<table>
<thead>
<tr>
<th>Title</th>
<th>Research and development aspects on chemical preparation techniques of photoanodes for dye sensitized solar cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Asim, Nilofar; Ahmadi, Shideh; Alghoul, M. A.; Hammadi, F. Y.; Saeedfar, Kasra; Sopian, K.</td>
</tr>
<tr>
<td>Date</td>
<td>2014</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/18905">http://hdl.handle.net/10220/18905</a></td>
</tr>
<tr>
<td>Rights</td>
<td>Copyright © 2014 Nilofar Asim et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.</td>
</tr>
</tbody>
</table>
Review Article

Research and Development Aspects on Chemical Preparation Techniques of Photoanodes for Dye Sensitized Solar Cells

Nilofar Asim, 1 Shideh Ahmadi, 2 M. A. Alghoul, 1 F. Y. Hammadi, 1 Kasra Saeedfar, 3, 4 and K. Sopian 1

1 Solar Energy Research Institute, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
2 NOVITAS, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798
3 School of Chemical Science & Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
4 Department of Chemistry, Faculty of Science, K. N. Toosi University of Technology, Tehran, Iran

Correspondence should be addressed to Nilofar Asim; asimnilofar@gmail.com and M. A. Alghoul; dr.alghoul@gmail.com

Received 5 August 2013; Revised 19 November 2013; Accepted 21 November 2013; Published 12 January 2014

Academic Editor: Mahmoud M. El-Nahass

Copyright © 2014 Nilofar Asim et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The importance of dye sensitized solar cells (DSSCs) as a low-cost and environmentally friendly photovoltaic (PV) technology has prompted many researchers to improve its efficiency and durability. The realization of these goals is impossible without taking into account the importance of the materials in DSSCs, so the focus on the preparation/deposition methods is essential. These methods can be either chemical or physical. In this study, the chemical applied methods that utilize chemical reaction to synthesize and deposit the materials are covered and categorized according to their gas phase and liquid phase precursors. Film processing techniques that can be used to enhance the materials’ properties postpreparation are also included for further evaluation in this study. However, there is a variety of consideration, and certain criteria must be taken into account when selecting a specific deposition method, due to the fact that the fabrication conditions vary and are unoptimized.

1. Introduction

Dye sensitized solar cells (DSSCs) as a novel photovoltaic (PV) technology have the potential to compete with other traditional solar cell because they are low-cost and an environmental friendly solar cell. Their low weight, flexibility, transparency, varied color, and superior performance in darker conditions make them more popular and have attracted considerable company investment and government funding.

The power conversion efficiency of a DSSC is highly reliant on its materials, which puts them at the forefront of research. However, it is not alone in its importance, as other areas are equally crucial in the quest to realize a stable, efficient, and low-cost dye sensitized solar cells [1–3].

Although there are many interesting research findings based on the development of nanomaterial and new hybrid materials [4, 5], there is still room for progress and the solving of different issues dealing with dye sensitized solar cells. The preparation and deposition methods are critical vis-à-vis the properties of DSSC.

Weerasinghe et al. [6] have reviewed the technological development of DSSC on flexible polymer substrates, paying attention to factors that are imperative to the preparation of the slurry, film deposition, and electrode processing intended to enhance the mechanical and photovoltaic properties of a device.

The aim of this review is to demonstrate the different preparation and deposition methods, which have been used in DSSC, emphasizing their advantages and disadvantages, in order to allow a researcher to carefully choose and optimize a given method. Chemical methods are further categorized according to their reaction medium or precursors, such as gas and liquid. We tried to categorize these methods by considering this concept, although overlapping does occur from time to time.
2. Gas Phase Precursors

2.1. Chemical Vapor Deposition (CVD). The process that is called chemical vapor deposition (CVD) of films and coatings is the result of chemical reactions that occur between the gaseous reactant close to or adjacent to the surface of a heated substrate (Figure 1). The flexible nature of CVD makes it one of the preferred methods of thin film deposition and coatings. The applications of CVD coated thin films are, but not limited to, semiconductors for microelectronics; optoelectronics, energy conversion devices; dielectrics for microelectronics; refractory ceramic materials for hard coatings, corrosion protection, oxidation, or as diffusion barriers; metallic films for microelectronics and for protective coatings; and fiber production and coating [7].

2.1.1. Advantages and Disadvantages of CVD. On top of its complex chemical system, some of the advantages of CVDs are [7] as follows.

(a) Being able to produce extremely dense and pure materials and allowing manipulation at the atomic or nanometer scales.
(b) The films are highly uniform and have good reproducibility and adhesion, with acceptable deposition rates.
(c) Due to its good throwing power and nonline of sight nature, it can be used to uniformly coat complex-shaped components and deposit films with reasonable conformal coverage, which is significantly advantageous compared to the physical vapor deposition (PVD) processes.
(d) Properties such as crystal structure, surface morphology, and orientation of the products can be manipulated and customized via the CVD's process parameters.
(e) It is capable of producing a variety of coatings, such as single layer, multilayer, composite, nanostructured, and functionally graded coating materials, along with well-controlled dimension and unique structure at low processing temperatures.
(f) The rate of deposition can be readily adjusted. Low deposition rates are favored for the growth of epitaxial thin films for microelectronic applications, while high deposition rates are preferred for the deposition of thick protective coatings.
(g) The processing cost for the conventional CVD technique is quite low.
(h) The CVD technique allows the usage of a wide variety of chemical precursors, such as halides, hydrides, and organometallics, which enables the deposition of a large spectrum of materials that encompasses metals, carbides, nitrides, oxides, sulphides, III–V, and II–VI materials.
(i) The low deposition temperatures allow the desired phases to be deposited in-situ at low energies via vapor phase reactions, or nucleation and growth on the substrate's surface. This, in turn, allows the deposition of refractory materials at a fraction of their respective melting temperatures.

However, the drawbacks of this technique include the following:

(a) the inherent chemical and safety hazards that might be instigated by the use of toxic, corrosive, flammable, and/or explosive precursor gases. Recently however, these issues have been mitigated by using variants of CVD methods such as electrostatic spray-assisted vapor deposition (ESAVD) and combustion chemical vapor deposition (CCVD) methods, which employ more environmental-friendly precursors;
(b) the difficulty encountered when trying to deposit multicomponent materials with well-controlled stoichiometry via multisource precursors, due to the fact that different precursors adhere to different vaporization rates. However, this limitation can be negated via the utilization of single source chemical precursors;
(c) the high level of sophistication in the reactor or vacuum system in CVD variants such as low pressure or ultrahigh vacuum CVD, plasma-assisted CVD, and photo-assisted CVD tends will inevitably increase the cost of production. However, there are exceptions to this case, such as aerosol assisted chemical vapor deposition (AACVD) and flame-assisted chemical vapor deposition (FACVD), where it might be a viable alternative that guarantees low production costs [7].

2.1.2. Variants of CVD Methods. Both the conventional CVD and thermal activated CVD (TACVD) rely upon thermal energy to activate chemical reactions. However, other sources of energy are also viable for this purpose. The advancements and uniqueness of different variants of the CVD method are discussed and detailed by Choy [7], while Figure 2 represents the relationship between different parameters and coating properties.

In all of the CVD processes, several basic functions must be provided. This includes free movement of the reactants and diluents gases to the deposition surface, utilizing different source to provide reactant’s activation energy, and maintain...
a specific system pressure and temperature, optimizing the chemical deposition method, and the complete removal of by-product gases. The provisions of these functions, however, require adequate control, high effectiveness, and foolproof safety.

Atmospheric-pressure CVD (APCVD) uses the low-temperature (below 600°C) rotary vertical-flow reactors and a continuous, in-line conveyored reactors with various gas distribution features, mostly for depositing oxides, binary and ternary silicate glass coatings for solid-state devices. Low-pressure CVD (LPCVD) (typically 0.1–10 torr) in the low-, mid-, or high-temperature range uses resistance-heated hot-wall reactors of tubular, bell-jar, or close-spaced designs. The advantage and wide usage of LPCVD over APCVD are attributed to the fact that, in LPCVD, no carrier gases are needed, particle contamination is reduced, and film uniformity and conformity are superior in conventional APCVD reactor systems [8].

In a metalorganic chemical vapor deposition (MOCVD), the copyrolysis of various combinations of organometallic compounds and hydrides is employed for the growth of thin epitaxial layers of compound semiconducting materials. Composite layers of accurately controlled thickness and dopant profile are required to produce structures of optimal designs for device fabrication [9].

Photo-enhanced chemical vapor deposition (PHCVD) uses electromagnetic radiation, usually short-wave ultraviolet radiation in order to activate the reactants in the gas or vapor phase. The selective absorption of photonic energy by the reactant molecules or atoms initiates the process by forming reactive free-radical species that will then interact to form a desired film product. In laser-induced chemical vapor deposition (LCVD), a laser beam prepares a highly localized heat in a substrate, which will then induce film deposition via CVD surface reactions [8]. Table 1 presents some research results on materials’ preparation using CVD methods for DSSC application.

2.2. Atomic Layer Deposition (ALD). The atomic layer deposition (ALD) method is considered a self-imposed film growth method that is defined by the alternating exposure of the chemical species in a layer-by-layer manner. ALD is divided into four crucial steps: (1) the exposure of the metal precursor, (2) evacuation or purging of the precursors and any byproducts from the chamber, (3) exposure of the other reactant species (nonmetal precursor), for example, nitrogen containing reducing agents for nitrides or reducing agents for metals, and (4) evacuation or purging of the reactants and by product molecules from the chamber (Figure 3). The most imperative requirement in the initial step is self-imposed limitation on the precursor molecule’s adsorption process. In most cases, this requirement is met via the ligands that are linked to the metal atoms present in the precursors, which includes halogen or organic ligands. This will inevitably curtail further adsorption by the metal precursor via the passivation of the adsorption sites on the saturation coverage of one monolayer or less.
Table 1: Some research results on DSSC using different CVD methods.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>Efficiency ($\eta$)%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene-based multiwalled carbon nanotubes (GMWNTs)</td>
<td>Drop casting and low pressure chemical vapor deposition (LPCVD)</td>
<td>3.0</td>
<td>[130]</td>
</tr>
<tr>
<td>Nanostructured TiO$_2$</td>
<td>Flat-flame chemical vapor deposition</td>
<td>&gt;4</td>
<td>[131]</td>
</tr>
<tr>
<td>Graphene-CoS</td>
<td>Low pressure thermal chemical vapor deposition (LPCVD)</td>
<td>3.42</td>
<td>[78]</td>
</tr>
<tr>
<td>ZnO/TiO$_2$</td>
<td>Thermal chemical vapor deposition</td>
<td>—</td>
<td>[132]</td>
</tr>
<tr>
<td>ZnO nanostructures coated on vertically aligned carbon nanotubes (CNTs)</td>
<td>Thermal chemical vapor deposition</td>
<td>1.94</td>
<td>[133]</td>
</tr>
<tr>
<td>MWNTs (multiwall carbon nanotubes)</td>
<td>Thermal chemical vapor deposition</td>
<td>0.99</td>
<td>[134]</td>
</tr>
<tr>
<td>TiO$_2$ thin film</td>
<td>Metalorganic chemical vapor deposition (MOCVD)</td>
<td>—</td>
<td>[135]</td>
</tr>
<tr>
<td>InN deposited over TiO$_2$ nanoparticle (NP) films</td>
<td>Metalorganic chemical vapor deposition (MOCVD)</td>
<td>7.07</td>
<td>[136]</td>
</tr>
<tr>
<td>Mesoporous TiO$_2$ with polymer electrolyte</td>
<td>Initiated chemical vapor deposition (iCVD)</td>
<td>2.8</td>
<td>[137]</td>
</tr>
<tr>
<td>TiO$_2$ thin films</td>
<td>Atmospheric pressure chemical vapor deposition (APCVD)</td>
<td>—</td>
<td>[138]</td>
</tr>
<tr>
<td>Nanocrystalline TiO$_2$ thin films</td>
<td>Chemical vapor deposition</td>
<td>0.17</td>
<td>[139]</td>
</tr>
</tbody>
</table>

Figure 3: Atomic layer deposition (ALD) [10].

2.2.1. Advantages and Limitations. ALD is sequential, self-limiting surface reaction process that enables atomic layer control (angstrom or monolayer level) and excellent conformal deposition [11]. This aspect results in excellent step coverage and conformal deposition on high aspect ratio structures. ALD can produce continuous, smooth, and pinhole-free film. It is possible to obtain high quality materials and low processing temperatures with the ALD method.

ALD processing also includes enormous substrates and parallel processing of multiple substrates as well. Due to the fact that the precursors to the ALD are gas phase molecules, the entire space will be filled with it regardless of the substrate’s geometry. The line-of-sight to the substrate vis-à-vis the substrate in this process is also unimportant, along with problems such as unpredictable vaporization rates of solid precursors. ALD possesses excellent reproducibility and is capable of producing multilayer structures in a continuous process [12, 13]. ALD is also capable of producing sharp interfaces and superlattices, allowing for the possibility of interface modification.

One major limitation of the ALD method is its lack of speed, resulting in only a fraction of a monolayer being deposited in a single cycle. However, the recent developments help the commercial ALD tools in realizing cycle times of $<$5 seconds, resulting in the deposition of a 100 nm film in less than an hour. Recent advances in roll-to-roll ALD are allowing for an even faster throughput.

The materials for the films grown by ALD are numerous, which also includes technologically strategic materials such as Si, Ge, and Si$_3$N$_4$. However, certain multicomponent oxides and metals cannot be grown or deposited by ALD in an economical manner, which renders their deposition unfeasible.

Another limitation of ALD is that it is confined by the size of its reaction chamber. In addition, due to the fact that it is a chemical technique, there is always a chance that chemical residues from the precursor might remain in the chamber. Table 2 presents the results of DSSC prepared using ALD methods.
Table 2: Results of DSSC using ALD method.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>Efficiency (η) %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃-coated TiO₂ (core–shell)</td>
<td>Atomic layer deposition (ALD)</td>
<td>8.4</td>
<td>[140]</td>
</tr>
<tr>
<td>Hafnium oxide (HfO₂) and aluminum oxide (Al₂O₃) on mesoporous TiO₂</td>
<td>Atomic layer deposition (ALD)</td>
<td>7.1</td>
<td>[141]</td>
</tr>
<tr>
<td>Al₂O₃ overlayers on porous TiO₂</td>
<td>Atomic layer deposition (ALD)</td>
<td>—</td>
<td>[142]</td>
</tr>
<tr>
<td>Highly ordered and vertically oriented TiO₂ nanotube arrays</td>
<td>Template-assisted method using atomic layer deposition (ALD) and reactive ion etching (RIE)</td>
<td>1.17</td>
<td>[143]</td>
</tr>
</tbody>
</table>

2.3. Thermal Oxidation. The method of thermal oxidation produces a thin layer of oxide on a wafer’s surface. It forces the diffusion of an oxidizing agent into the wafer at high temperatures and induces a reaction within it. The Deal-Grove model predicts the rate the oxide growth. Figure 4 shows a thermal oxidation furnace.

ZnO nanobelts and nanotetrapods are fabricated via the thermal oxidation reaction technique. The process begins by heating the zinc paste that was prepared from zinc powder (purity 99.9%), which was then mixed with a hydrogen peroxide solution (30 wt.%) at a temperature of 1000 °C under normal atmosphere for a few minutes. The best results of DSSCs were the short circuit current ($J_{sc}$) of 1.25 mA/cm², the open circuit voltage ($V_{oc}$) of 0.45 V, a fill factor (FF) of 0.65%, and the overall energy conversion efficiency ($\eta$) of 0.68% [15].

ZnO nanonetwork structures with high porosities were fabricated for use in the photoelectrodes of binder-free dye-sensitized solar cells (DSSCs) by the PVD method of DC sputtering, followed by thermal oxidation. The nano-network of Zn was successfully transformed into ZnO without undergoing a morphological change through annealing in open atmosphere [16].

Moreover, Ti–TiO₂ structure has been used in the fabrication of numerous TiO₂-based devices, such as solar cells, electrocatalytic electrodes, and noble metal–TiO₂–Ti chemical sensors. Hossein-Babaei and Rahbarpour [17] fabricated Ti–TiO₂–Ti and Ag–TiO₂–Ti structures on a thermally oxidized titanium chip and analyzed their electronic behaviors at different biasing, thermal, and atmospheric conditions.

3. Liquid Phase Precursor

Due to the fact that the liquid phase chemical methods are considered a bottom-up approach, the morphology of nanomaterials in the thin film can be tuned in order to allow for better control of particle size, shape, size distribution, particle composition, and degree of particle agglomeration, while the chemical deposition methods are inexpensive, which allows the synthesis of thin films materials containing complex chemical compositions. Lokhande et al. [18] investigated the deposition of nanocrystalline metal oxide thin films, using chemical methods, and the relation of their respective morphology in their various applications.

3.1. Electrochemical Deposition (ECD). The electrochemical deposition of metals and alloys revolves around the reduction of metal ions from aqueous, organic, and fused-salt electrolytes (see Figure 5). This process is represented by (1)

$$M^{z+}_{\text{solution}} + ze \rightarrow M_{\text{lattice}}$$

(1)

This is achievable via two different processes: (1) an electrodeposition process, where $z$ electrons (e) are provided by an external power supply, and (2) an electroless (autocatalytic) deposition process, where a reducing agent in the solution is the electron source (sans an external power supply). Both processes are representative of electrochemical deposition [19].

The electrochemical method counts among the simplest and most effective method of fabricating 1D semiconductor nanostructures. Among variants of the electrochemical method in preparing oriented 1D film are template-assisted electrochemical synthesis and direct electrochemical growth via capping reagents [20]. Among the advantages of the electrochemical methods is the ability to customize and control the compositions and morphologies of nanostructured materials. Different types of electrochemical deposition such as electroplating, electrolytic anodization, and electrophoretic deposition can be used for the synthesis of materials. In Electrophoretic Deposition, dissociated colloidal cations and anions disperses onto a conductive substrate. After applying an electric field, the colloidal charged particles migrate to the substrate, get discharged, and form a film. Similar to thermal oxidation in Electrolytic anodization, an oxide film is formed on the substrate; the difference is that the anode is oxidized because of the negative ions in the electrolyte and forms a nonporous and well-adhering oxide or a hydrated...
oxide coating on semiconductors and on a few specific metals. During oxidation, the hydrogen gas evolves at the cathode. Electroplating can be used for the deposition of metallic coatings on the cathode's substrate when applying an electrical current to an electrolytic cell consisting of an anode, cathode, and an electrolyte solution (containing the metal ions) [8]. Table 3 summarizes the different type of electrochemical synthesis that is employed for DSSC.

3.2. Solvothermal/Hydrothermal Methods. Both the solvothermal and hydrothermal methods are effective tools in the generalization and systematic control of the syntheses of nanomorphologies. Figure 6 shows the typical autoclave for solvothermal/hydrothermal synthesis.

The solvothermal/hydrothermal methods are important technologies with regard to the production of semiconductor nanowires at low temperatures. Zou et al. [22] discussed nanowire growth from mainly four aspects in the solvothermal/hydrothermal processes: (1) materials with highly anisotropic crystal structures, (2) coordination directing/mixed solvents, (3) surfactants/capping reagents, and (4) reactions at relatively high temperatures.

Both the hydrothermal and solvothermal methods have some poignant differences. These differences include the fact that the solvothermal method (using non-water as a solvent) can practically halt oxidation, a factor that is especially imperative to the synthesis of a variety of nonoxides [22].

“Hydrothermal synthesis” is defined by the heterogeneous reactions in aqueous media above 100°C, at 1 bar of pressure [24]. It remains one of the preferred methods in fabricating pure fine oxide powders. Figure 7 details the schematic of the hydrothermal synthesis.

For hydrothermal experiments, the prerequisites for the starting materials are (i) knowing the composition, (ii) being as homogeneous as possible, (iii) being as pure as possible, and (iv) being as fine as possible [26]. Sōmiya and Roy [26] described some of different types of hydrothermal synthesis methods (see Table 4).

3.2.1. Advantages and Disadvantages of Hydrothermal/Solvothermal Synthesis. The advantages include the following.

(1) Most of the materials that are involved can be induced to solubility via heat and pressure applied to the system up to its critical point.

(2) It offers a significant enhancement to the chemical activities of the reactant, the possibility to replace the solid-state synthesis, and materials, which may not be obtained via solid-state reaction but may be prepared through hydrothermal/solvothermal synthesis.

(3) Products of intermediate state, metastable state and specific phases may be easily produced, and novel compounds of metastable state and other specific condensed state may be synthesized.

(4) Simplified and precise control of the size, shape, distribution, and crystallinity of the end product via the adjustment of parameters such as reaction temperatures and time, the types of solvents, surfactants and precursors can be achieved.

(5) Substances that are low in melting points and high in vapor pressures and tendency towards pyrolysis will be obtained.

The disadvantages of hydrothermal/solvothermal synthesis are as follows:

(1) the need of expensive autoclaves;

(2) safety issues during the reaction process;

(3) impossibility of observing the reaction process ("black box") [27].

Researchers have used both the hydrothermal and solvothermal methods extensively. Some of most recent researches
Table 3: Different electrochemical deposition methods used in DSSC.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>Efficiency (η)%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous ZnO on carbon nanotube (CNT) coated polymer</td>
<td>Electrochemical deposition</td>
<td>2.5</td>
<td>[144]</td>
</tr>
<tr>
<td>Vertical ZnO nanotube (ZNT)</td>
<td>Electrochemical deposition followed by a selective etching process</td>
<td>1.01</td>
<td>[145]</td>
</tr>
<tr>
<td>Well-crystallined ZnO-eosin Y hybrid thin films</td>
<td>Two-step cathodic electrodeposition</td>
<td>0.21</td>
<td>[146]</td>
</tr>
<tr>
<td>Crystalline nanoporous layers of ZnO</td>
<td>Gas template electrodeposition</td>
<td>2.1</td>
<td>[147]</td>
</tr>
<tr>
<td>ZnO/dye hybrid thin films</td>
<td>Cathodic electrodeposition (electrochemically self-assembled)</td>
<td>—</td>
<td>[148]</td>
</tr>
<tr>
<td>ZnO nanobelt array films</td>
<td>Electrodeposition method with liquid crystal template</td>
<td>2.6</td>
<td>[149]</td>
</tr>
<tr>
<td>ZnO porous film on a plastic substrate</td>
<td>Electrophoresis deposition (EPD) process with UV-O3 treatment</td>
<td>4.04</td>
<td>[150]</td>
</tr>
<tr>
<td>ZnO photoanode on plastic</td>
<td>Electrochemical deposition</td>
<td>4.17</td>
<td>[151]</td>
</tr>
<tr>
<td>Nanowires and hierarchical ZnO nanostructures</td>
<td>Anodization and subsequent electrochemical deposition</td>
<td>—</td>
<td>[152]</td>
</tr>
<tr>
<td>Branched hierarchical ZnO nanowire arrays</td>
<td>Two-step electrochemical deposition process</td>
<td>0.88</td>
<td>[153]</td>
</tr>
<tr>
<td>Mesoporous platinum</td>
<td>Electrochemical deposition</td>
<td>7.6</td>
<td>[154]</td>
</tr>
<tr>
<td>Platinum/graphene hybrid film</td>
<td>Electrochemical deposition</td>
<td>7.88</td>
<td>[155]</td>
</tr>
<tr>
<td>Graphene-Pt/ITO (ITO-PG)</td>
<td>Electrochemical deposition</td>
<td>7.57</td>
<td>[156]</td>
</tr>
<tr>
<td>Platinum nanoparticle</td>
<td>Electrochemical deposition</td>
<td>6.4</td>
<td>[157]</td>
</tr>
<tr>
<td>Thin Pt counter electrode</td>
<td>Pulsed electrodeposition method</td>
<td>6</td>
<td>[158]</td>
</tr>
<tr>
<td>Platinum nanoparticles on plastic substrates</td>
<td>Electrophoretic deposition</td>
<td>5.8</td>
<td>[159]</td>
</tr>
<tr>
<td>Platinum (Pt) layer on ITO</td>
<td>Electroless deposition</td>
<td>6.46</td>
<td>[160]</td>
</tr>
<tr>
<td>Composite (PProDOT-Et2/Pt)</td>
<td>Electropolymerization</td>
<td>6.65</td>
<td>[161]</td>
</tr>
<tr>
<td>Closely packed titania nanoparticles</td>
<td>Electrochemical deposition</td>
<td>6.27</td>
<td>[162]</td>
</tr>
<tr>
<td>Coaxial TiO₂/ZnO nanotube arrays</td>
<td>Electrochemical deposition</td>
<td>2.8</td>
<td>[163]</td>
</tr>
<tr>
<td>(ClO₄⁻ PEDOT/TiO₂/FTO)</td>
<td>Electrochemical deposition</td>
<td>4.78</td>
<td>[164]</td>
</tr>
<tr>
<td>Nanocrystalline anatase TiO₂</td>
<td>Reductive electrodeposition</td>
<td>5.1</td>
<td>[165]</td>
</tr>
<tr>
<td>TiO₂/dye hybrid films</td>
<td>Anodic electrodeposition</td>
<td>—</td>
<td>[166]</td>
</tr>
<tr>
<td>Ordered titanate nanotube (TNT) films</td>
<td>Electrophoretic deposition</td>
<td>3.79</td>
<td>[167]</td>
</tr>
<tr>
<td>Titanate nanotubes</td>
<td>Hydrothermal process and electrophoretic deposition</td>
<td>6.71</td>
<td>[168]</td>
</tr>
<tr>
<td>Mesoporous TiO₂ film on a titanium (Ti) foil</td>
<td>Electrophoretic deposition</td>
<td>6.5</td>
<td>[169]</td>
</tr>
<tr>
<td>Mesoporous TiO₂ photoanode film on plastic substrate</td>
<td>Electrophoretic deposition</td>
<td>4.37</td>
<td>[170]</td>
</tr>
<tr>
<td>TiO₂-B nanoribbon films</td>
<td>Electrophoretic deposition</td>
<td>0.87</td>
<td>[171]</td>
</tr>
<tr>
<td>Highly ordered TiO₂ nanotube arrays</td>
<td>Electrophoretic deposition</td>
<td>6.28</td>
<td>[172]</td>
</tr>
<tr>
<td>Titanium oxide (TiO₂) thin films</td>
<td>Cathodic electrolysis</td>
<td>2.33</td>
<td>[173]</td>
</tr>
<tr>
<td>Nanostructured TiO₂ films</td>
<td>Plasma electrolytic oxidation combined with chemical and thermal post-treatments</td>
<td>2.194</td>
<td>[174]</td>
</tr>
<tr>
<td>Combined TiO₂ structure with nanotubes and nanoparticles</td>
<td>Electrochemical anodization</td>
<td>5.75</td>
<td>[175]</td>
</tr>
<tr>
<td>Titanium dioxide (TiO₂) nanotube arrays</td>
<td>Anodizing</td>
<td>4.38</td>
<td>[176]</td>
</tr>
<tr>
<td>Non-annealed anatase TiO₂ film</td>
<td>Anodizing and sputtering</td>
<td>—</td>
<td>[177]</td>
</tr>
<tr>
<td>Titan nanotube arrays</td>
<td>Electrochemical anodization</td>
<td>—</td>
<td>[178]</td>
</tr>
<tr>
<td>TiO₂ nanotube arrays</td>
<td>Anodizing, detachment and transfer method</td>
<td>1.78</td>
<td>[179]</td>
</tr>
<tr>
<td>Aligned high-aspect ratio TiO₂ nanotube bundles</td>
<td>Rapid breakdown anodizing (electrochemical)</td>
<td>—</td>
<td>[180]</td>
</tr>
<tr>
<td>Well-aligned TiO₂ nanotube arrays</td>
<td>Electrochemical etching</td>
<td>2.13</td>
<td>[181]</td>
</tr>
</tbody>
</table>
Table 3: Continued.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>Efficiency (η)%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-nanotube array electrode</td>
<td>Arc ion plating (AIP) deposition and anodically oxidizing</td>
<td>1.88</td>
<td>[182]</td>
</tr>
<tr>
<td>Nanocrystalline TiO$_2$ films</td>
<td>Microplasma oxidation (MPO) method (process combines electrochemical oxidation with a high-voltage spark treatment in an electrolyte bath)</td>
<td>0.092</td>
<td>[183]</td>
</tr>
<tr>
<td>Nanostructured TiO$_2$ films</td>
<td>Plasma electrolytic oxidation (PEO) combined with chemical and thermal posttreatments</td>
<td>2.194</td>
<td>[174]</td>
</tr>
<tr>
<td>Functionalized and nonfunctionalized fullerene thin films on ITO glasses</td>
<td>Electrolytic micelle disruption method (the electrolysis method)</td>
<td>—</td>
<td>[184]</td>
</tr>
<tr>
<td>Arborous structure SnO$_2$ porous films on Ti substrate</td>
<td>Pulse-potential technique (electrodeposition)</td>
<td>0.47</td>
<td>[185]</td>
</tr>
<tr>
<td>Crystalline CuSCN films</td>
<td>Cathodic electrodeposition</td>
<td>—</td>
<td>[186]</td>
</tr>
<tr>
<td>(PProDOT-Et2)</td>
<td>Electrochemical polymerization (electropolymerization)</td>
<td>7.88</td>
<td>[187]</td>
</tr>
<tr>
<td>High conductive transparent substrates were fabricated with nickel grids</td>
<td>Electroplating process</td>
<td>4.3</td>
<td>[188]</td>
</tr>
<tr>
<td>Polyaniline nanofiber/carbon film</td>
<td>Electrochemical deposition</td>
<td>6.85</td>
<td>[189]</td>
</tr>
<tr>
<td>Polyaniline nanofibers</td>
<td>Pulse electropolymerization</td>
<td>5.13</td>
<td>[190]</td>
</tr>
</tbody>
</table>

3.2.2. Microwave Irradiation. The hydrothermal method plays a defining role in the shaping of the microstructures of TiO$_2$. However, conventional hydrothermal processing is usually reliant upon high temperatures and pressures, along with extended processing times and complex procedures for the synthesis of TiO$_2$ nanocrystals [36, 37]. This paves the way for microwave processing of inorganic compounds, which forms an attractive field in modern material science. To this end, many inorganic materials had been synthesized via microwave ovens [38–42], mostly through rapid microwave-material interactions. This technique is also viable for the synthesis of nanosized TiO$_2$ powder possessing high degrees of crystallinity and monodispersed crystallites [43–45]. It has also been reported that the integration of microwave irradiation has effectively enhanced the efficiency of the hydrothermal method vis-à-vis the preparation of inorganic materials [46–53]. Microwave-assisted method has the unique advantage of uniform, rapid, and volumetric heating compared to its conventional counterpart. Moreover, microwave-assisted hydrothermal method significantly reduces both the processing time and temperatures, which...
results in rapid crystallization and the simplification of the whole process [37]. In most cases, TiO\textsubscript{2} nanoparticles are produced via the hydrothermal treatment. A multimode microwave heating system, operating at a frequency of 28 GHz, is utilized in order to induce rapid processing [45]. The synthesis of ZnO nanorods electrodes utilizing microwaves also demonstrated marked performance improvements [54].

It has been determined that the usage of organometallic or inorganic precursors in microwave-assisted methods resulted in remarkable improvements in all aspects. This is demonstrated in the work of Bhatte and coworkers [55], where they employed Zn (CH\textsubscript{3}COO\textsubscript{2})\textsubscript{2} as an additive-free synthesis of nanocrystalline zinc oxide via the microwave technique. Also, Brahma and Shivashankar [56] reported the utilization of the microwave method for depositing thin films and thick coatings of metal oxides via a liquid medium involving the microwave irradiation of an inorganic complex solution and zinc acetylacetone in a dielectric solvent. In this work, ZnO nanoflowers and ZnGly micro- and nanoplates are synthesized via a very rapid and convenient microwave-assisted polyol method. ZnO nanoflower based solar cell fabrication on metallic sheets was both prepared using the chemical deposition method, and have been used in DSSC as counter electrodes [72, 73].

Meanwhile, it must be considered that microwave technique can be used with other methods such as chemical bath deposition, which requires heating and calcination.

### 3.2.3. Ultrasonic Technique

The method of sonochemical processing has proven itself useful in fabricating novel materials with unique properties [58, 59]. The working principle behind the chemical effect of ultrasound is derived from acoustic cavitation, which is the formation, growth, and implosive collapse of bubbles in a liquid. This in turn generates localized hot spots via adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. These formed hot spots are demonstrated to possess a transient temperature of about 5000 K, pressure of 1800 atm, and cooling rates exceeding 108 Ks\textsuperscript{-1} [59]. The specific application of ultrasound in the synthesis of a variety of materials has been analyzed by Suslick and Price [60].

Wang et al. [61] employed ultrasonic waves to fabricate mesoporous TiO\textsubscript{2} under different conditions for DSSC applications.

#### 3.3. Chemical Bath Deposition (CBD)

The chemical bath deposition (CBD) method, also known as controlled precipitation or solution growth method, or quite simply, chemical deposition, has recently been vaunted as a viable method for the deposition of both metal chalcogenide and metal oxide thin films. CBD is essentially a simple method, requiring only a hot plate with a magnetic stirrer. The precursor chemicals are widely available and cost little. The CBD method allows the coating of a large number of substrates in a single cycle, provided that a proper jig is designed to do so. In the context of this method, the electrical conductivity of the substrate is unimportant. Any part of the surface that is insoluble and can be accessed by the solution will make a suitable deposition substrate. The deposition process happens at low temperatures, which circumvents the occurrence of oxidation and corrosion of metallic substrates. Chemical deposition usually results in the absence of pinholes, and uniform deposits are easily obtained, since their basic building blocks are ions instead of atoms. The parameters are easily controlled, which allows us to gain better orientations and grain structures. The formation of the film occurs when the ionic product allows us to gain better orientations and grain structures.

### Table 4: Hydrothermal synthesis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrothermal crystal growth</td>
<td>Hydrothermal treatment</td>
</tr>
<tr>
<td>Hydrothermal degeneration</td>
<td>Hydrothermal dehydration</td>
</tr>
<tr>
<td>Hydrothermal extraction</td>
<td>Hydrothermal reaction sintering</td>
</tr>
<tr>
<td>Hydrothermal sintering</td>
<td>Corrosion reaction</td>
</tr>
<tr>
<td>Hydrothermal oxidation</td>
<td>Hydrothermal precipitation—hydrothermal crystallization</td>
</tr>
<tr>
<td>Hydrothermal decomposition</td>
<td>Hydrothermal hydrolysis—hydrothermal precipitation</td>
</tr>
<tr>
<td>Hydrothermal electrochemical reaction</td>
<td>Hydrothermal mechanochemical reaction</td>
</tr>
<tr>
<td>Hydrothermal + ultrasonic</td>
<td>Hydrothermal + microwave</td>
</tr>
</tbody>
</table>

3.4. Successive Ionic Layer Adsorption and Reaction (SILAR) Method

Successive ionic layer adsorption and reaction (SILAR) is a recently developed method for the deposition of metal chalcogenide thin films, although it has undergone less scrutiny by researchers [75, 76]. The method is based on the immersion of a substrate into anionic and cationic precursors, followed by rinsing of the substrate between every
immersion in double distilled water in order to circumvent homogeneous precipitation. Figure 9 graphically summarizes this method. During the immersion into a cationic precursor, cations are adsorbed onto the substrate’s surface. The act of rinsing after immersion will separate the unabsorbed or excess ions, while simultaneously preventing homogeneous precipitation. Similarly, when immersed in an anionic precursor solution, the anions will react with the preadsorbed cations. The remaining unreacted/powdery material can be expelled via rinsing. The whole process of immersion and rinsing in both the cationic and anionic precursor is regarded as one full cycle. After a few repetitions of these cycles, a multilayer film of desired thickness would be formed. The quality and thickness of these respective films are highly dependent on the preparation parameters. A review by Pathan and Lokhande [77] outlines the advantages of SILAR over the CBD method. In the former, the deposition of a sufficiently thick film requires an extended period of time, which makes it crucial that it is operated with microprocessor or computer [18].

Das et al. [78] have prepared CoS-implanted graphene (G-CoS) film electrode using chemical vapor deposition and SILAR for DSSC. The prepared electrode was characterized in a dye sensitized solar cells (DSSCs). It reached better efficiency $\eta = 3.42\%$, while $J_{sc}$ (mA/cm$^2$), $V_{oc}$ (V), and FF (%) was 12.8, 0.72, and 36.4, respectively.

Thin ZnSe layers were deposited on ZnO nanowires using SILAR method by Chung et al. [79] for DSSC application. The facilitation of electron transfer increased the $J_{sc}$, which was followed by improved efficiency.

### 3.5. Spray Pyrolysis Method

Spray pyrolysis is regarded as one of the most attractive and promising film preparation methods. It basically mirrors a film processing technique called the pyrosol technique, where a source solution is sprayed onto a heated substrate for it to be deposited in the form of a film. The mechanism of the process is as follows. The source solution is atomized, where small droplets splash and vaporize on a substrate, which results in the formation of a dry precipitate and thermal decomposition [80]. Figure 10 shows a schematic of the whole process.

#### 3.5.1. Advantage and Disadvantages

Advantage and Disadvantages are as follows:

(i) does not require high quality targets or substrates;
(ii) being of low cost;
(iii) does not require a UHV system;
(iv) continuously produces the material;
(v) chemical reaction occurs within the created micron to submicron sized liquid droplets—a microcapsule reactor.

The technique is quite empirical, with a number of variables that can affect the final product such as solute concentration, atomization technique, temperature, temperature gradient, residence time in furnace, and carrier gases [80]. Table 5 represents research results using SPD method in preparation of DSSC. Figure 11 represents the comparison between spin coating and spray pyrolysis methods.

### 3.6. Sol-Gel Coating

The sol-gel process is also known as the chemical solution deposition, and it is classified as a wet chemical technique that is widely being applied in fields of materials science and ceramic engineering (Figure 12). It is mostly used for materials’ synthesis (typically a metal oxide), initiated from a chemical solution that acts as the precursor for an integrated network (or gel) of discrete particles or network polymers. Some common precursors include metal alkoxides and chlorides, which are pegged to undergo multiple forms of hydrolysis and polycondensation reactions. Metal oxides are formed via the linkage of metal ions with o xo (M–O–M) or hydroxo (M–OH–M) bridges, which results in a metal-oxo or metal-hydroxo polymers forming in
Figure 10: Schematic representation of spray pyrolysis method [18].

Table 5: SPD methods in preparation of DSSC.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>Efficiency (η)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine-doped tin oxide (FTO) films coated on indium-tin oxide (ITO) films</td>
<td>Spray pyrolysis deposition (SPD)</td>
<td>3.7</td>
<td>[191, 192]</td>
</tr>
<tr>
<td>ITO-Pt semiconductor powder containing nanoscale noble metal particles</td>
<td>Spray pyrolysis</td>
<td>—</td>
<td>[193]</td>
</tr>
<tr>
<td>TiO₂ blocking layer</td>
<td>Spray pyrolysis</td>
<td>—</td>
<td>[194, 195]</td>
</tr>
<tr>
<td>Porous TiO₂ films</td>
<td>Spray pyrolysis deposition</td>
<td>3.2–5.1</td>
<td>[81, 196]</td>
</tr>
<tr>
<td>TiO₂ nanocrystalline electrode</td>
<td>Atomized spray pyrolysis (ASP)</td>
<td>8.2</td>
<td>[197]</td>
</tr>
<tr>
<td>Nb₂O₅ blocking layer</td>
<td>Spray pyrolysis</td>
<td>3.35</td>
<td>[198]</td>
</tr>
<tr>
<td>Boron-doped zinc oxide (B₉ZnO) electrode</td>
<td>Spray pyrolysis deposition</td>
<td>1.53</td>
<td>[199]</td>
</tr>
<tr>
<td>ZnO nanostructures</td>
<td>Spray pyrolysis</td>
<td>4.7</td>
<td>[200]</td>
</tr>
</tbody>
</table>

Thus, the sol gravitates towards a gel-like biphasic system of both liquid and solid, whose morphologies ranges from discrete particles to continuous polymer networks. The sol-gel technique is considered as a bridge for nanoparticles in the DSSC working electrodes such as TiO₂ nanoparticles (P25 and P90) on polyethylene naphthalate (PEN) plastic sheet [82] and metal oxide semiconductor nanostructured such as zinc titanate (ZT), zinc oxide (ZO), and titanium dioxide (TD). The highest loading amount of dye and the best interaction between the semiconductor and dye are related to ZO, which has higher efficiency than the other cells. Due to its high electron conductivity, ZnO has the potential to enhance dye adsorption and highlight transmittance of a composite film [83]. Generally, the sol-gel process results in a highly pure product, homogenous, high adhesion, and strength and low temperature processing.

The Sol-gel method is one of the most used methods for materials preparation in DSSC. Certain recent research achievements using the sol-gel methods include TiO₂ film and nanoparticles, ZnO, ZT preparation for DSSC.
Figure 11: Comparison between spin coating and SPD methods [81].

Figure 12: Schematic of sol-gel procedure and their products [84].
application [82, 83, 85–90]. Some researchers employ the sol-gel method in combination with physical deposition methods such as dip coating, spin coating, and electrospinning in order to synthesis TiO₂, doped TiO₂, and TiO₂ composites [90–95].

Kwon et al. [96] used the sol-gel combustion method for the preparation of nanoporous F-doped tin dioxide films. The resulting DSSC managed to achieve an efficiency of 1.2%.

3.7. Template Method. Among the many methods that can be used to fabricate ordered porous films (sputtering, chemical vapor deposition (CVD), spray pyrolysis and sol-gel process), the template method is the one that is mostly used, due to the fact that the pore's dimensions are determined by the size of the ordered template beads [97–100]. The result of this method is a material that is homogenous, pure, possessing novel morphology, structure, and properties.

However, it is commonly acknowledged that without being combined with another physical and chemical method, the end product of the template method is not up to par. The combination of template growth and sol-gel coating results in the fabrication of fine nanostructure of desired features [101–110]. Jiu et al. [102] reported template growth of porous TiO₂ films with mixed polymers of Pluronic F-127 and cetyltrimethylammonium bromide. Zukalová et al. [111] reported a similar structure with Pluronic P-123. Both works produce end products with very high surface areas but small pore diameters of 4–7 nm [102] and 6–8 nm [101], respectively.

Dionigi et al. presented a colloidal composite consisting of monodispersed polystyrene (PS), coated with a titanium oxide precursor named TALH that acts as a “structure director” for the fabrication of TiO₂ films [112]. Meanwhile, Meng et al. assembled a highly ordered three-dimensional porous structure with commercial nanosized crystalline TiO₂ particles via a cooperative method, where the fabrication of the template and the infiltration of its voids occur simultaneously [113]. Also, highly ordered TiO₂ porous films were synthesized via a single-step assembly method, where the porous structures were prepared using polystyrene microspheres, with diameters [114]. Liu et al. prepared porous ZnO thin films that are assembled by dip coating method [115]. Table 6 shows the result for DSSC prepared using template method.

3.8. Self-Assembly. Self-assembled nanosphere monolayers form the templates of nanosphere lithography and can usually be fabricated with techniques such as drop coating or spin coating [116–118] of polystyrene (PS) latex nanospheres. However, the difficulty in producing a low-defect and large-area nanosphere monolayer using this method is also noted [119].

Jhang et al. [119] have used spin-coating that in combination with the water transfer technique produced self-assembled layer for preparation of nanostructured Pt counter electrodes. This electrode achieved $V_{oc}$ (V), $J_{sc}$ (mA/cm²), FF, and $\eta$ (%) of 0.71, 14.45, 0.70, and 7.18, respectively. Template-free chemically induced self-transformation (CIST) method has been employed by Yu et al. [120] for preparation of hollow anatase TiO₂ spheres. The fabricated DSSC has been reached at $J_{sc}$ (mA/cm²), $V_{oc}$ (V), FF (%), and $\eta$ (%) of 14.7, 0.599, 0.547, and 4.82, respectively. Mesostructured titania thick films have been synthesized employing of evaporation-induced self-assembly using nonionic triblock copolymers as templating agents by Malfatti et al. [121].

3.9. Mechanical Methods. There are many mechanical techniques such as spraying, spinning, dipping and draining, flow coating, and roller coating, which are done for depositing coatings from a liquid media that subsequently reacted chemically to form the inorganic thin film product. These techniques are also classified in different ways compared to the physical deposition method, which requires a whole other discussion.

4. Film Processing Techniques

There are some techniques which can be used to enhance the materials’ properties after their preparation, as well as their application for the preparation mix with some other preparation methods, namely, microwave or ultrasonic.

The deposited electrode materials on flexible substrate like polymers require an additional processing step to improve the necessary interparticle contact for their effective performance as an electrode material, as well as to improve the mechanical stability, namely, good film-substrate adhesion. Organic binders were used in making flexible DSSCs, but the absence of high temperature sintering of the metal oxide film on polymer substrates resulted in incomplete necking of the particles due to the presence of residual organics in the film [122]. UV/ozone and UV radiation treatments of the deposited metal oxide films were used by several groups as a method for eliminating adsorbed organic impurities on the surface of metal oxide films and improving the interparticle connection as another low temperature sintering method for flexible DSSCs [6, 123–127].

In order to realize the selective heating of organic-inorganic composite films, microwave processing seems to be the most promising choice. Uchida et al. [128] used a 28 GHz microwave irradiation process to produce a flexible DSSC. This particular technique is also applicable in the fabrication of PET-ITO film electrodes. A photoelectron energy conversion efficiency of 2.16% is realized for all-plastic cell fabricated by the 28 GHz microwave irradiation, at 1.0 kW for 5 minutes.

Gan et al. [129] succeeding in fabricating a hybrid ZnO nanowire/TiO₂ nanoparticle photoanodes for DSSCs using an ultrasonic irradiation assisted dip-coating method. The gap-filling efficiency of TiO₂ nanoparticles into the interstice voids of the ZnO nanowires was enhanced with the assistance of ultrasonic irradiation, which results in an increase of the total surface area, along with the light harvesting efficiency for the hybrid electrode. The effects of the ultrasonic treatment on the microstructure, the sensitization, and
Table 6: Some research work on DSSC that used template method.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>Efficiency (η)%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-crystalline TiO₂ nanoparticles as a thin-film</td>
<td>Mixed template of copolymer and surfactant</td>
<td>8.24</td>
<td>[102]</td>
</tr>
<tr>
<td>Mesoporous titania nanocrystals</td>
<td>Sol-gel synthesis using surfactant as template</td>
<td>4.08</td>
<td>[201]</td>
</tr>
<tr>
<td>Organized mesoporous TiO₂ films</td>
<td>Supramolecular templating with an amphiphilic triblock copolymer</td>
<td>—</td>
<td>[111]</td>
</tr>
<tr>
<td>Multilayered mesoporous TiO₂ films</td>
<td>Supramolecular templating and layer-by-layer deposition</td>
<td>5.12</td>
<td>[202]</td>
</tr>
<tr>
<td>Nanocrystalline mesoporous titania</td>
<td>Surfactant-assisted templating method and doctor-blading technique</td>
<td>8.06</td>
<td>[203]</td>
</tr>
<tr>
<td>Ordered nanoporous TiO₂</td>
<td>Different silica templates and the squeeze printing technique</td>
<td>3.6</td>
<td>[204]</td>
</tr>
<tr>
<td>Hollow spherical TiO₂</td>
<td>Colloidal carbon spheres as templates</td>
<td>5.64</td>
<td>[205]</td>
</tr>
<tr>
<td>Mesoporous anatase-TiO₂</td>
<td>Sol-gel using soft template and a hard template</td>
<td>6.71</td>
<td>[206]</td>
</tr>
<tr>
<td>Anatase TiO₂ hollow spheres</td>
<td>Chemical template method</td>
<td>3.79</td>
<td>[207]</td>
</tr>
<tr>
<td>Ordered porous TiO₂ thin films</td>
<td>Colloid crystal template</td>
<td>1.269</td>
<td>[208]</td>
</tr>
<tr>
<td>Mesoporous TiO₂</td>
<td>Sol-gel using water miscible ionic liquid template</td>
<td>—</td>
<td>[209]</td>
</tr>
<tr>
<td>Porous TiO₂ films</td>
<td>Templated sol-gel method</td>
<td>—</td>
<td>[210]</td>
</tr>
<tr>
<td>Mesoporous nanocrystalline TiO₂ films</td>
<td>Hydrolysis-limited sol-gel process using block copolymer as template</td>
<td>0.31</td>
<td>[211]</td>
</tr>
<tr>
<td>Center hollow ZnO and TiO₂ nanotubes arrays</td>
<td>Electrodeposition, chemical etching, and sol-gel process assisted by templates</td>
<td>1.2</td>
<td>[212]</td>
</tr>
<tr>
<td>Ferrocene-derivatized ordered mesoporous carbon</td>
<td>Hard template method</td>
<td>7.89</td>
<td>[213]</td>
</tr>
<tr>
<td>Ordered mesoporous carbon (OMC)</td>
<td>Evaporation-induced triconstituent coassembly method using soft-template method employing triblock copolymer</td>
<td>7.46</td>
<td>[214]</td>
</tr>
<tr>
<td>MWCNT/mesoporous carbon nanofibers composites</td>
<td>Electrospinning, template etching, and thermal process</td>
<td>6.35</td>
<td>[215]</td>
</tr>
<tr>
<td>Nanoporous NiO films</td>
<td>NiCl₂ in water/ethanol mixed solution, using triblock copolymers as template</td>
<td>—</td>
<td>[216]</td>
</tr>
<tr>
<td>Hollow silver microspheres</td>
<td>Chemical deposition using sacrificial templating method</td>
<td>—</td>
<td>[217]</td>
</tr>
</tbody>
</table>

the performance of hybrid ZnO NW/TiO₂ NP electrodes were thoroughly analyzed.

5. Lessons Learned

Taking into account the contents that are presented, it can be surmised that choosing an appropriate method is incumbent upon its parameters. For example, if the deposition rate is the primary parameter being considered, then the ALD and SIALR methods are ruled out, as they are detrimental in the context of deposition rates. If safety is of vital importance, then the use of CVD, ALD, and solvothermal/hydrothermal methods is not recommended. Furthermore, if one needs to synthesize materials that are unobtainable via solid-state reaction, the usage of solvothermal/hydrothermal method might be most suitable.

The preparation of thin films is highly reliant on the minute control of the materials at a molecular and atomic level, which encompasses surface modifications, deposition, and structuring. The preparation techniques and methods of thin film preparation have been significantly enhanced in the past decade due to better understanding of the physics and chemistry of thin films, along with their fundamental aspects, microstructural evolution, and their respective properties.

6. Conclusion

The selection of a specific deposition method needs variety of consideration and criteria such as thin film application, material characteristics, and process technology. It is found that there is no general guideline for choosing the best deposition method. However, different preparations and deposition technologies with materials’ and substrates’ type, specified application, cost, and requested efficiency allow the researchers to select a more appropriate technique for their research. Future work focuses more on the fabrication conditions and accounts for more parameters in order to compare the available chemical preparation methods in terms of their effect on DSSC efficiency, stability, durability cost, and optimization of the working conditions.
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors would like to thank the UKMDIP-2012-22 and DLP-2013-015 Research Funds for providing financial support to this study.

References


[34] C. Lao, Y. Chui, L. Su et al., “Mix-solvent-thermal method for the synthesis of anatase nanocrystalline titanium dioxide used


[99] L. J. Fu, T. Zhang, Q. Cao, H. P. Zhang, and Y. P. Wu, "Preparation and characterization of three-dimensionally ordered mesoporous titania microparticles as anode material for lithium ion battery," *Electrochemistry Communications*, vol. 9, no. 8, pp. 2140–2144, 2007.


Submit your manuscripts at http://www.hindawi.com

Hindawi Publishing Corporation
http://www.hindawi.com

International Journal of

Inorganic Chemistry

Analytical Methods in Chemistry

Journal of Chemistry

Advances in Physical Chemistry

Spectroscopy

The Scientific World Journal

Medicinal Chemistry

Chromatography Research International

Journal of Spectroscopy

Catalysts

Journal of Theoretical Chemistry

The Scientific World Journal

Journal of Applied Chemistry

Journal of Analytical Methods in Chemistry

Journal of Quantum Chemistry

Organic Chemistry

Bioinorganic Chemistry and Applications

Electrochemistry International Journal of

International Journal of Medicinal Chemistry

International Journal of Carbohydrate Chemistry

International Journal of Photoenergy

International Journal of Inorganic Chemistry

International Journal of Analytical Chemistry

Bioinorganic Chemistry and Applications

Journal of Spectroscopy

International Journal of Quantum Chemistry

Organic Chemistry

International Journal of Analytical Methods in Chemistry

Bioinorganic Chemistry and Applications

Electrochemistry International Journal of

International Journal of Medicinal Chemistry

International Journal of Carbohydrate Chemistry

International Journal of Photoenergy

International Journal of Inorganic Chemistry

International Journal of Analytical Chemistry

Bioinorganic Chemistry and Applications

Journal of Spectroscopy

International Journal of Quantum Chemistry

Organic Chemistry

International Journal of Analytical Methods in Chemistry

Bioinorganic Chemistry and Applications

Electrochemistry International Journal of

International Journal of Medicinal Chemistry

International Journal of Carbohydrate Chemistry

International Journal of Photoenergy

International Journal of Inorganic Chemistry

International Journal of Analytical Chemistry

Bioinorganic Chemistry and Applications

Journal of Spectroscopy

International Journal of Quantum Chemistry

Organic Chemistry

International Journal of Analytical Methods in Chemistry

Bioinorganic Chemistry and Applications

Electrochemistry International Journal of

International Journal of Medicinal Chemistry

International Journal of Carbohydrate Chemistry

International Journal of Photoenergy

International Journal of Inorganic Chemistry

International Journal of Analytical Chemistry

Bioinorganic Chemistry and Applications

Journal of Spectroscopy

International Journal of Quantum Chemistry

Organic Chemistry

International Journal of Analytical Methods in Chemistry

Bioinorganic Chemistry and Applications

Electrochemistry International Journal of

International Journal of Medicinal Chemistry

International Journal of Carbohydrate Chemistry

International Journal of Photoenergy

International Journal of Inorganic Chemistry

International Journal of Analytical Chemistry

Bioinorganic Chemistry and Applications

Journal of Spectroscopy

International Journal of Quantum Chemistry

Organic Chemistry

International Journal of Analytical Methods in Chemistry

Bioinorganic Chemistry and Applications

Electrochemistry International Journal of