



# Dynamic shadowing growth and its energy applications

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The unique features of dynamic shadowing growth (DSG) in structural and compositional design of nanomaterials are discussed. Their recent applications in energy storage, fuel cell, and solar energy conversion have been reviewed briefly. Future directions for applying DSG nanostructures in renewable energy applications are presented.

**Keywords:** dynamic shadowing growth, glancing angle deposition, super capacitor, hydrogen storage, Li<sup>+</sup> battery, fuel cell, photovoltaics, solar water splitting

Dynamic shadowing growth (DSG) or glancing angle deposition (GLAD) is a versatile nanofabrication technique based on the self-shadowing effect during a thin-film deposition process (Young and Kowal, 1959; Motohiro and Taga, 1989; Robbie and Brett, 1997; Robbie et al., 1998; Messier et al., 2000; He and Zhao, 2011). For a conventional physical vapor or chemical vapor thin-film deposition process, as long as the incident vapor possesses certain directionality and there are protrusions (shadowing centers) on the substrate, as shown in **Figure 1A**, a self-shadowing effect will occur, i.e., there will be an area around the protrusion opposite to the incident vapor direction that cannot receive vapor to grow further. This will cause a preferred growth of the protrusion toward the vapor incident direction. There are several consequences resulting from this self-shadowing effect. First, film growth front that is dominated by the self-shadowing effect is unstable, which results in overhangs on the substrate (Lichter and Chen, 1986; Roland and Guo, 1991; Krug and Meakin, 1993; Yao and Guo, 1993; Drotar et al., 2000). This induces preferred growth of taller surface features and generates large roughness or nanostructures. Second, the growth is site specific, i.e., preferred growth mostly occurs on the locations of protrusions. Finally, the growth is asymmetric, i.e., only one side of the protrusions receives the incoming vapors to continue the growth.

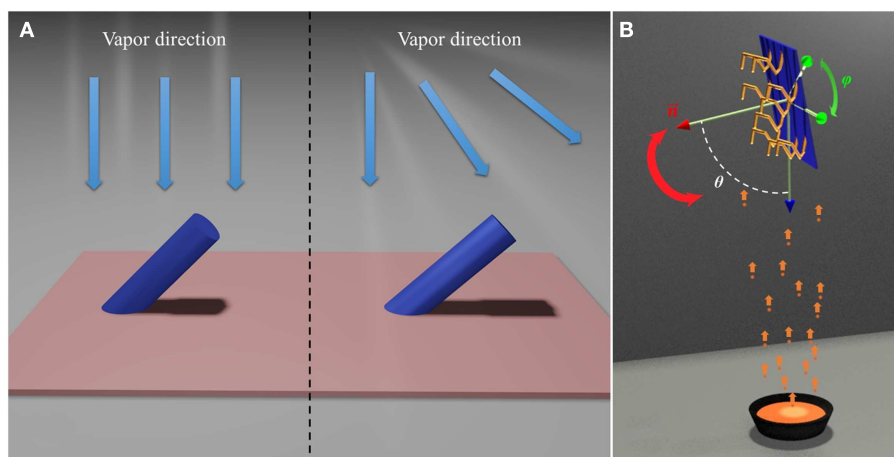
Any conventional thin-film deposition technique could naturally exhibit the self-shadowing effect due to the uneven surface features formed thermodynamically during deposition and the directionality of the local incident vapor. However, in order for the self-shadowing effect to be the dominant growth mechanism, highly directional vapor is required and surface smoothening effects such as surface diffusion should be limited. Many physical vapor deposition methods working in high vacuum or ultra-high vacuum, such as thermal evaporation (Beydaghyan et al., 2008), electron beam evaporation (Zhao et al., 2002a,b), and molecular beam epitaxy (Robbie et al., 2004), can be used to generate pronounced self-shadowing effects due to the intrinsic directionality occurring at long vapor striking distances. Other

low vacuum deposition techniques, such as sputtering growth (Sit et al., 1999; Lintymer et al., 2003; Zhou and Gall, 2006), pulsed laser deposition (Vick et al., 1999), and chemical vapor deposition (Ma et al., 2010a), can also produce significant self-shadowing effects if the depositing vapor beam is properly arranged, i.e., a collimator can be used to direct the growth vapor.

Once the self-shadowing effect becomes the dominant growth mechanism, by combining substrate rotation together with different thin-film growth configurations, such as multilayer deposition and co-deposition, one can alter the direction of the incident vapor with respect to the shadowing centers to generate nanostructures with different morphology and composition. Specifically, the polar angle  $\theta$  between surface normal of the substrate and the vapor direction and the azimuthal angle  $\varphi$  in the substrate plane (**Figure 1B**) can be dynamically programmed to design different nanostructures. Compared to other nanofabrication and synthesis techniques, DSG offers the following unique features (Robbie and Brett, 1997; Zhao et al., 2003; He et al., 2007a,b, 2008b,c, 2010; Steele and Brett, 2007; Zhou et al., 2008; He and Zhao, 2009a; Smith and Zhao, 2009).

## MORPHOLOGICAL SCULPTURE

To use the self-shadowing effect to produce well-separated nanorod arrays, the angle  $\theta$  should be larger than  $70^\circ$  (Robbie and Brett, 1997; Zhao et al., 2003; He et al., 2007a,b, 2008b,c, 2010; Steele and Brett, 2007; Zhou et al., 2008; He and Zhao, 2009a; Smith and Zhao, 2009). By programming the locations and motions of both angles  $\theta$  and  $\varphi$ , nanorods of different morphology can be formed as shown in **Figures 2A–F**. The simplest morphology is the tilted nanorod array (**Figure 2A**) formed by oblique-angle deposition (OAD), where  $\theta$  ( $\geq 70^\circ$ ) is fixed with no azimuthal rotation. The angle  $\theta$  can be used to tune the density, the diameter, and the tilting angle of the nanorod array. Other deposition conditions such as substrate temperature can also be used to adjust the abovementioned morphological parameters, and at the same time, tune the crystallinity of the resulting nanostructures



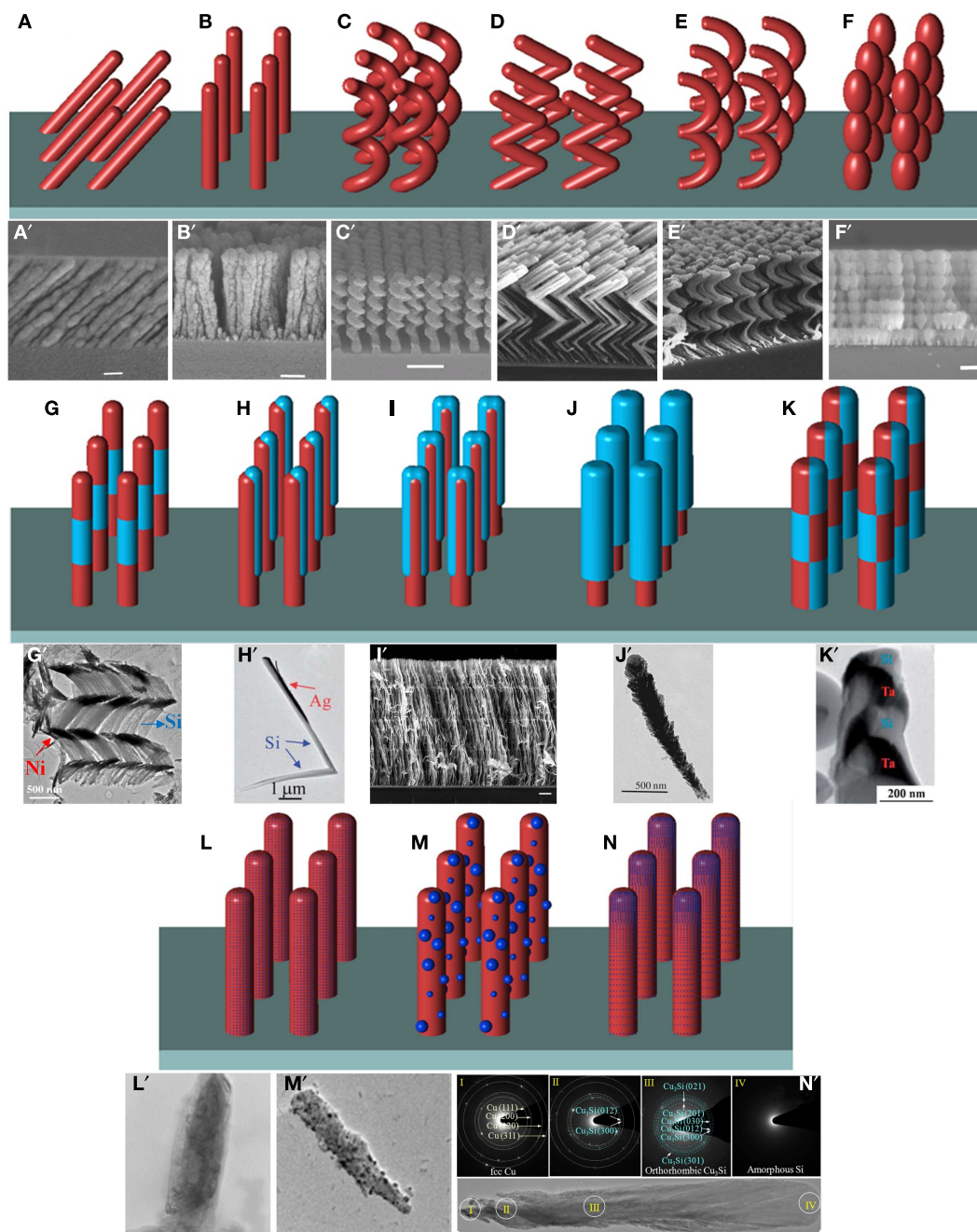
**FIGURE 1 | (A)** Self-shadowing effect: collimated parallel vapor beam (left) and divergent vapor beam (right). **(B)** The general deposition configuration of DSG.

(Schubert et al., 2006; Patzig and Rauschenbach, 2008). If  $\theta$  ( $>70^\circ$ ) is fixed, but the substrate is rotating azimuthally with a constant speed, a vertically aligned nanorod array (**Figure 2B**, at a relatively fast rotation speed) or a helical nanorod array (**Figure 2C**, at a very slow rotation speed) will be fabricated. For the helical structure, the pitch height, the helical diameter, and the length are determined by the rotation speed and the nanorod deposition rate. Thus, by programming the azimuthal rotation, one can generate nanorods with different morphology. For example, by periodically rotating substrate  $180^\circ$  azimuthally and quickly after a period of OAD, zigzag nanorods can be produced (**Figure 2D**). The number of bends and the length of each arm are programmed by the azimuthal rotation. If the fast rotation angle is set to be smaller than  $180^\circ$ , such as  $120^\circ$  and  $90^\circ$ , polygonal helices can be constructed. Similarly, one can also program the rotation of the polar angle  $\theta$  to create the zigzag nanorods; after a period of OAD,  $\theta$  can be quickly rotated to  $-\theta$  (i.e., the surface normal in **Figure 1B** changes to its mirror location with respect to the incident vapor direction). If the  $\theta$  angle is programmed to move periodically in between  $\theta_{\min}$  and  $\theta_{\max}$  ( $0 < \theta_{\min} < \theta_{\max} < 90^\circ$ ), a C-shape nanorod array (**Figure 2E**) or a bead-like nanorod array (**Figure 2F**) can be designed, depending on the rotation speed and deposition rate. The idea of programming the angular rotations can be extended to produce periodic structures with morphological modulation, such as helical-straight nanorod structures, or zigzag-straight rod structure. If a regular two-dimensional template is provided as a substrate, then the site-specified growth of the self-shadowing effect can ensure the fabrication of a regularly aligned nanorod array. Thus, the beauty of the DSG (GLAD) fabrication technique lies in that all the structural parameters of three-dimensional nanorod arrays can be controlled by computer programming, which is unique compared to other nanofabrication techniques.

### HETERO-NANOSTRUCTURE DESIGN

The advantage of morphological sculpture can be combined with conventional thin-film multilayer deposition technique to design

different heterostructured nanorods with tunable morphology. A natural extension for structures in **Figures 2A–F** is to add a layer of nanorod with different material but similar morphology. One example is shown in **Figure 2G**, the multilayered hetero-nanorods can be easily fabricated by keeping the same rotation program while alternating the deposition material. Such multilayered nanorod structures, like straight nanorods, zigzag nanorods, and helical structures, have been realized by different research groups (He and Zhao, 2011). In addition to the multilayered heterostructures, side-coated structures are possible if one utilizes the asymmetric deposition feature of the self-shadowing effect. In this case, the aligned nanorod array itself can serve as a substrate, and the angle between the surface normal of the nanorod side surface and the vapor incident direction determines the shadowing effect. By fixing  $\theta$  at a relatively small angle ( $<40^\circ$ ), an additional layer of different material can be deposited on one side of the vertical nanorods (**Figure 2H**). The coverage or the length of the coating is determined by  $\theta$  and the separation among adjacent nanorods. If during the deposition, the polar angle is programmed to swing between  $\theta$  and  $-\theta$  periodically while there is no azimuthal rotation, sandwiched nanorods shown in **Figure 2I** can be created. However, if the azimuthal angle is programmed to rotate continuously for the second layer deposition while keeping  $\theta$  fixed, core-shell nanorods (**Figure 2J**) will be fabricated. The thickness of the shell is determined by the growth rate, the angle  $\theta$ , and the deposition time. If the angles  $\theta$  and  $\varphi$  as well as multilayer deposition can be programmed simultaneously, complicated heterostructures like checkerboard structure can be fabricated as shown in **Figure 2K**. This can be realized by first creating a side-coated nanorod array (**Figure 2H**), then depositing side-coated nanorods by making sure that there is a  $180^\circ$  phase shift in  $\varphi$  direction during the second deposition. Repeating the procedure will give a multilayered structure. Furthermore, with the advantage of morphological sculpture, the heterostructures one can design using DSG are not limited to straight nanorods shown in **Figures 2G–K**. Three-dimensional nanostructures can also be created. Finally, DSG can be combined



**FIGURE 2 | Illustrations of typical nanorod arrays fabricated by DSG and representative SEM or TEM images of the corresponding structures from published literature (below each illustration).**

**I.** Morphological sculpture: **(A)** tilted nanorods and **(a')** tilted Si nanorods deposited at  $\theta = 80^\circ$  (Zhao et al., 2003); **(B)** vertically aligned nanorods and **(b')** vertically aligned Si nanorods at  $\theta = 86^\circ$  (Zhao et al., 2003); **(C)** helical nanorods and **(c')** regular array of helical Si nanorods (Zhao et al., 2003); **(D)** and **(d')** zigzag nanorods (Hawkeye and Brett, 2007); **(E)** C-shape nanorods and **(e')** C-shape  $MgF_2$  nanorod array (Robbie and Brett, 1997); and **(F)** bead-like nanorods and **(f')** bead-like Si nanorod array (Zhao et al., 2003). **II.** Heterostructure design: **(G)** multilayer nanorods and **(g')** multilayer helical Si/Ni nanorod array (He et al., 2007a); **(H)** side-coated nanorods and **(h')** Ag side-coated L-shaped Si nanorods [Reprinted with permission from (He

et al., 2007b). Copyright 2007 American Chemical Society]; **(I)** sandwiched nanorods and **(i')** V/Mg sandwiched nanoblades for hydrogen storage [Reproduced from (He and Zhao, 2009a) with permission from the PCCP Owner Societies]; **(J)** core-shell nanorods and **(j')**  $WO_3/TiO_2$  quasi core-shell nanorods for effective photocatalyst (Smith and Zhao, 2009); and **(K)** checkerboard nanorods and **(k')** Ta/Si checkerboard nanorods (Zhou et al., 2008). **III.** Composition tunability: **(L)** homogenous composite nanorods and **(l')** homogenous composite Ti-doped Mg nanorods (He et al., 2008c); **(M)** nanoparticle-decorated nanorods and **(m')** embedded Ag nanoparticles in  $MgF_2$  nanorods (He et al., 2008b) and **(N)** composition-graded nanorods and **(n')** Si/Cu composition-graded nanorods for improved  $Li^+$  battery anodes [Reprinted with permission from (He et al., 2010). Copyright 2010 American Chemical Society].

with other nanofabrication techniques to develop many unique material systems.

### COMPOSITION TUNABILITY

From a materials science point of view, conventional thin-film deposition techniques not only can generate thin films with single components or single compounds but composite thin films can also be produced if two or more sources are simultaneously used during the deposition. Therefore, the combination of co-deposition configuration with the DSG principle can be used to design composite nanorod arrays (He and Zhao, 2011). Based on the physical and chemical properties of the two (or three, or more) materials for co-deposition, nanorod arrays with a homogenous mixture (Figure 2L) or with nanoparticle decoration (Figure 2M) can be fabricated, provided that the deposition rates of the two materials are fixed throughout the deposition process. If the ratio of the deposition rates of the two materials is programmed dynamically during growth, a composition-graded nanorod array can be produced (Figure 2N). The co-deposition combined with multilayer deposition and DSG can be used to design many new nanocomposites with different layered structure and nanorod morphology.

In summary, DSG is a versatile and simple nanofabrication technique to design three-dimensional, well-aligned, and heterostructured nanorod arrays, and it has the following specific advantages:

- (1) DSG naturally forms high aspect ratio aligned nanorod arrays with high surface areas and tunable layered structures.
- (2) The size, separation, and density of the nanorods can be controlled by deposition conditions and templates.
- (3) The shape, alignment, and orientation of the nanorods can be easily changed by programming the substrate rotation procedure.
- (4) Three-dimensional nanorod structures can be sculptured by programming the rotations of the angles  $\theta$  and  $\varphi$ .
- (5) Different configurations of heterostructured nanorods can be designed.
- (6) The composition of composite nanorods can be programmed.
- (7) There is virtually no constraint on the material that can be used for DSG, as long as the material can be evaporated and the vapor can be collimated.
- (8) The process is compatible to the conventional microfabrication processes, which makes scale-up fabrication possible. In fact, the Brett group has recently demonstrated the feasibility of roll-to-roll DSG (GLAD) fabrication (Krause et al., 2013).

These advantages make DSG an excellent nanofabrication technique to design different nanomaterials for energy applications. To date, while promising results have already been demonstrated, the potential for DSG to further energy research has not been fully realized.

Due to the high surface area of DSG films and aligned nanorod arrays, energy storage applications of DSG thin films have been explored. Electrochemical performance of carbon nanostructures fabricated by DSG has been studied by the Brett group to investigate the potential application as supercapacitors (Kiema and Brett,

2004). They found that post-deposition treatment was needed to improve the electrode reactivity. The use of DSG nanostructures for hydrogen storage has been explored extensively. Early works showed that LaNi<sub>5</sub> (Devi et al., 2001), Cr-coated TiNi (Singh et al., 2007), and MnNi<sub>4.5</sub>Al<sub>0.5</sub> (Jain et al., 2000, 2008) thin films deposited by OAD at high  $\theta$  angles had better hydrogen storage performance. Very recently, different groups have shown that Mg can form nanoblade morphology due to OAD growth, and they exhibit improved hydrogen storage thermodynamics (Tang et al., 2007; He et al., 2008a,c). Once the surface of the Mg nanoblades were decorated with catalysts such as Pt, Pd, or V, both the thermodynamics and the kinetics of the hydrogen adsorption and desorption could be improved (He and Zhao, 2009a,b; Bayca et al., 2011; Liu et al., 2011; Liu and Wang, 2012). The amount of reversible hydrogen in V decorated Mg nanoblades was found to be less than 6 wt.%, which was slightly smaller than the theoretical value 7.6 wt.% of MgH<sub>2</sub>. The material could absorb hydrogen to saturation within 7 min at 570 K, and desorb hydrogen almost completely within 15 min at 570 K (He and Zhao, 2009a). The absorption activation energy was estimated to be  $35.0 \pm 1.2$  kJ/mol H<sub>2</sub> and desorption activation energy  $65.0 \pm 0.3$  kJ/mol H<sub>2</sub>. Both were much lower than the desorption energy of 141 kJ/mol H<sub>2</sub> for MgH<sub>2</sub> film (Cecchetto et al., 2005) and 156 kJ/mol H<sub>2</sub> for MgH<sub>2</sub> powder (Huot et al., 1999). If the catalyst decorated nanoblades are protected by polymer (Parylene) coating through vapor deposition, air stable hydrogen storage material can be achieved (Liu et al., 2013a).

Dynamic shadowing growth has also been used to fabricate electrodes for battery applications, especially the anodes of Li<sup>+</sup> battery. Si nanorods fabricated by DSG have demonstrated >3000 mAh/g capacity by Brett and Lu group (Fleischauer et al., 2009; Teki et al., 2009). However, silicon exhibits large volume changes (about 300%) upon Li insertion and extraction. The stress induced by this volume change causes cracking, pulverization, and peeling of the underlying current collector, which leads to loss of electrical contact, formation of additional solid-electrolyte-interphase layer, and eventual fading of capacity. To circumvent this problem, stress compliant layer has been engineered. Lu group designed a carbon nanorod/Al capped layer to release the stress of Si nanorods during the Li<sup>+</sup> shuttling (Krishnan et al., 2011), while Zhao group used the Si–Cu composite nanorods and Si–Cu composition-graded nanorods to reduce the stress effect (Au et al., 2011; He et al., 2012). Recently Mullins' group showed that control oxidation of Si nanorods or Si<sub>1-x</sub>Ge<sub>x</sub> composite nanorods could greatly improve the anode performance (Abel et al., 2012, 2013a). Other anode materials fabricated by DSG, such as Al (Au et al., 2010; Sharma et al., 2013), Ge (Abel et al., 2013b), TiO<sub>2</sub> (Lin et al., 2011), and WO<sub>3</sub> (Figueroa et al., 2007), have also been explored for Li<sup>+</sup> battery applications.

The porous nature of DSG thin films also has found applications as fuel cell electrodes or catalyst supporting structures. Both Gall and Karabacak groups showed that the Pt nanoparticles/nanorods fabricated by DSG could improve the oxygen reduction reaction with a high mass-specific performance (Gasda et al., 2009; Khudhayer et al., 2011). The catalytic performance of fuel electrodes was further improved by multilayer Pt/Ru nanorods (Yoo et al., 2010) and Pt–Ni alloy nanorods (Kariuki et al., 2013). In fact, the mass-specific activity of the Pt–Ni alloy nanorods was



found to be a factor of 2.3–3.5 higher than that of pure Pt nanorods of the same dimensions. Conductive DSG nanorods, such as Ti (Bonakdarpour et al., 2008), C (Gasda et al., 2010), Cr (Khudhayer et al., 2012), Ni (Francis et al., 2013), and niobium oxides (Bonakdarpour et al., 2012), were also used as catalyst supporting structures to reduce the loading of Pt in fuel cell electrodes.

The use of DSG nanostructures for solar application has been studied more extensively compared to other applications. Most works have focused on dye-sensitized solar cells (DSSC), organic solar cells (OSC), and related surface coating. For DSSC, DSG-produced TiO<sub>2</sub> nanorods were mainly used (Kiema et al., 2005; Yang et al., 2009; Wong et al., 2010; Gonzalez-Garcia et al., 2011). An early report by Brett group showed that the annealed TiO<sub>2</sub> nanostructures gave better performance, and a photoelectric conversion efficiency of 4.1% could be achieved (Kiema et al., 2005). Recent work by Wong et al. (2010) demonstrated a higher cell efficiency of 6.1%. Li and Forrest (2009) reported an OSC consisted of chloroaluminum phthalocyanine (ClAlPc) and C<sub>60</sub> grown by OAD, and demonstrated an efficiency of 2.0–2.8%. Other OSC-based semiconductors such as copper phthalocyanine (CuPc) (Van Dijken et al., 2011; Yang et al., 2013), ClAlPc (Yang et al., 2013), and lead phthalocyanine (PbPc) (Liu et al., 2013b) were also made into nano-columnar structures by OAD, and the donor-acceptor hetero-junctions were characterized. Furthermore, high surface area nanorod electrodes made by DSG, such as indium tin oxide (ITO) (Yu et al., 2010; Rider et al., 2011), SnO<sub>2</sub>:Sb (ATO) (Xiao et al., 2010), and C<sub>60</sub> fullerene (Thomas et al., 2011, 2012), were used for OSC construction. Besides DSSC and OSC, hybrid inorganic–organic solar cells (HIOSCs) were incorporated with DSG nanostructures (Ma et al., 2010b). Using a modified hot wire chemical vapor deposition system (Guo et al., 2011) was able to grow crystalline Si nanorod array, coated with amorphous Si shell. After spin-coating 3-hexylthiophene (P3HT), a HIOSC with 1% conversion efficiency was achieved (Ma et al., 2010b). Similar inorganic nanorod acceptor-organic donor structures, such as TiO<sub>2</sub>–P3HT (Gerein et al., 2010), TiO<sub>2</sub>–porphyrin (Castillero et al., 2010), and ZnO–InN–PbPc (Chen and Chen, 2012), were fabricated, but the measured conversion efficiency was less than 0.2%. In addition to solar cells, DSG nanostructures were also utilized as photoelectrodes for solar water splitting. Wolcott et al. (2009) demonstrated a 0.1% photo-to-hydrogen efficiency with OAD TiO<sub>2</sub> nanorods, and they further showed that TiO<sub>2</sub>–WO<sub>3</sub> core-shell nanorods could further extend the photoconversion to visible wavelength range (Smith et al., 2011). Other TiO<sub>2</sub>-based nanostructures, such as Cr doped (Larsen et al., 2011) and CdSe decorated (Larsen et al., 2012) TiO<sub>2</sub> nanorods, were explored as the photoelectrodes for water splitting. Finally, since DSG can tune the optical property of each layers, it has been used widely to create antireflection coating for solar cell application (Poxson et al., 2009, 2011), especially based on ITO nanostructure, to improve the light trapping efficiency and conversion efficiency (Chhajed et al., 2008; Yu et al., 2009; Yao et al., 2012).

Compared to materials made from other nanofabrication techniques, the nanostructures made by DSG have not been extensively studied in renewable energy area. This is due to several reasons. First, the crystallinity of the nanorod arrays fabricated by DSG is poor. In order to form the well-separated nanorod arrays

during DSG process, the self-shadowing effect shall dominate the growth process while the adatom diffusion needs to be minimized. This requires the deposition occurring at lower temperature. The films grown at near room temperature are usually amorphous for most compound materials and polycrystalline for metals. For applications requiring high-quality crystalline nanostructures, post-deposition annealing is usually performed. However, the improvement in crystallinity is typically insignificant. Second, high-quality heterojunction interfaces are lacking. The low temperature grown nanorods by DSG usually have rough surfaces. Thus, the deposition of an additional layer on the rough, porous, and amorphous nanorods to generate heterostructures does not result in good-quality interface. Many defects could exist at the interface that can impair the charge transport properties. To overcome abovementioned shortcomings, the adatom diffusion has to be increased to improve the quality of the nanostructures. Recently, high temperature DSG has been explored by Suzuki et al. (2006, 2011) and Brett groups (Taschuk et al., 2013; Beaudry et al., 2014). They show vapor–liquid–solid-like growth of single crystalline nanowires with directions controlled by the incident vapor. Another alternative method is to use energetic beam-assisted deposition. It is well-known that the presence of energetic ions during conventional thin-film deposition can greatly improve the quality of the films, and sometimes can even achieve low temperature epitaxial growth (Takagi et al., 1975; Takagi, 1982; Hirvonen, 1991; Mohan and Krishna, 1995; Monteiro, 2001; Manova et al., 2010; Popok, 2011). Brett group investigated the oxide nanorod growth using ion-assisted GLAD. Under Ar<sup>+</sup>-assisted deposition (390 eV and 6 mA with 45° ion incident angle), they found that the density and tilting angle of SiO<sub>2</sub> and TiO<sub>2</sub> nanorods were both increased (Sorge and Brett, 2010). They also investigated the morphology of 12 different oxides and fluorides fabricated using a similar technique, and reached a similar conclusion (Sorge et al., 2012). Third, the composition of the most DSG materials studied so far is either single element or single compound, while many energy-related applications require multi-element compounds or composites. New material discovery also requires the tunability of material composition. As discussed above, co-deposition DSG has the capability to program the composition during the deposition. Some of the current studies on composite nanostructures used in battery, fuel cell, and photocatalyst have already demonstrated the advantages of complex materials or composite materials. Yet, there are not many groups that have the capability to perform co-deposition DSG. In spite of these temporary drawbacks, progress is being made, and once the structure sculpture, composition design, and high-quality fabrication have been combined and integrated perfectly, the DSG technique will become an indispensable nanofabrication technique for many different energy applications.

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