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Perspective—A Brief Perspective on the Fabrication of Hierarchical Nanostructure for Solar Water Splitting Photoelectrochemical Cells

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A Brief Perspective on the Fabrication of Hierarchical Nanostructure for Solar Water Splitting Photoelectrochemical Cells

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Among various solar energy generation methods, a water splitting photoelectrochemical (PEC) cell have been anticipated as a one of the promising source to generate hydrogen by natural sunlight. Owing to unique electrical, electrochemical and optical properties, the nanostructured metal oxides were intensively investigated to adopt as a main material in the water splitting PEC cell. However, most of nanostructured metal oxides have an improper bandgap size/position for splitting water molecule, it needs to be engineered to shift a level of the energy bandgap. In this prospective review, we will briefly discuss solution-processed fabrication methods for water splitting applications.

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Current Status

Sunlight-driven energy generation systems have been broadly studied to establish a clean and sustainable energy source. Water splitting photoelectrochemical (PEC) cell is one of the next-generation hydrogen generation technology.^{1–3} Since metal oxides have unique electrical, electrochemical and optical properties, it usually was adopted as a main material for the water splitting PEC cell. At this time, the metal oxides were fabricated to have nanoscale structure. Typically, the nanostructured materials have different chemical, electrical and optical characteristics, largely depended on the size.⁴ One of the featured characteristics for the nanoscale materials is large surface to volume ratio, which indicates that it offers many chemical reaction sites. Moreover, the nanostructured materials own minimized defects and shortened migration distance for electrons/holes, which decreases electron-hole recombination and eventually leads high photoresponse efficiency.⁵ Nanomaterials were engineered as various shapes and structures such as thin film,⁶ porous frameworks,^{7,8} nature-mimicked branched systems^{9,10} and hierarchical structures^{11,12} to obtain maximize surface areas. Among the various structures, the hierarchical metal oxide nanostructure has been broadly studied for the electrochemical applications due to a simple structure form as well as a capability of modulation for the electrical property. Regarding the hierarchical structure is basically consisted of an inner core and an outer surrounding, the core material fabrication process firstly needs to be determined. At the early stage of research, metal oxide-based hierarchical nanostructures were generally synthesized via vapor-liquid-solid process, mostly conducted under vacuum environment. However, several pioneer researchers have introduced a hybrid fabrication process using both dry and wet methods to get hierarchical nanostructure.

Synthesis of Metal Oxide Nanostructure by Hydrothermal Process for Water Splitting Applications

Over several decades, nanostructured metal oxides were synthesized by various vacuum-based synthesis methods such as evaporator,^{13,14} sputtering,¹⁵ chemical vapor deposition (CVD),^{16–19} pulsed laser deposition (PLD)²⁰ and other techniques. Recently, a hydrothermal reaction was practiced to make metal oxide nanostructure as a core material for the hierarchical nanostructure. The hydrothermal reaction is a solution-based process that can synthesize a crystalline material by using metal precursor and aqueous solution. By adjusting synthetic conditions including concentrations of metal precursor, reaction time and reaction temperature, it is possible to grow a target material within wet environment. Various metal oxides such as copper oxide (CuO),²¹ iron oxide (Fe₂O₃),^{22,23} tungsten oxide (WO₃),² titanium dioxide $(TiO_2)^{25}$ and zinc oxide $(ZnO)^{26}$ can be synthesized into a nanoscale structure though this manner. The hydrothermally synthesized nanostructured metal oxides were employed for the water splitting applications as shown in Table I. In particular, Grätzel group have been reported series of nanostructure hematite (α -Fe₂O₃) photoanode for water oxidation.^{6,27–32} At the beginning of their study, hematite thin film was formed by CVD process.²⁷ After several years, they represent that hematite was successfully grown in the nanorod shapes by solution process and shown good chemical stability within a strong basic solution.³² While the hydrothermally synthesized metal oxide nanostructure brings good crystalline structure with a short reaction time, a nature property of the metal oxides has some flaws such as a large bandgap size and inappropriate position to absorb sunlight for splitting water. Therefore, several surface treatments have been executed to shift the bandgap level of the metal oxides and to extend absorbable wavelength region of the sunlight.

Surface Engineering Routes for Metal Oxide Nanostructure

As aforementioned, when a bulk state material turned to nanoscale material, specific characteristics of the material were changed by its size. By changing dimensions of nanostructured metal oxides including length, diameter and thickness, metal oxide nanomaterials could be functioned to get a desirable property. However, an additional surface treatment is performed because a dimensional control of the nanomaterial cannot satisfy for all cases.

Thermal oxidation.—Thermal oxidation is a simple way to make hierarchical nanostructure by oxidation for the target material in oxygen-rich or ambient condition. This process began with a single-phase material, which could be transformed different phases at the elevated temperature. J. Han et al. demonstrated Cu₂O/CuO composite photocathode by H_2/O_2 flame oxidation.³³ The fabricated copper

	CuO	Cu ₂ O*	α-Fe ₂ O ₃ (Hematite)	WO ₃	TiO ₂ (Rutile)	ZnO
Bandgap (eV)	1.5	2.1	2.2	2.8	3.0	3.2
Types	p-type	p-type	n-type	n-type	n-type	n-type
Thickness	150 nm	3.5 µm	600 nm	500–1,000 nm	3 µm	1 μm
Electrolyte (pH)	0.1 M Na ₂ SO ₄ (5.84)	0.5 M Na ₂ SO ₄ (6.82)	1 M KOH (13.6)	0.1 M HCl (1.0)	1 M KOH (13)	0.25 M Na ₂ S + 0.35 M Na ₂ SO ₄ (N/A)
Current Density (mA/cm ²)	-3.1 @ 0 V vs RHE	–0.82 @ 0 V vs RHE	0.105 @ 0.2 V vs Ag/AgCl	0.45 @ 1.23 V vs RHE	0.8 @ 1.23 V vs RHE	0.5 @ 0.2 V vs SHE under 380 nm wavelength
Stability	89% in 20 minutes	65% in 10 minutes	92% in 60 minutes	80% in 90 minutes	N/A	95% in 200 seconds
Reference	21	33	22	24	35	53

Table I. List of the basic properties of the intact metal oxide nanostructures by hydrothermal growth for water splitting photoelectrochemical cell.

*Note that Cu2O grown onto CuO by thermal oxidation.

oxides composite was initially originated from copper foil. Carraro et al. reported polymorph Fe₂O₃ nanostructure for hydrogen generation.³⁴ By controlling thermal annealing condition including total pressure, O₂ flow and water vapor, they successfully synthesized α , β and ϵ phase of Fe₂O₃ nanostructure.

Dopant doping for bandgap engineering.—Doping is implant of impurities purposely into the target materials to modulate electrical conductivity and energy bandgap. In semiconductor fabrication process, doping process is frequently performed to increase or decrease semiconductor property by using each of n-type and p-type dopant. Since dopant doping into the intrinsic material affect the electrical property of the material, it also adopted to the synthesis of metal oxide nanostructure for the water splitting applications. Dopant doping to the metal oxide nanostructure can be achieved in two ways: after formation of metal oxide nanostructure or during at the synthesis stage of metal oxide. In particular, the latter case can be processed in a wet method.

For the first case, the mechanism of doping was diffusion of dopant atoms. Typically, diffusion process is conducted within high vacuum environment and/or high temperature condition, which influences to diffusion rate. As examples, flame spray pyrolysis enabled rapidly carbon doping for the TiO₂ nanostructure at the temperature condition of 1,000°C, obtained C-doped TiO₂ nanostructure.³⁵ The C-doped TiO₂ shifted the level of the valence band, resulting smaller bandgap energy. Yang et al. and Li et al. reported independently the fabrication of Sn-doped Fe₂O₃ nanostructure on the FTO glass for decreasing electron-hole recombination.^{36,37} In here, Sn was diffused from the FTO glass after several hours annealing. While those methods were performed at 500 and 800°C, respectively, both doping methods were provided an improved photoresponse reaction by visible wavelength.

Meanwhile, doping could be attained in solution-based way by adding dopant precursor to the metal oxide precursor solution. At this point, dopant precursor worked as an additive component. H.J. Lee et al. represented Li-doped ZnO nanostructure though modified hydrothermal process.³⁸ The fabricated Li-doped ZnO photoanode showed over 200% increased solar-to-hydrogen conversion efficiency without applied bias. Shen et al. conducted a simple solution-based doping process for the Ag-doped hematite nanorod.³⁹ In this study, a concentration of Ag ion solution was finely controlled as 0, 0.005, 0.01, 0.05 and 0.1. After annealing process at 750°C, Ag-content in the hematite experienced oxidation, forming Ag-doped thin film and AgO nanoparticle on the hematite nanorod. Consequently, they found that the ideal molar ratio of Ag/Fe is 0.05 for the high-efficiency PEC cell.

Formation of hierarchical metal oxide nanostructure.—Metal oxide nanostructure is modified into heterojunction structure such as core/shell, branched and hierarchical shapes. Those surface modifications ultimately provide co-catalysis and trigger sites for surface plasmonics on the metal oxide nanostructure. Since noble metals such as Ag, Au, Ir, Pd and Pt have high chemical, photochemical and corrosion stability, it is broadly employed for surface modification. Recently, quantum dots (QDs) are also extensively adopted due to a property of quantum confinement and bandgap engineering by forming hierarchical nanostructure along with metal oxide nanostructure.

Deposition process.—Deposition process is widely used in the semiconductor fabrication process to form thin film structures. Likewise, the deposition process was naturally imported to make hierarchical nanostructure in terms of formation thin film structure on the metal oxide nanostructure. The deposition process was conducted by using various vacuum-based equipment such as atomic layer deposition (ALD),^{40–43} chemical-vapor deposition,²¹ E-beam evaporator,^{44,45} pulsed laser deposition (PLD)^{46,47} and sputtering⁴⁸ on the metal oxide nanostructures. By this way, a robust and dense thin film structure was accurately formed from only several nanometers to tens of nanometers onto the metal oxide nanostructure, obtained hierarchical nanostructure by controlling deposition processing conditions. However, most of deposition techniques were essentially required vacuum environment, elevated temperature condition and long processing time.

Two-step hydrothermal process.—Two-step hydrothermal process is a process that fabrication of hierarchical metal oxide nanostructure though successive hydrothermal process. At the first hydrothermal process, a scaffold metal oxide nanostructure was fabricated. Afterward, the second hydrothermal process is continuously practiced by using the same or another metal precursor. In particular, this process spontaneously provides core-shell nanostructure when different metal precursor solutions are separately used. For example, Y. Xie et al. demonstrated TiO₂ branched arrays though successive hydrothermal process.⁴⁹ Particularly, in order to obtain well-branched structure, the second hydrothermal process time took for 24 hours. Chen et al. represented a ZnO hierarchical nanostructure, consisted of ZnO nanowire and branched ZnO nanodisks for large surface area to absorb sunlight.⁵⁰ On the other hand, F. Xu et al. conducted TiO₂/ZnO hybrid nanostructure by using titanium precursor and following zinc precursor, respectively.⁵¹

Photoreduction process.—Photoreduction process is solutionbased process and a kind of photocatalytic synthesis, which reduces metal ion into metal nanoparticles by external light energy to make hierarchical nanostructure. The mechanism of the photoreduction is that the electrons, generated by the metal oxide in response to the external light, meet with the metal ion in the precursor solution and are reduced as metal nanoparticle forms.⁵² T. Wang et al. conducted



Figure 1. Examples of FDTD simulation of i) ZnO nanostructure and ii) ZnO/Ag hierarchical nanostructure. A largely enhanced surface resonance was observed at the case of the ZnO/Ag hierarchical nanostructure. Note that the simulation conditions of the ZnO nanostructure dimension was 50 nm of diameter and 100 nm of length while the diameter of Ag nanoparticles (AgNPs) were 20 nm.

photoreduction process on the vertically aligned ZnO nanowire arrays for ZnO/Ag nanostructure.⁵³ A similar research carried out with different experimental conditions for ZnO/Ag hierarchical nanostructure. In here, the fabricated ZnO/Ag hierarchical nanostructure was connected with lab-made supercapacitors for showing solar energy generation and storage platform, simultaneously.⁵⁴ However, when an external voltage was over around 1.5 V vs Ag/AgCl, Ag nanoparticles showed extremely weak electrochemical stability and destructive surface morphology due to corrosive nature at that threshold voltage condition. A hematite/Ag hierarchical nanostructure was also fabricated by photoreduction process.⁵⁵ While the photoreduction process is capable to obtain hierarchical nanostructure with a facile preparation and processing, it cannot make complicated materials such as complex compounds.

Chemical bath deposition.—Chemical bath deposition, also known as dip coating, is a simple process that the target metal oxide nanostructure is immersed in a liquid solution of precursor and coated with metal/QD nanoparticles. F. Lin and S. W. Boettcher showed NiO_x or IrO_x film deposition by using each precursor solution on the TiO_2 nanostructure.⁵⁶ The TiO_2 nanostructure was immersed into each precursor solution and annealing at 300°C for 3 min, precursor decomposes to form NiO_x or IrO_x film. Similarly, K. Kim et al. executed that Au nanoparticles were formed on the surface textured TiO₂ nanostructure.⁵⁷ Moreover, H. Han et al. performed hollow 3D structured hematite/TiO₂ photoanode that was used ZnO nanostructure as a sacrificial template.⁵⁸ In this study, TiO₂ was hydrothermally grown on the ZnO nanostructure and hematite nanoflakes were deposited by immersing into the iron precursor solution. Particularly, complex hierarchical nanostructures could be synthesized through chemical bath deposition. For instance, CdS/Au/TiO₂ sandwich nanorod structure was fabricated by J. Li et al.⁵⁹ Likewise, S. Park et al. reported the fabrication of CdS/TiO₂/Sb:SnO₂ hierarchical nanostructure that TiO₂ branch and CdS nanoparticles were formed by typical chemical bath deposition.⁶⁰ Additionally, Z. Liu et al. conducted trilaminar nanostructure of TiO2/In2S3/AgInS2 for enhancing charge transfer process, which consisted of core, buffer layer and shell structure, respectively.⁶¹ Unlike typical vacuum-based deposition processes, the deposited nanomaterials were randomly located onto metal oxide nanostructure and weak adhesive strength to metal oxide nanostructure.

Mechanisms of the Enhanced Photoelectrochemical Property for the Surface Engineered Metal Oxide Nanostructure

The major objective of the surface engineering on the nanostructured metal oxides is extension of absorbable wavelength region of sunlight. The ideal bandgap structure of the metal oxide is that the conduction band level should be more negative than the redox potential of $\rm H^+/H_2$ along with the valence band level should be more positive than the redox potential of O₂/H₂O.⁵ Most of metal oxides locate in the unsuitable bandgap position or possess too large bandgap energy. In order to tune bandgap level, doping process was introduced and could lift the valence band level of the metal oxide with only small molar volumes of dopant. On the other hand, structure engineering came with dramatically structural changes such as core/shell, bundled and hierarchical structure. Especially, the hierarchical nanostructure has actively been studied and significant developed to obtain an enhanced photochemical activity. The structure engineering brought increased surface areas as well as an improved charge-transfer process and a unique optical phenomenon, surface plasmon effect, when it associated with additional nanomaterials such as metal nanoparticles on the metal oxide nanostructure.^{62,63} Commonly, high density electron clouds are generated at the surface of the metal nanoparticle when external wavelength, which is larger than the particle size, is stimulated.^{64,65} In other word, a large electromagnetic enhancement can be occurred near interacting metal nanoparticles. When metal particles are illuminated with light, where resonance with the particle localized surface plasmon resonance (LSPR) frequency, the electromagnetic enhancement will be particularly strong. The LSPR from the metal nanoparticle is basically ruled by size, shape, surrounding medium and nearby, inter-particles coupling effect. To achieve a highly enhance surface plasmon effect, metal oxide structure along with additional nanostructured decorations were needed to be wellordered and to possess periodical patterned structure.^{11,66-68} Although the wet-based processes for the additional structure on the nanostructured metal oxide were enabled random deposition of metal oxide nanoparticles with arbitrary formation, this manner also provided optically enhanced property for the water splitting applications.⁶⁹ As shown in Figure 1, metal nanoparticles on the metal oxide nanostructure were occurred surface plasmon resonance, which accelerated electron generation by sunlight, and eventually resulted in improved solar-to-hydrogen efficiency for water splitting applications.

Future Needs and Prospects

- (i) Electrolytes: Most of water splitting PEC cells were tested under high base electrolyte conditions such as 1 M NaOH or 1 M KOH solution. For the broad device accessibility, it should be operated within common solutions including neutral solutions, rainwater and even sea water.
- (ii) Fabrication cost: While several solution-based fabrication methods were proposed a possibility of the low-cost fabrication processing for the water splitting PEC cells, more intuitive and advanced process is needed.
- (iii) Long-term stability/reliability: The long-term stability of the solution-processed hierarchical nanostructure is still in a veil and a controversy issue.
- (iv) Large-area affinity: Current water splitting PEC cells are confined (small) shapes and only lab-scale size. In order to achieve

economy of scale, large-area cell fabrication process is highly required.

- (v) Energy storage platform: The generated electricity or hydrogen from the solar water splitting PEC cells should be connected with energy storage devices such as battery and super capacitors for the long-time usability. Regarding that storing of the generated energy is as important as energy generation, realistic researches related to this is currently rarely reported.
- Flexible compatibility: Water splitting devices anticipate to (vi) have flexible forms, given mobility and further applications.

Conclusions

To date, most of solar water splitting photoelectrodes have been fabricated under highly controlled conditions that uses high-cost vacuum technology. Some pioneer researchers tried to introduce a partial wet process and they successfully demonstrated its feasibility. All solution-processed hierarchical nanostructures for water splitting PEC cells were showed facile processing steps, enough photoelectrochemical performances and moderate stability in the controlled conditions such as high base solution and lower bias voltage.

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