geometry that was a ta-C/Ni/Al₂O₃ multilayered film on Si/SiO₂ insulating substrate, in which Al₂O₃ layer acted as diffusion barrier to inhibit the outward diffusion of carbon atoms. As expected, amorphous carbon was directly converted into few layer graphene (FLG) mainly on the substrate/Ni interface via Ni catalysis after annealing. In addition, the influence of Al₂O₃ thickness on the quality, number of layers of graphene was also discussed.

The ta-C/Ni/Al₂O₃ films were deposited in turn on insulating substrate (Si/SiO₂; 15 mm × 15 mm × 0.5 mm) by home-made double bend filtered cathode vacuum arc (FCVA), direct current magnetron

* Corresponding author.

** Corresponding author. Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, China.

E-mail addresses: wangzy@nimte.ac.cn (Z. Wang), aywang@nimte.ac.cn (A. Wang).

<https://doi.org/10.1016/j.vacuum.2023.112106>

Received 10 February 2023; Received in revised form 23 March 2023; Accepted 15 April 2023

Available online 16 April 2023

0042-207X/© 2023 Elsevier Ltd. All rights reserved.

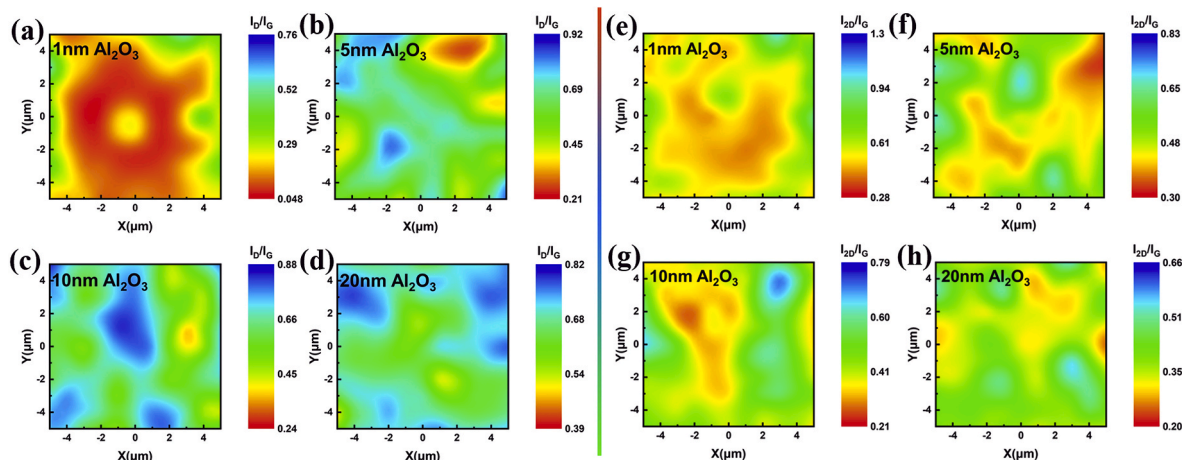


Fig. 1. Raman spectra mapping images of the substrate/FLG obtained by annealing substrate/ta-C/Ni/Al₂O₃ samples at 700 °C. The ratios of I_D/I_G and I_{2D}/I_G at different thickness of Al₂O₃ layer: (a) (e) 1 nm, (b) (f) 5 nm, (c) (g) 10 nm and (d) (h) 20 nm.

sputtering (DCMS) and atomic layer deposition (ALD), respectively. The ta-C film with 2 nm thick was deposited at the Ar flowing rate of 1.5 sccm. The arc current of the graphite target was fixed at 50 A, and the DC substrate bias was set to -80 V. Then, Ni layer with 80 nm thick was deposited on ta-C layer; sputter power of Ni target (purity, 99.9%), substrate bias voltage, and Ar flow rate were set to 0.2 kW, -50 V and 40 sccm, respectively. After that, the sample was put into ALD equipment (CARBOZEN LAB) and Al₂O₃ layer with different thickness of 1 nm, 5 nm, 10 nm and 20 nm, was deposited at 250 °C under the vacuum degree of 2.0×10^{-2} Torr. During the deposition of Al₂O₃, trimethyl aluminum (Al(CH₃)₃, TMA) and H₂O were introduced as reaction sources. The pulse lengths were 1 s in Al₂O₃ deposition sequence, and the purge was always 6 s. The growth rate of Al₂O₃ was 0.1 nm cycle⁻¹. After finishing the deposition process, the substrate/ta-C/Ni/Al₂O₃ sample was placed in a rapid thermal processing furnace (RTP-3S04, Wuhan Jouleyacht Co., Ltd) for annealing treatment. Annealing test was performed at 700 °C and 800 °C for 1 h under the vacuum degree of 2.0×10^{-3} Torr.

When the sample was cooled down to room temperature, FLG would be obtained via etching Ni layer with 1 mol/L FeCl₃ solution for 6–12 h. The obtained FLG covered on substrate after etching Ni layer was named as substrate/FLG.

The surface morphology of the annealed substrate/ta-C/Ni/Al₂O₃ sample was characterized by scanning electron microscope (SEM). The quality of the substrate/FLG was analyzed using Raman spectroscopy (Renishaw inVia Reflex) with a 532 nm excitation wavelength and transmission electron microscope (TEM, Talos F200X) and high-resolution TEM (HRTEM). The optical transmittance of graphene was tested on spectrophotometer (Perkin-Elmer Lambda 950) in the range of 400–1200 nm.

Fig. 1 shows the Raman spectra mapping of the substrate/FLG obtained by annealing substrate/ta-C/Ni/Al₂O₃ sample at 700 °C. The Raman results of as-deposited ta-C, without annealing, can refer to our previous work [8,9]. The ratio of I_D/I_G can reflect the quality of FLG, that the lower ratio suggests a lower defect density [10]. The ratio of

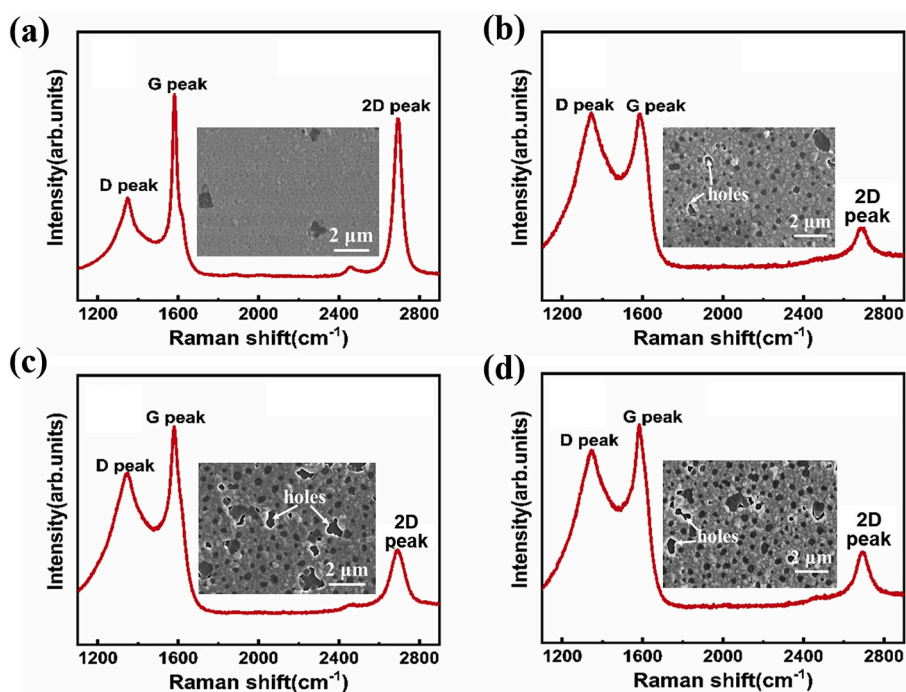


Fig. 2. Raman spectra of the substrate/FLG and corresponding surface morphologies (inserted images) of substrate/ta-C/Ni/Al₂O₃ samples annealed at 800 °C with different thickness of Al₂O₃ layer: (a) 1 nm; (b) 5 nm; (c) 10 nm; (d) 20 nm.

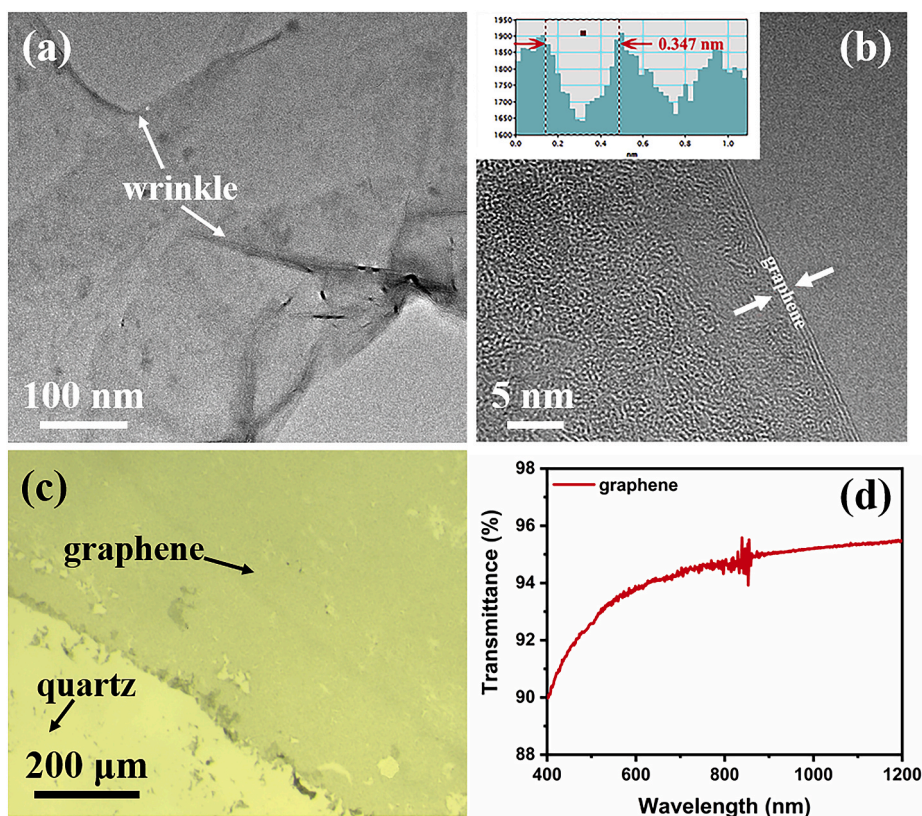


Fig. 3. (a–b) TEM images of the substrate/FLG obtained at the annealing temperature of 800 °C with 1 nm thick Al₂O₃, (c) optical microscope image and (d) transmittance of graphene on quartz substrate.

I_{2D}/I_G represents the number of layers of graphene [11,12]. The ratio mappings of I_D/I_G and I_{2D}/I_G within $10 \mu\text{m} \times 10 \mu\text{m}$ area were shown in Fig. 1a–d and Fig. 1e–h, respectively. When the thickness of Al₂O₃ layer was 1 nm, the ratio of I_D/I_G ranged from 0.048 to 0.29 (Fig. 1a). Fig. 1b illustrated that the ratio of I_D/I_G was varied from 0.21 to 0.75 as the thickness of Al₂O₃ layer increasing to 5 nm, which suggested that the quality of graphene decreased somewhat. With further increase in the thickness of Al₂O₃ layer (10 nm and 20 nm), the ratio of I_D/I_G raised to

over 0.4, as shown in Fig. 1c and d. These results demonstrated that the graphene was obtained when the thickness of Al₂O₃ layer was 1 nm. As displayed in Fig. 1e, when the thickness of Al₂O₃ layer was 1 nm, the I_{2D}/I_G value was between 0.6 and 0.9, which indicates that the generated graphene is of few layers or multilayers. As the thickness of Al₂O₃ layer increased to 5–20 nm, the I_{2D}/I_G value was varied from 0.3 to 0.6, suggesting that the generated graphene is of multilayer. Consequently, according to our findings, the number of graphene layers was difficulty

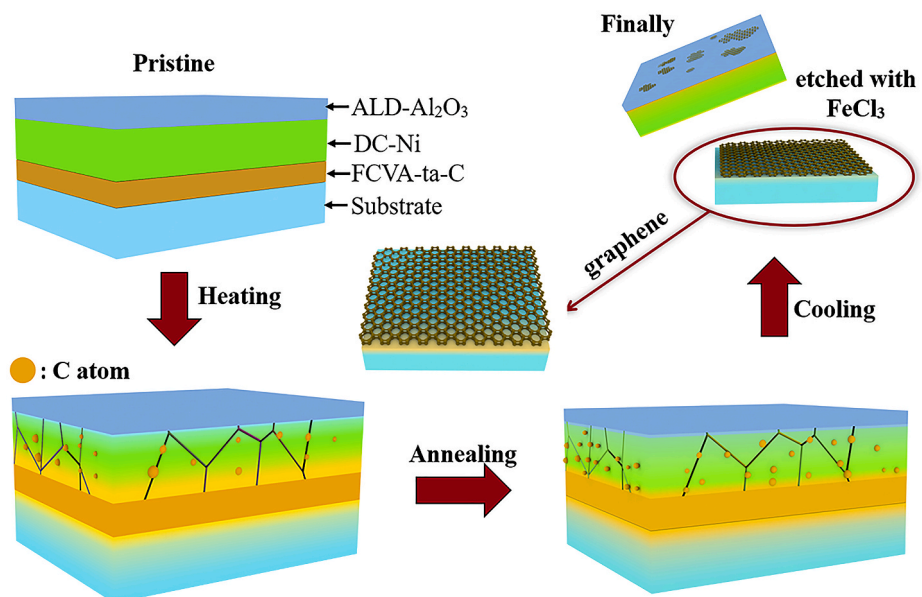


Fig. 4. The schematic diagram of in-situ growth of FLG on substrate surface.

to regulate when thickness of Al₂O₃ layer was over 5 nm.

To exclude the influence of annealing temperature on the quality of FLG, annealing treatment at 800 °C was further performed. Fig. 2 shows the Raman spectra of the substrate/FLG and the surface morphologies of the substrate/ta-C/Ni/Al₂O₃ samples annealed at 800 °C. The results indicated that when the thickness of Al₂O₃ layer was 1 nm, the obtained graphene exhibited the best quality. The ratios of I_D/I_G and I_{2D}/I_G were determined to be 0.35 and 0.81, respectively, indicating that the graphene with few layers was formed. However, the ratios of I_D/I_G and I_{2D}/I_G were changed to be 1.03 and 0.21, respectively, for the sample with 5 nm thick Al₂O₃ layer. This demonstrated the graphene has been seriously damaged, consistent well with the results at 700 °C. When the thickness of Al₂O₃ is 10 nm and 20 nm, the quality of graphene was also poor. This indicated that the thickness of Al₂O₃ layer should be controlled at below 1 nm. Thicker Al₂O₃ layer is not conducive to the crystallization of graphene. In addition, as illustrated in the inserted images of Fig. 2, noted that the sample with 1 nm thick Al₂O₃ layer exhibited more homogeneous and less hole defects compared to other ones.

Fig. 3a and b are the TEM images of the substrate/FLG sample obtained at the annealing temperature of 800 °C for the substrate/ta-C/Ni/Al₂O₃ samples with 1 nm thick Al₂O₃. The wrinkled graphene could be observed from Fig. 3a, originating from the difference of thermal expansion coefficient between graphene and substrate [13]. To further accurately determine the number of layers of graphene, the graphene flakes were characterized by HRTEM (Fig. 3b). The interlayer spacing was identified to be 0.347 nm, which was close to the interlayer spacing of graphene [14], demonstrating the transformation of amorphous carbon to graphene. After the thickness measurement, the number of layers of graphene was found to be 3–4. Fig. 3c and d show the optical micrograph and transmittance of graphene on quartz substrate. The graphene covered on the quartz could be clearly seen (Fig. 3c). The optical transmittance of graphene at 550 nm is 93% (Fig. 3d), which indicated that the graphene prepared by this method has the great potential to be applied in the field of optical devices as transparent thin film.

Fig. 4 shows the schematic diagram of in-situ growth of FLG on substrate surface. When the annealing progress was conducted for the substrate/ta-C/Ni/Al₂O₃ sample, carbon atoms diffused outwardly mainly along the grain boundaries of the Ni layer [5]. However, carbon atoms were difficultly to diffuse horizontally when they reached to surface of Ni layer due to the blocking effect from ALD-Al₂O₃ layer. As a consequence, large amounts of carbon atoms would return to the Ni/substrate interface when the annealing process approached to the cooling stage. At the same time, the carbon atoms transformed into graphene under the catalysis of Ni layer. After etching the Ni layer with FeCl₃ solution, FLG was obtained on substrates. Many attempts have been made on the van der Waals epitaxial growth of graphene on c-plane (0001) sapphire by CVD without a metal catalyst [15,16], where a highly single crystalline dielectric substrate is indispensable. However, ALD-Al₂O₃ layer inherently exhibits amorphous structural feature, hence graphene transformation here accounts for the catalysis of Ni layer not the ALD-Al₂O₃ layer.

In conclusion, we investigated the in-situ growth of FLG by annealing the substrate/ta-C/Ni sample covered with ALD-Al₂O₃ which acted as a diffusion barrier layer. The quality of the formed substrate/FLG was highly dependent on the thickness of the Al₂O₃ layer. When the thickness of Al₂O₃ layer was 1 nm, 3–4 layers of graphene with integrity and

homogeneity surface was achieved. In addition, graphene behaved a good transmittance (93%) under the light source of 550 nm. Our experiments gave insights into the in-situ growth of FLG synthesized from a solid carbon source.

CRediT authorship contribution statement

Anfeng Zhang: Writing – original draft, Data curation. **Li Wang:** Methodology, Formal analysis. **Zhenyu Wang:** Writing – review & editing, Project administration, Investigation. **Rende Chen:** Investigation, Data curation, Conceptualization. **Xiaoping Li:** Supervision, Resources. **Yuanbing Wang:** Funding acquisition, Formal analysis. **Aiying Wang:** Supervision, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The research was supported by National Natural Science Foundation of China (U20A20296), Science and Technology Innovation 2025 Major Project of Ningbo (2022Z011, 2020Z023), Natural Science Foundation of Ningbo (2021J227). The authors would like also to acknowledge Dr. Hanchao Li at Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Science for experimental investigation.

References

- [1] M. Sang, J. Shin, K. Kim, K.J. Yu, *Nanomaterials* 9 (3) (2019) 374.
- [2] J. Baek, M. Lee, J. Kim, J. Lee, S. Jeon, *Carbon* 127 (2018) 41–46.
- [3] I.I. Kondrashov, M.G. Rybin, E.A. Obraztsova, E.D. Obraztsova, *Phys. Status Solidi B* 256 (2019), 1800688.
- [4] H. Li, X. Li, J. Wei, Z. Wang, P. Guo, P. Ke, H. Saito, P. Cui, A. Wang, *Diam. Relat. Mater.* 101 (2020), 107556.
- [5] H. Li, D. Shi, P. Guo, J. Wei, P. Cui, S. Du, A. Wang, *Mater. Lett.* 278 (2020), 128468.
- [6] R.N. Tiwari, M. Tripathi, M. Yoshimura, A. Kumar, *Mater. Res. Bull.* 107 (2018) 147–153.
- [7] R.S. Weatherup, C. Baecht, B. Dlubak, B.C. Bayer, P.R. Kidambi, Raoul Blume, R. Schloegl, S. Hofmann, *Nano Lett.* 13 (2013) 4624–4631.
- [8] J. Wei, P. Guo, L.L. Liu, H.C. Li, H. Li, S.Y. Wang, P.L. Ke, A.Y. Wang, *Appl. Surf. Sci.* 516 (2020), 146115.
- [9] J. Wei, P. Guo, H. Li, P.L. Ke, A.Y. Wang, *J. Mater. Sci. Technol.* 97 (2022) 29–37.
- [10] P. Kumar, P.K. Kanaujia, G. Vijaya Prakash, A. Dewasi, I. Lahiri, A. Mitra, *J. Mater. Sci.* 52 (2017) 12295–12306.
- [11] H. Lim, H.C. Lee, M.S. Yoo, A. Cho, N.N. Nguyen, J.W. Han, K. Cho, *Chem. Mater.* 32 (2020) 10357–10364.
- [12] J. Liu, P. Li, Y. Chen, Z. Wang, J. He, H. Tian, F. Qi, B. Zheng, J. Zhou, W. Lin, W. Zhang, *J. Alloys Compd.* 615 (2014) 415–418.
- [13] F. Long, P. Yasaei, W. Yao, A. Salehi-Khojin, R. Shahbazian-Yassar, *ACS Appl. Mater. Interfaces* 9 (2017) 20922–20927.
- [14] S. Park, R.S. Ruoff, *Nat. Nanotechnol.* 4 (2009) 217–224.
- [15] J. Hwang, M. Kim, D. Campbell, H.A. Alsaman, J.Y. Kwak, S. Shivaraman, A. R. Woll, A.K. Singh, R.G. Hennig, S. Gorantla, M.H. Rummeli, M.G. Spencer, *ACS Nano* 7 (2013) 385–395.
- [16] M.A. Fanton, J.A. Robinson, C. Puls, Y. Liu, M.J. Hollander, B.E. Weiland, M. LaBella, K. Trumbull, R. Kasarda, C. Howsare, J. Stitt, D.W. Snyder, *ACS Nano* 5 (2011) 8062–8069.