



HOKKAIDO UNIVERSITY

Title	Switching of the products by changing the size and shape of catalytic nanoparticles during CVD growth of MoS ₂ nanotubes
Author(s)	Weng, Mengting; Yanase, Takashi; Uehara, Fumiya et al.
Citation	Crystengcomm, 19(28), 3915-3920 https://doi.org/10.1039/c7ce00608j
Issue Date	2017-07-28
Doc URL	https://hdl.handle.net/2115/71072
Type	journal article
File Information	Revised version2.pdf



Switching of the products by size and shape of catalytic nanoparticles during CVD growth of MoS₂ nanotubes

Weng Mengting,^a Takashi Yanase,^a Fumiya Uehara,^a Sho Watanabe,^a Takuya Miura,^a
Taro Nagahama^a and Toshihiro Shimada^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Nanowires of layered materials are important because the highest sensitivity as electrically-detected chemical sensors is expected. MoS₂ nanowires have been synthesized by the catalytic chemical vapor deposition method on silicon substrates drop-coated with FeO nanoparticles of different shapes. Switching of the products (MoS₂ nanowires to SiO₂ nanowires) has been observed when the shapes and sizes of the FeO nanoparticles changed. MoS₂ nanowires were grown in the presence of six-horned octahedral nanoparticles, whereas SiO₂ nanowires were formed in the presence of spherical nanoparticles. The morphology, crystal structure and elemental composition have been fully investigated to elucidate the growth mechanism of the nanowires. The kinetics of the grown SiO₂ and MoS₂ nanowires is competing, giving rise to the observed switching.

Introduction

Semiconductor nanowires have been a hot topic over the past decades. One of their major applications is in nanoscale sensor arrays, which is important, for example, as the interface between a bio-system and information technologies.^{1,2} The sensitivity of the nano-sensors depends on the capping layer on the surfaces, which is primarily introduced for the protection of the semiconductor from the surrounding solution or atmosphere. The capping layer can also be used to provide a selectivity to the sensing species. For the conventional semiconductors, such as Si or GaAs, the surface is chemically active and has to be capped by oxides or organic species, which sometimes reduces their sensitivity, and the long-term stability is still problematic. The highest sensitivity and stability is expected from the layered materials such as graphene and transition metal dichalcogenides (TMDs). Graphene can be made into nanowires, *i.e.*, carbon nanotubes, and their application in nanoscale sensors is promising.^{3–5} However, the physical property of carbon nanotubes is strongly dependent on their chirality that is difficult to control.^{6,7} Therefore, it is worth studying the nanotubes of TMDs, in which no strong chirality effects have been reported.

Molybdenum dioxide (MoS₂), a representative TMD material, has a broad range of applications including field effect transistors (FET),^{8–10} gas sensors,^{11–13} lithium batteries^{14–16} and solar cells.^{17–20} Several methods have been used to grow MoS₂ nanowires, such as the vapor transport reaction with MoS₂ powders,^{21,22} H₂S reduction of molybdenum oxides mixtures,²³ thermal decomposition of the precursor (NH₄)₂MoS₄ using the template method,²⁴ hydrothermal

treatment of LiMoS₂ lamella,²⁵ and sulfurization of the precursor Mo₆S₄I₆ nanowires.²⁶ Nevertheless, progress towards the control of the nanowires growth has still been limited. It is necessary to investigate the mechanism for their growth process to control the size of the nanowires and optimize their properties.

In this paper, we focus on the chemical vapor deposition (CVD) with solid catalyst nanoparticles of MoS₂ nanowires. This approach is successful for the growth of carbon nanotubes, Si, GaAs and ZnO. In our previous study, it was found that FeO and other metal oxides can function as catalysts for the growth of the MoS₂ nanotubes.²⁷ In this study, we focus on the impact of the size and shape of the chemically synthesized FeO nanoparticles on the nanowire growth.

FeO is one of the common iron oxides, which consist of goethite (α -FeOOH), hematite (α -Fe₂O₃), magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃) etc. Among them, FeO is the most chemically reactive, as a result of its defective NaCl structure which is non-stoichiometric with an O-vacancy.²⁸ As reported, Sun's group has synthesized FeO nanoparticles with two shapes, *i.e.*, octahedral and spherical.²⁹ It is of great interest to investigate whether the shape has an effect on the catalytic reactivity of the FeO nanoparticles. Actually, we found switching of the products from MoS₂ and SiO₂ as described in the following sections.

Results and Discussion

^a Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan.

^b (ESI) available: See DOI: 10.1039/x0xx00000x

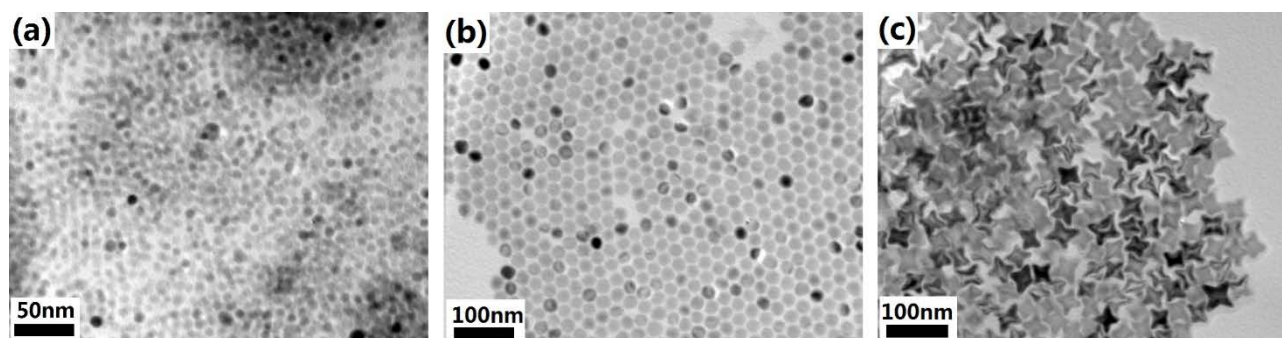


Fig. 1 TEM images of FeO nanoparticles: (a) 9 nm, (b) 24 nm spherical and (c) 30 nm six-horned octahedral nanoparticles.

Figure 1 shows the typical TEM images of the synthesized FeO nanoparticles. As already reported²⁹, the shapes and sizes of the particles are controlled by changing the reaction conditions. In this study, we synthesized 9 nm spherical nanoparticles (Figure 1(a)) by heating the mixture of iron(III) acetylacetonate [Fe(acac)₃], oleic acid (OA) (4 ml) and oleylamine (OAm) (6 ml) at 220 °C, then at 300 °C, each for 30 min. Under the same conditions, 30 nm six-horned octahedral nanoparticles (Figure 1(c)) were acquired by the decomposition of Fe(acac)₃ mixed with OA (5.5 ml) and OAm (5 ml).

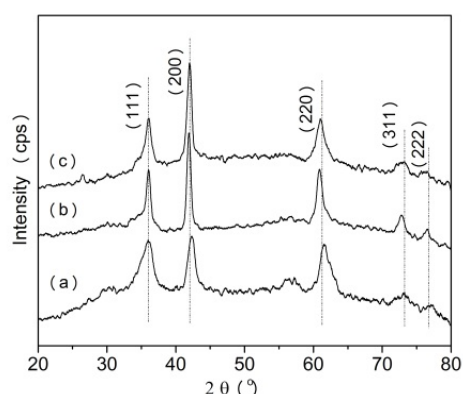


Fig. 2 XRD patterns of FeO nanoparticles: (a) 9 nm, (b) 24 nm and (c) 30 nm nanoparticles.

Additionally, we found that stirring is another essential factor to control the shape of the particles during the decomposition. For example, heating a mixture of Fe(acac)₃, OA (5.5 ml) and OAm (5 ml) without stirring at 220 °C for 1h, then at 300 °C for 30 min, formed 50 nm six-horned octahedral nanoparticles (Figure S1), whereas 24 nm spherical nanoparticles (Figure 1(b)) were obtained by continuous stirring. The flow chart of the synthesis process is shown in Figure S2.

The crystal structures of the 9 nm and 24 nm spherical particles and 30 nm six-horned octahedral particles were characterized by XRD, as shown in Figure 2. It is clear that all the samples exhibit the 111, 200, 220, 311 and 222 characteristic peaks of the FeO structure, indicating that the synthesized nanoparticles are almost pure FeO. Raman were also taken, as shown in Figure S3. The morphologies of the nanoparticles heated to 1000 °C on SiO₂/Si substrates are shown in Figure S4, and their corresponding Raman spectra and XRD are shown in Figure S5 and S6. Even though some morphology change has occurred to the nanoparticles due to **their agglomeration at** the high temperature, it is obvious that the size and shape of the nanoparticles are distinct from each other. We admit that very thin residual carbon might exist on the surface of catalysts, but the coverage of the carbon is the same for all the catalysts.

The nanowires were grown on 285 nm SiO₂/Si substrates in a CVD reactor made of quartz tube (Figure S7)^{30,31} at 1000 °C with MoO₃ and S using the 9 nm, 24 nm spherical, 30 nm and 50 nm six-horned octahedral particles as catalysts. Powders of 0.15g MoO₃ and 1.5g S were evaporated at 650 °C and 280 °C, respectively. The gas flow of MoO₃ and S lines were started when the temperature reached 1000 °C. The pressure in the growth tube was 1 atm and the growth time was 1 hour.

The SEM images of the products after CVD using the 9 nm, 24 nm, 30 nm and 50 nm FeO are shown in Figures 3 (a), (b), (c) and S8 respectively. TEM equipped with EDS was employed to investigate their crystal structures and morphologies, as shown in Figure 4. In the case of the 9 nm spherical catalyst particles, high-aspect ratio nanowires with a diameter of 40 nm and length of 10 μm, were found to grow in a high density. The EDS and diffraction results show that they are amorphous SiO₂ nanowires with a particle cap. The EDS analysis revealed that the particles consist of Mo, Fe and S.

When the diameter of the spherical particles increased to 24 nm, as shown in Figure 3(b), low-density nanowires and particles

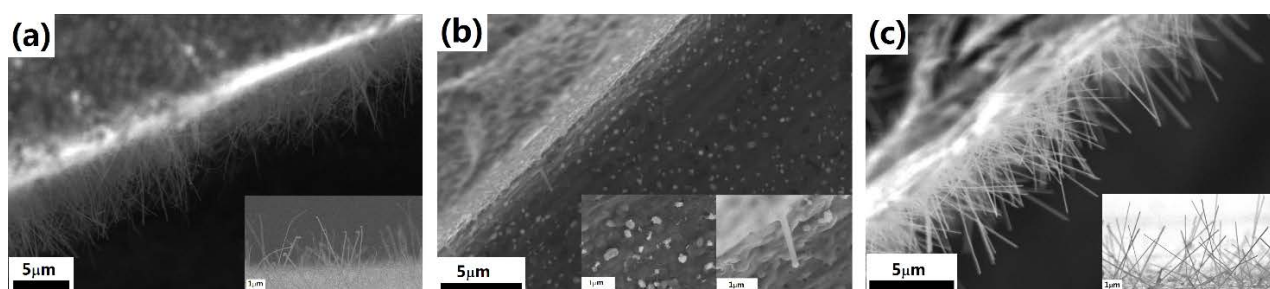


Fig. 3 SEM images after CVD with (a) 9 nm, (b) 24 nm and (c) 30 nm catalyst nanoparticles.

covered by MoS₂ films were observed. Similar to the ones grown with the 9 nm particles, a particle can be found at the tip of a nanowire (Figure 3b inset). From the Raman spectra and EDS results, the nanowires were SiO₂. Compared to Figure 3(a), the diameter of the nanowire increased and the length became shorter.

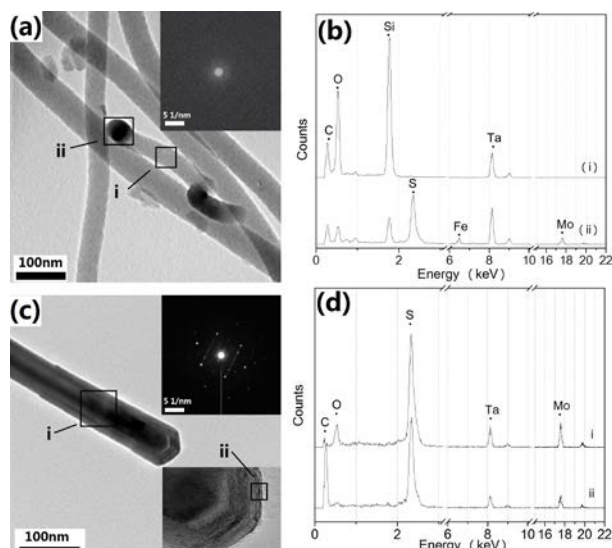


Fig. 4 TEM images of (a) SiO₂ and (c) MoS₂ nanowires. (b) and (d) are the EDS results corresponding to (a) and (c), respectively.

When the shape of the catalyst nanoparticles changed from spherical to 30 nm six-horned octahedra, nanowires with no particle caps were found (Figure S9). The nanowires are typically a few micrometers in length with diameters from 40 to 80 nm. Based on the EDS, they were composed of Mo and S. The peaks in the TEM diffraction (Figure 4(c) inset) and Raman spectra (Figure S10)

of the nanowires correspond to those of MoS₂. The two peaks in the Raman spectra, centered at 380 and 406 cm⁻¹, were assigned as the E_{2g} and A_{1g} modes, respectively.³²⁻³⁴ In the case of 50 nm, low-density MoS₂ nanowires were obtained (Figure S8), which were evidenced by TEM-EDS (Figure S11).

We have now observed drastic switching of the CVD product depending on the size and shape of the FeO nanoparticle catalysts. This result is summarized in the first row of Table 1. In order to study the growth mechanism, CVD experiments with only flowing MoO₃ (no S) were conducted. The SEM images are shown in Figure S12, and no nanowires were observed in them. Instead, the particles randomly dispersed on the substrates.

These products were characterized by Raman spectroscopy. Figures 5 (a), (b) and (c) are the results of using the 9 nm, and 24 nm spherical and 30 six-horned octahedral catalysts, respectively. In the 9 nm case, peaks of both MoO₂ and FeO_x (x=1, 3/2, 4/3) were found in contrast to the one of the 24 nm spherical nanoparticles, in which no MoO₂ peaks could be found, indicating that MoO₃ could be deposited on the smaller spherical particles. When the shape of the particles changed to six-horned octahedra, significant peaks of MoO₂ could be observed, as shown in Figure 5(c). It is proposed that the sharp edges and acute angles in the six-horned octahedra contribute to the deposition of MoO₃.

Based on the results of the above experiments summarized in Table 1, the growth mechanism can be described as follows.

Although SiO₂ has a very low vapour pressure at 1000 °C, SiO can be vaporized under reducing conditions from the substrate surface and furnace wall. We suggest that based on the reaction SiO₂ + S → SiO + SO₂, SiO (~1.33 Pa, 1000 °C)³⁷ is the source of the SiO₂ nanowires. The MoO₃ vapor pressure in the furnace is estimated to be 4 Pa, which is described in the supporting information. Based on this value, the competition between the SiO and MoO₃ vapor gives rise to the formation of two different nanowires with the assistance of the different shapes of the catalyst nanoparticles, as illustrated in Figure 6.

Table 1. Summary of the CVD products.

Catalysts (FeO particles)	9 nm sphere	24 nm sphere	30nm truncated octahedra
Growth of nanowires (MoO ₃ and S flow)	SiO ₂ nanowires	few SiO ₂ nanowires	MoO ₃ nanowires
MoO ₂ Raman peaks (only MoO ₃ flow)	weak	none	strong

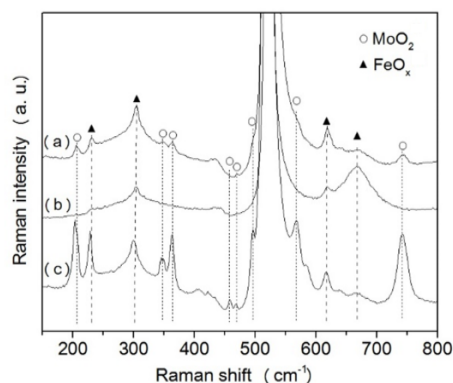


Fig. 5 Raman spectra after CVD with (a) 9-nm spherical FeO+MoO₃, (b) 24-nm spherical FeO+MoO₃ and (c) 30-nm six-horned octahedral FeO + MoO₃. Raman peaks were identified using Refs. 35 and 36.

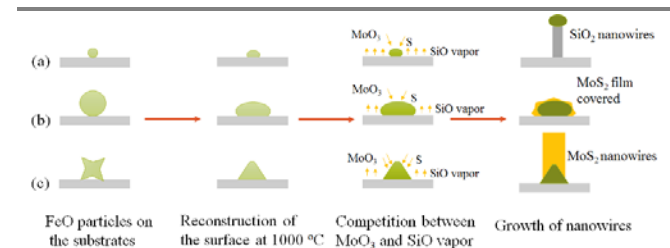


Fig. 6 Mechanism of switching between SiO₂ and MoS₂.

By using 9-nm particles, the particles consisting of Mo, Fe and S were observed at the top of the SiO₂ nanowires, indicating that the SiO₂ nanowire growth proceeded through a vapor-liquid-solid (VLS) or vapor-solid-solid (VSS) mechanism.³⁸⁻⁴² In the VSS mechanism, the growth temperature is lower than the eutectic temperature (50-90% of the reported eutectic temperature) and more facets of the catalysts at the top would be observed due to the lower solubility of the precursor atoms.^{41, 42} The round particle shape of the catalyst existing at the top of the nanowire in Figure 4(a) illustrates that the growth of the SiO₂ nanowire is not explained by the VSS mechanism. The reaction temperature at 1000 °C, higher

than the eutectic point ($\leq 940^\circ\text{C}$, because of the size effect) in the FeO-FeS system,^{43, 44} makes it possible to explain it by the VLS mechanism. At 1000°C , Ar gas carrying MoO_3 and sulfur from the low-temperature region starts to flow, depositing Mo, O and S atoms onto the particles. Some sulfur atoms react with FeO, leading to the formation of the FeO-FeS system. When the FeS content in the particle reached a certain value, a liquid alloy drop will be formed. Whereas MoO_3 tends to quickly evaporate rather than diffuse into the particles. Additionally, an experiment without MoO_3 (only S) was also conducted, as shown in Figure S13. SiO_2 nanowires did not grow in this case, which demonstrates that the Mo absorbed into the drop played an important role in its catalyzing effect.

With the increasing size of the nanoparticles, the growth of the SiO_2 nanowires seems to become more difficult. As shown in Figure 3(b), lower-density nanowires were found compared with Figure 3(a). With the increasing size of the nanoparticles, the surface to volume ratio decreased, leading to fewer active sites for interaction with the chemical adsorbate.⁴⁵ Thus, the absorbance of the S, MoO_3 , SiO become lower than that in the smaller particles. For example, as shown in Figure 5(b) and Table 1, compared with the weak peaks in the 9 nm particles, no MoO_x peaks were found in the case of the larger particles. However, due to the increased volume of the particles, more atoms need to be absorbed to grow SiO_2 nanowires by the VLS mechanism. In other words, it required a longer time to form the supersaturated alloy drop, whereas at the same time, MoS_2 thin films are formed with the presence of the MoO_3 and S vapors, which is not affected by the nanoparticles. Thus, less SiO_2 nanowires were formed as the size of the nanoparticles increased, instead, the particles tended to be covered by the MoS_2 thin films.

When the shape of the catalyst nanoparticles changed from spherical to six-horned octahedra, MoS_2 nanowires were formed. Unlike the SiO_2 nanowires, no particle cap at the tip of the MoS_2 nanowires were ever found, indicating that the mechanism of MoS_2 cannot be the VLS mechanism. As the temperature increased to 1000°C , six-horned octahedral FeO nanoparticles start forming frustums, as shown in Figure S4(c). The sharp edges and acute angles of which contribute the deposition of MoO_3 (Figure 5(c) and Table 1). At a high temperature, an oxygen deficiency in the deposited MoO_3 would occur,^{46, 47} which can be incorporation sites for sulfur atoms, leading to the nucleation of MoS_2 . With the orientation effect of the sharp edges of the catalyst, MoS_2 nanowires were then formed. Thus, we suggest that the mechanism of the MoS_2 nanowires is the VS mechanism. Compared with the VLS mechanism of SiO_2 nanowires, the MoS_2 nanowires with the VS mechanism can be understood as a simple surface reaction system, while the mechanism of the SiO_2 nanowire growth is more complex because it involves diffusion and precipitation of silicon atoms into the alloy drops. Additionally, when the nanoparticle size increased to 50 nm, lower-density MoS_2 nanowires were grown, indicating that the increase in the size of nanoparticles slowed down the growth of MoS_2 nanowires.

Conclusions

In this study, high-aspect-ratio MoS_2 and SiO_2 nanowires have been successfully fabricated by catalytic CVD, in which FeO nanoparticles with different and well-defined shapes were used as catalysts. It was found that switching of the composition of the nanowires occurred when the shapes of the nanoparticle catalysts changed. In the case of spherical nanoparticles, high-density SiO_2 nanowires were fabricated, whereas in the case of six-horned octahedral nanoparticles, MoS_2 nanowires were formed. This switching can be explained by the competition between the growth of the SiO_2 nanowires by the VLS mechanism and MoS_2 nanowires grown by the VS mechanism. The deposition of MoO_2 species on the catalyst seems critical in controlling the process.

Experimental

Synthesis

Catalysts. FeO nanoparticles were synthesized by the thermal decomposition of iron (III) acetylacetonate [$\text{Fe}(\text{acac})_3$] (99.9%, Sigma-Aldrich), according to a previous report.²⁹ Briefly, 0.7g $\text{Fe}(\text{acac})_3$ was mixed with either 4 ml oleic acid (OA), 6ml oleylamine (OAm) or 5ml OA and 5ml OAm. The solutions were heated at 220°C and 300°C under Ar (99.9999%) for 1-2h to yield FeO nanoparticle solutions with different sizes and shapes. The flow chart is shown in the supporting information of Figure S2.

Nanowires. MoS_2 nanowires were grown using a CVD apparatus, as shown in the supporting information. The furnace tube had a 28-mm diameter and separated into three zones; zones A, B and C. MoO_3 (99.5%) and S powders were purchased from Kanto Chemistry. MoO_3 (0.15g) was placed into a quartz tube in zone A, and the S powders (1.5 g) were placed in an alumina boat in another heating apparatus.

Si wafers with 500 nm SiO_2 layers were drop-coated with the catalyst FeO solution (0.1 mmol/L) after RCA cleaning. The substrates were then transferred to zones B and C of the tube furnace. In typical experiments, after the furnace and S apparatus were heated to the set temperature, the Ar gases carrying the MoO_3 (40 sccm) and S (800 sccm) were flowed into the furnace. The temperatures of the zones were 280°C for the sulfur source, 650°C in zone A, and 1000°C in zones B and C. After holding the temperature for 1 h, the furnace were naturally cooled to room temperature. The experiment was conducted under atmospheric pressure.

Characterization

The FeO catalyst nanoparticles and MoS_2 nanowires have been characterized by a 200 kV JEOL JEM-2010 transmission electron microscope (TEM) equipped with an energy-dispersive (EDS) analyzer. The crystallinity of the nanoparticles were examined by a Rigaku Rint Ultima 2000 X-ray diffractometer (XRD) using Cu K α radiation ($\lambda = 0.1541$ nm). The morphology of the nanowires was characterized by a JSM-6510LA scanning electron microscope (SEM) and JSM-6500F field emission scanning electron microscope (FE-

SEM). Raman spectroscopy (Renishaw Invia) with 532 nm excitation was used.

Acknowledgements

The present work is partly supported by CREST-JST grant. Instrumental analysis was supported by Nanotechnology platform at Hokkaido University by METI, Japan.

Notes and references

- 1 B. Tian, P. Xie, T. J. Kempa, D. C. Bell and C. M. Lieber, *Nat Nanotechnol*, 2009, **4**, 824-829.
- 2 B. Tian, T. Cohen-Karni, Q. Qing, X. Duan, P. Xie and C. M. Lieber, *Science*, 2010, **329**, 830-834.
- 3 J. Wang and M. Musameh, *Anal Chem*, 2003, **75**, 2075-2079.
- 4 M. G. Zhang, A. Smith and W. Gorski, *Anal Chem*, 2004, **76**, 5045-5050.
- 5 R. J. Chen, H. C. Choi, S. Bangsaruntip, E. Yenilmez, X. W. Tang, Q. Wang, Y. L. Chang and H. J. Dai, *J Am Chem Soc*, 2004, **126**, 1563-1568.
- 6 F. Yang, X. Wang, D. Zhang, J. Yang, D. Luo, Z. Xu, J. Wei, J. Wang, Z. Xu, F. Peng, X. Li, R. Li, Y. Li, M. Li, X. Bai, F. Ding and Y. Li, *Nature*, 2014, **510**, 522-524.
- 7 F. Qin, W. Shi, T. Ideue, M. Yoshida, A. Zak, R. Tenne, T. Kikitsu, D. Inoue, D. Hashizume and Y. Iwasa, *Nat. Commun.*, 2017, 14465.
- 8 B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti and A. Kis, *Nat. Nanotechnol.*, 2011, **6**, 147-150.
- 9 S. Das, H. Chen, A. V. Penumatcha and J. Appenzeller, *Nano Lett.*, 2013, **13**, 100-105.
- 10 D. Sarkar, W. Liu, X. Xie, A. C. Anselmo, S. Mitragotri and K. Banerjee, *ACS Nano*, 2014, **8**, 3992-4003.
- 11 H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang and H. Zhang, *Small*, 2012, **8**, 63-67.
- 12 Q. He, Z. Zeng, Z. Yin, H. Li, S. Wu, X. Huang and H. Zhang, *Small*, 2012, **8**, 2994-2999.
- 13 B. Cho, M. G. Hahm, M. Choi, J. Yoon, A. R. Kim, Y. Lee, S. Park, J. Kwon, C. S. Kim, M. Song, Y. Jeong, K. Nam, S. Lee, T. J. Yoo, C. G. Kang, B. H. Lee, H. C. Ko, P. M. Ajayan and D. Kim, *Sci. Reports*, 2015, **5**, 8052.
- 14 C. Feng, J. Ma, H. Li, R. Zeng, Z. Guo and H. Liu, *Mater. Res. Bull.*, 2009, **44**, 1811-1815.
- 15 J. Xiao, D. Choi, L. Cosimbescu, P. Koech, J. Liu and J. P. Lemmon, *Chem. Mater.*, 2010, **22**, 4522-4524.
- 16 K. Chang and W. Chen, *ACS Nano*, 2011, **5**, 4720-4728.
- 17 M. Shanmugam, T. Bansal, C. A. Durcan and B. Yu, *Appl. Phys. Lett.*, 2012, **100**, 153901.
- 18 J. Lin, C. Chan and S. Chou, *Chem. Commun.*, 2013, **49**, 1440-1442.
- 19 M. Tsai, S. Su, J. Chang, D. Tsai, C. Chen, C. Wu, L. Li, L. Chen and J. He, *ACS Nano*, 2014, **8**, 8317-8322.
- 20 I. Jeon, D. Kutsuzawa, Y. Hashimoto, T. Yanase, T. Nagahama, T. Shimada and Y. Matsuo, *Org. Electron.*, 2015, **17**, 275-280.
- 21 M. Remskar, A. Mrzel, Z. Skraba, A. Jesih, M. Ceh, J. Demsar, P. Stadelmann, F. Levy and D. Mihailovic, *Science*, 2001, **292**, 479-481.
- 22 S. Fathipour, M. Remskar, A. Varlec, A. Ajoy, R. Yan, S. Vishwanath, S. Rouvimov, W. S. Hwang, H. G. Xing, D. Jena and A. Seabaugh, *Appl. Phys. Lett.*, 2015, **106**, 022114.
- 23 H. A. Therese, N. Zink, U. Kolb and W. Tremel, *Solid State Sci.*, 2006, **8**, 1133-1137.
- 24 E. M. Rivera-Munoz, *J. Appl. Phys.*, 2007, **102**, 094302.
- 25 V. Lavayen, N. Mirabal, C. O'Dwyer, M. A. Santa Ana, E. Benavente, C. M. Sotomayor Torres and G. Gonzalez, *Appl. Surf. Sci.*, 2007, **253**, 5185-5190.
- 26 M. Remskar, A. Mrzel, M. Virsek, M. Godec, M. Krause, A. Kolitsch, A. Singh and A. Seabaugh, *Nanoscale Res. Lett.*, 2011, **6**, 26.
- 27 M. Weng, T. Yanase, F. Uehara, S. Watanabe, T. Miura, Y. Hashimoto, T. Nagahama and T. Shimada, 2017, submitted.
- 28 R. M. Cornell and U. Schwertmann, *The iron oxides : structure, properties, reactions, occurrence, and uses*. VCH, Weinheim ; New York, 1996.
- 29 Y. Hou, Z. Xu and S. Sun, *Angew. Chem.*, 2007, **119**, 6445-6448.
- 30 T. Yanase, S. Watanabe, M. Weng, T. Nagahama and T. Shimada, *J. Nanosci. Nanotech.* 2016, **16**, 3223-3227.
- 31 T. Yanase, S. Watanabe, M. Weng, M. Wakeshima, Y. Hinatsu, T. Nagahama and T. Shimada, *Crystal Growth & Design* 2016, **16**, 4467-4472.
- 32 C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *ACS Nano*, 2010, **4**, 2695-2700.
- 33 H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier and D. Baillargeat, *Adv. Funct. Mater.*, 2012, **22**, 1385-1390.
- 34 S. Sahoo, A. P. S. Gaur, M. Ahmadi, M. J. F. Guinel and R. S. Katiyar, *J. Phys. Chem. C*, 2013, **117**, 9042-9047.
- 35 M. Dieterle and G. Mestl, *Phys. Chem. Chem. Phys.*, 2002, **4**, 822-826.
- 36 D. de Faria, S. V. Silva and M. T. de Oliveira, *J. Raman Spectrosc.*, 1997, **28**, 873-878.
- 37 ULVAC Inc., *Vacuum Handbook*, Ohm-sha; Tokyo, 2002.
- 38 J. L. Elechiguerra, J. A. Manriquez and M. J. Yacaman, *Appl. Phys. A*, 2004, **79**, 461-467.
- 39 K. Kolasinski, *Current Opinion in Solid State and Materials Science*, 2006, **10**, 182-191.
- 40 Z. Xiao, L. Zhang, G. Meng, X. Tian, H. Zeng and M. Fang, *J. Phys. Chem. B*, 2006, **110**, 15724-15728.
- 41 J. L. Lensch-Falk, E. R. Hemesath, D. E. Perea and L. J. Lauhon, *J. Mater. Chem.*, 2009, **19**, 849-857.
- 42 C. Y. Wen, M. C. Reuter, J. Tersoff, E. A. Stach and F. M. Ross, *Nano Lett.*, 2010, **10**, 514-519.
- 43 S. J. Groves, J. Williamson and A. Sanyal, *Fuel*, 1987, **66**, 461-466.
- 44 M. C. Mayoral, M. T. Izquierdo, J. M. Andres and B. Rubio, *Thermochimica Acta*, 2002, **390**, 103-111.
- 45 B. R. Cuenya, *Thin Solid Films*, 2010, **518**, 3127-3150.
- 46 L. E. Firment and A. Ferretti, *Surf Sci.*, 1983, **129**, 155-176.
- 47 G. Mestl, C. Linsmeier, R. Gottschall, M. Dieterle, J. Find, D. Herein, J. J. Ger, Y. Uchida and R. Schlogl, *Journal of Molecular Catalysis A: Chemical*, 2000, **162**, 463-492.