# **Chapter 11 Plant-Assisted Fabrication of SnO**<sub>2</sub> and SnO<sub>2</sub>-Based Nanostructures **for Various Applications**



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### **11.1 Introduction**

Nanotechnology encompasses the understanding, manipulation, and control of matter at the nanoscale level obtained by a combination of engineering, physical, chemical, and biological approaches. It has enabled the development of advanced materials such as nanoparticles (NPs) and nanostructures with unique properties, including the novel optoelectronic, catalytic, and biological properties (Hong and Jiang [2017\)](#page-11-0). The extensive practical application of NPs could be attributed to their unique characteristics that establish their superiority over their bulk counterparts (Shamaila et al. [2016](#page-12-0)).

Different metal oxides such as  $TiO<sub>2</sub>$ ,  $ZnO$ ,  $SnO<sub>2</sub>$ , and  $CeO<sub>2</sub>$ , among others, are commonly synthesized and used widely as photocatalysts, especially in the heterogeneous photocatalysis (Kalathil et al. [2013](#page-11-1); Khan et al. [2013,](#page-12-1) [2014,](#page-11-2) [2015a](#page-11-3), [b](#page-11-4), Ansari et al. [2014a,](#page-10-0) [b](#page-11-5), [c](#page-11-6), [d,](#page-11-7) [2016](#page-11-8); Saravanan et al. [2015](#page-12-2)). This is due to their biocompatibility as well as exceptional stability in a variety of conditions and their capability to generate charge carriers when excited by the required amount of light energy. The favorable combination of the electronic structure, light absorption properties, charge-transport characteristics, and excited lifetimes of charge carriers in different metal oxides has made them a fine photocatalyst (Khan et al. [2015a](#page-11-3)). Among all these nanomaterials (NMs),  $SnO<sub>2</sub>$  NPs in particular can be utilized as gas sensors (Sun et al. [2005;](#page-12-3) Song et al. [2012](#page-12-4); Ahamed Fazil et al. [2015;](#page-10-1) Manjula et al. [2012\)](#page-12-5), photocatalysts (Haritha et al. [2016](#page-11-9)), semiconductors (Cheng et al. [2016](#page-11-10)), and antibacterial agents (Vidhu and Philip [2015a\)](#page-12-6).

 $SnO<sub>2</sub>$  semiconductor is an important n-type oxide semiconductor with wide bandgap (3.6 eV). It has good electrical, optical, and electrochemical properties and

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is known as the catalytic support material for solar cells, as the solid-state chemical sensors and for its high lithium-storage capacity. The active crystal surfaces of  $SnO<sub>2</sub>$ have an important role in determining its interesting properties including the sensing and catalytic ones (Das and Jayaraman [2014\)](#page-11-11).

The large bandgap (3.6 eV, which can only respond to UV illumination) and the high electron hole recombination rate are the main drawbacks of  $SnO<sub>2</sub>$  semiconductors. Doping the  $SnO<sub>2</sub>$  semiconductors with metal ions is one of the best methods to improve the visible light photocatalytic activity for the oxidative degradation of organic compounds. Many transition metals have been used to modify the electronic properties of  $SnO<sub>2</sub>$ . Due to the relative ionic radius and interstitial spacing in the  $SnO<sub>2</sub>$  structure, the most frequently tested transition metals for this modification include inter alia gold, manganese, silver, cobalt, and iron. These transition metals have similar or lesser ionic radius, so the atoms can easily replace or fit into the interstitial sites in the  $SnO<sub>2</sub>$  structure (Sabergharesou et al. [2013;](#page-12-7) Cheng et al. [2016;](#page-11-10) Tomer and Duhan [2016](#page-12-8); Sinha et al. [2017\)](#page-12-9).

Gas sensors of individual  $SnO<sub>2</sub>$  materials are attractive due to their high sensitivity, quick response, and good stability. The hetero-structured  $SnO<sub>2</sub>$  with other semiconducting metal oxides will provide another promising strategy to develop novel high-performance gas sensors due to the formation of different charge carriers. This would assist to overcome effectively the challenge of high recombination rate in  $SnO<sub>2</sub>$  by scavenging the charge carriers (electrons and holes from the conduction and valence band, respectively) through compositing  $SnO<sub>2</sub>$  with other metal oxides such as n-type TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, CaO, MgO, V<sub>2</sub>O<sub>5</sub>, and Nb<sub>2</sub>O<sub>5</sub> and p-type  $NiO, Co<sub>3</sub>O<sub>4</sub>, Sb<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>O, Ag<sub>2</sub>O, CeO<sub>2</sub>, etc. (Cheng et al. 2016; Sudhaparimala$  $NiO, Co<sub>3</sub>O<sub>4</sub>, Sb<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>O, Ag<sub>2</sub>O, CeO<sub>2</sub>, etc. (Cheng et al. 2016; Sudhaparimala$  $NiO, Co<sub>3</sub>O<sub>4</sub>, Sb<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>O, Ag<sub>2</sub>O, CeO<sub>2</sub>, etc. (Cheng et al. 2016; Sudhaparimala$ and Vaishnavi [2016](#page-12-10)).

 $SnO<sub>2</sub>$  NPs have also been used widely for effective photocatalytic degradation of dye effluents and water treatment applications, using the UV or solar irradiation. This photodegradation process converts dye molecules into nonhazardous compounds and by-products. The nanostructured  $\text{SnO}_2$  exhibits enhanced photocatalytic activity for the degradation of dyes and proves to be an effective means for the elimination of various water pollutants (Bhattacharjee et al. [2015](#page-11-12)). In addition, utility of SnO2 NPs has been reported for antimicrobial applications (Meena Kumari and Philip [2015](#page-12-11); Vidhu and Philip [2015a](#page-12-6), [b;](#page-12-12) Roopan et al. [2015](#page-12-13)). This report intends to elucidate the morphology and characteristics of phytosynthesized  $SnO<sub>2</sub>$  NPs and their diverse applications.

#### **11.2 Synthesis of Nanoparticles**

In general, there are chemical, physical, and biological methodologies (as shown in Fig. [11.1](#page-2-0)) that can be used to synthesize NPs. Chemical methods of producing the desired NPs usually involve the use of metal precursors and other chemicals to initiate the particular reaction and stabilize pH for favorable reaction condition.

<span id="page-2-0"></span>

Fig. 11.1 Different methods of nanoparticle synthesis

These methods include sol-gel technique, microemulsion technique, solvo-thermal method, hydrothermal method, and chemical vapor deposition (CVD) technique, among others. In the case of physical synthesis, dry and wet mechanical grindings are used for inexpensive NP preparation. For technological applications, wet grinding is preferable because it allows more options to control the NP size (Saleh [2016\)](#page-12-14). Other physical methods include ultrasonication, thermal evaporation, and lithography. Several NP preparation methods employ a combination of both physical and chemical synthesis procedures, such as the sonochemical technique based on chemical method and ultrasound technique as well as the microwave-assisted chemical syntheses. A proper combination of chemical and physical methods allows for the production of smaller NPs (Xia et al. [2008;](#page-12-15) Saleh [2016\)](#page-12-14).

The expansion of these synthesis procedures to a large-scale production has several limitations such as expensive production costs resulting from high energy consumption, use of toxic organic solvents, production of hazardous intermediates, and formation of harmful waste products, leading to environmental pollution and several biological risks. Generally, wet chemical synthesis of NPs dominates the production methods. Agglomeration or aggregation of NPs usually occurs during synthesis due to the presence of attractive forces among NPs. Therefore, some capping agent is used to prevent aggregation and attain the desired morphology of the product. Besides their toxic nature, these methods also have such drawbacks as slow production rate, limited growth, and distorted structure of synthesized NPs. Size reduction may also lead to increased reactivity and toxicity of the material synthesized. Therefore, prior to the large-scale implementation of these reactions, it is necessary to analyze the potential hazards to the ecosystem by considering the entire chemical procedure and tracking all the species involved (Shamaila et al. [2016](#page-12-0); Hong and Jiang [2017](#page-11-0); Sinha et al. [2017;](#page-12-9) Osuntokun et al. [2017\)](#page-12-16).

Biological methods have been considered as green (eco-friendly) alternatives to the existing chemical and physical methods. The biological tools include microorganisms such as fungi, bacteria, and yeast as well as plant tissues obtained usually from roots, barks, leaves, seeds, and fruits (Sun et al. [2005](#page-12-3); Song et al. [2012](#page-12-4); Ansari et al. [2014d](#page-11-7); Kamaraj et al. [2014;](#page-11-13) Khan et al. [2015b](#page-11-4); Meena Kumari and Philip [2015;](#page-12-11) Vidhu and Philip [2015a,](#page-12-6) [b](#page-12-12); Elango et al. [2015;](#page-11-14) Ahamed Fazil et al. [2015;](#page-10-1) Sudhaparimala and Vaishnavi [2016](#page-12-10); Ahmed et al. [2016](#page-10-2); Elango and Roopan [2016;](#page-11-15) Haritha et al. [2016;](#page-11-9) Diallo et al. [2016;](#page-11-16) Hong and Jiang [2017;](#page-11-0) Sinha et al. [2017;](#page-12-9) Osuntokun et al. [2017](#page-12-16)). Plant-mediated methods to produce the  $SnO<sub>2</sub>$  nanomaterials are very few and yet to be collated. Phyto-nanotechnology (plant-mediated technique) for NP synthesis has multiple advantages over the chemical and physical methods, including cost-effectiveness, eco-friendliness, biocompatibility, scalability, and medical applicability of NPs obtained (Singh et al. [2016](#page-12-17)). The nontoxic nature of plants ensures suitability of phyto-mediated NPs for applications in biomedical and environmental areas. Extracts of various plant parts contain compounds required for the synthesis of NPs. Active compounds such as polyphenols, flavonoids, and other secondary metabolites are believed to be primarily responsible for the biological synthesis. These compounds are capable of reducing or oxidizing the ions present in the precursors by forming intermediates. The resulting NPs, such as SnO2, are usually obtained after calcination at specified temperatures (Diallo et al. [2016;](#page-11-16) Hong and Jiang [2017](#page-11-0); Osuntokun et al. [2017](#page-12-16)).

## 11.3 **Plant-Assisted Fabrication of SnO<sub>2</sub> Nanostructures and Their Applications**

Given the current chemophobia and the awareness about the hazardous effects of many chemical synthetic routes, green chemistry tends to offer an appropriate alternative by ensuring that the fabrication of materials is eco-friendly. A befitting and cost-effective means of achieving this goal in NM synthesis is the adoption of plant extracts to replace the toxic chemicals. This area of green chemistry is very promising to achieve an eco-friendly synthesis route and has gained ground with some recent reports on phytosynthesis of  $SnO<sub>2</sub>$  NPs (Table [11.1](#page-4-0)) and their diverse applications (Fig. [11.2](#page-6-0)) (Roopan et al. [2015;](#page-12-13) Vidhu and Philip [2015b;](#page-12-12) Elango and Roopan [2016](#page-11-15); Diallo et al. [2016](#page-11-16); Hong and Jiang [2017](#page-11-0); Sinha et al. [2017;](#page-12-9) Osuntokun et al. [2017](#page-12-16)).

No.	Plant	Metal oxide nanoparticle	Particle size (nm)	Applications	Year	Reference
$\mathbf{1}$	Cotton fiber	SnO <sub>2</sub> microtubes	$5 - 15 \times 10^3$ (microtubes)	Gas sensing	2005	Sun et al. (2005)
$\overline{2}$	Cotton fiber	SnO <sub>2</sub> nanotubules	14.2	Gas sensing	2010	Zhu et al. (2010)
3	Ramie fiber	SnO <sub>2</sub> /C; original NaOH- treated degummed	$2.0 - 5.0$ $2.5 - 6.3$ $2.6 - 4.7$	Gas sensing	2011	He et al. (2011)
$\overline{4}$	<b>Brassica</b> campestris	SnO <sub>2</sub> microreactor	$40 - 55$	Gas sensing	2012	Song et al. (2012)
5	Cotton	SnO <sub>2</sub> /C	20	Lithium-ion batteries	2014	Li et al. (2014)
6	Cleistanthus collinus	SnO <sub>2</sub>	~149.26	Antimicrobial and antioxidant agents	2014	Kamaraj et al. (2014)
$\boldsymbol{7}$	Saraca indica	SnO <sub>2</sub>	$2.1 - 4.1$	Antibacterial and antioxidant agents	2014	Vidhu and Philip $(2015a)$
8	Ficus carica	SnO <sub>2</sub>	~132	$Hg^{2+}$ sensor	2015	Hu J (2015)
9	Peltophorum pterocarpum	$SnO2$ motifs	$16 - 25$	Gas sensing	2015	<b>Ahamed Fazil</b> et al. (2015)
10	Trigonella foenum- graecum	SnO <sub>2</sub>	$2.2 - 3.2$	Nanofluids, antibacterial, and antioxidant agents	2015	Vidhu and Philip $(2015b)$
11	Pomegranate	SnO <sub>2</sub>	$2.5 - 2.7$	Nanofluids. antibacterial, and antioxidant agents	2015	Meena Kumari and Philip (2015)
12	Annona squamosa	SnO <sub>2</sub>	$25 \pm 5$	Cytotoxicity toward HepG2	2015	Roopan et al. (2015)
13	Persea americana	SnO <sub>2</sub>	$-4$	Photocatalytic degradation (phenol red)	2015	Elango et al. (2015)
14	Cyphomandra betacea	SnO <sub>2</sub>	$-21$	Photocatalytic degradation (methylene blue)	2016	Elango and Roopan (2016)
15	Catunaregam spinosa	SnO <sub>2</sub>	$47 \pm 2$	Photocatalytic degradation (Congo red)	2016	Haritha et al. (2016)

<span id="page-4-0"></span>Table 11.1 Different SnO<sub>2</sub> nanostructures synthesized with plant-assisted methods and their applications

(continued)

No.	Plant	Metal oxide nanoparticle	Particle size (nm)	Applications	Year	Reference
16	Aloe vera	Coupled $SnO_2-ZnO$	~22.27	Photocatalytic degradation (methylene orange), antimicrobial agent	2016	Sudhaparimala and Vaishnavi (2016)
17	Aspalathus linearis	SnO <sub>2</sub>	$2.1 - 19.3$	Photocatalytic degradation (methylene blue, Congo red, and eosin Y.)	2016	Diallo et al. (2016)
18	<b>Brassica</b> oleracea L. var. botrytis	SnO <sub>2</sub>	$3.62 - 6.34$	Photocatalytic degradation (methylene blue)	2017	Osuntokun et al. (2017)
19	Litsea cubeba	SnO <sub>2</sub>	~20	Photocatalytic degradation (Congo red), antioxidant agent	2017	Hong and Jiang (2017)
20	Saccharum officinarum	Ag doped SnO <sub>2</sub>	$\sim 9$	Photocatalytic degradation (methylene blue, rose Bengal, methyl violet 6B, and 4-nitro phenol), antimicrobial and antioxidant agents	2017	Sinha et al. (2017)
21	Piper nigrum	SnO <sub>2</sub>	$8.85 \pm 3.5$ at 300 °C; $12.76 \pm 3.9$ at 500 °C; $29.29 \pm 10.9$ nm at 900 $\degree$ C	Cytotoxicity toward cancer cells	2017	Tammina et al. (2017)

**Table 11.1** (continued)

## *11.3.1 Synthesis of Undoped SnO2*

Vidhu and Philip [\(2015a\)](#page-12-6) reported a cost-effective and environmentally benign method of synthesizing bioactive SnO<sub>2</sub> NPs of 2.1–4.1 nm, using *Saraca indica* flower. The synthesized NPs exhibited antibacterial activity against the gram-negative bacteria *Escherichia coli* and proved to be a good antioxidant and antibacterial agent. In another work, they synthesized  $SnO<sub>2</sub>$  NPs in the size range of 2.2–3.2 nm, using the fenugreek seeds. These particles found applications in nanofluids and biomedical field due to their unique properties such as viscosity and thermal conductivity and their antibacterial and antioxidant potential (Vidhu and Philip [2015b\)](#page-12-12).

<span id="page-6-0"></span>

**Fig. 11.2** Reported applications of  $SnO<sub>2</sub>$  nanostructure synthesized by using plants

Similarly, Kamaraj and coworkers prepared  $SnO<sub>2</sub>$  NPs using the methanol extract of *Cleistanthus collinus* plant as the reducing and capping agent. The average crystallite size of the NPs formed was 49.26 nm, and they were identified to possess antioxidant property due to their activity against DPPH radicals (Kamaraj et al. [2014](#page-11-13)). Quantumconfined spherical  $SnO<sub>2</sub>$  NPs have also been fabricated using different quantities of the pomegranate fruit extract as the reducing/oxidizing agent and capping agent, while tin (IV) chloride (SnCl<sub>4</sub>  $\times$  H<sub>2</sub>O) as the precursor. The prepared NPs showed excellent antibacterial and antioxidant activity, thus emerging as a potential bioactive material (Kumari and Philip [2015](#page-12-11)).

Aqueous extract of dried peel of sugar apple (*Annona squamosa*), an agricultural waste, was used in the rapid synthesis of stable  $SnO<sub>2</sub>$  NPs. At specific concentrations they exhibited moderate cytotoxicity toward the hepatocellular carcinoma (HepG2) (Roopan et al. [2015\)](#page-12-13). Elango et al. [\(2015\)](#page-11-14) synthesized  $SnO<sub>2</sub>$  nanoparticles of 4 nm size, using the methanol extract of *Persea americana* seeds as reducing/oxidizing agents as well as capping agents and tin chloride as the precursor. These particles could cause photocatalytic degradation of phenols under ultraviolet irradiation, depicting their applicability in such processes as dye effluents pollution abatement (Elango et al. [2015](#page-11-14)). In another study, these authors used methanol extract of *Cyphomandra betacea*. The NPs produced were rod-shaped with an average size of 21 nm and showed photocatalytic ability when used for degrading methylene blue (Elango and Roopan [2016](#page-11-15)).

Likewise, Hu  $(2015)$  $(2015)$  synthesized SnO<sub>2</sub> NPs from tin chloride in aqueous mixture of fig (*Ficus carica*) leaf extract. The NPs produced were about 132 nm in size and could be used as an electrode modifier for electrochemical detection of mercury in water. Its application as a  $Hg^{2+}$  sensor proved useful for water purification and pollutant detection. Haritha et al. [\(2016](#page-11-9)) synthesized  $SnO<sub>2</sub> NPs$  (47  $\pm$  2 nm) using an aqueous extract of *Catunaregam spinosa* root bark. These particles were able to degrade the toxic Congo red dye and raise the degradation percentage up to 92% after 45 min and therefore may be useful for the purpose of pollutant abatement. SnO2 NPs have also been synthesized using the *Aspalathus linearis* natural extract as an effective chelating agent and SnCl<sub>4</sub> as the precursor, without adding any acid or base standard compounds. These particles  $(2.1-19.3 \text{ nm in size})$  exhibited enhanced photocatalytic responses to several organic water contaminants such as methylene blue, Congo red, and eosin Y (Diallo et al. [2016](#page-11-16)).

Recently, SnO<sub>2</sub> NPs were produced using the extracts from *Litsea cubeba* fruits as reducing agent and tin chloride as the precursor. These NPs (approximately 30 nm) with irregular morphology showed high antioxidant capacity against DPPH radicals and good photocatalytic activity toward Congo red and were found to be useful for photocatalytic and cosmetic applications (Hong and Jiang [2017\)](#page-11-0). Similar efforts were made using the aqueous extract of fresh cauliflower (*Brassica oleracea* L. var. *botrytis*) after annealing at two different temperatures (300 and 450 °C). Due to the smaller particle sizes, the samples prepared at 300  $^{\circ}$ C exhibited greater degradation efficiency than those annealed at 450 °C. It was concluded that the  $SnO<sub>2</sub>$ NPs so synthesized can be utilized in applications for degradation of toxic organic dyes and purification of effluent water (Osuntokun et al. [2017](#page-12-16)).

Tammina et al.  $(2017)$  $(2017)$  synthesized tetragonal  $SnO<sub>2</sub>$  NPs of different sizes using *Piper nigrum* seed extract at three different calcination temperatures (300, 500, and 900 °C). Their cytotoxicity test proved them to be toxic against the colorectal (HCT116) and lung (A549) cancer cell lines, depending on their size and dose. The cytotoxicity was attributed to the formation of reactive oxygen species (ROS), which was more abundant with the smaller NPs than with the larger ones. The reported IC50 values of SnO<sub>2</sub> NPs with average particle sizes of  $8.85 \pm 3.5$ , 12.76 ± 3.9, and 29.29 ± 10.9 nm were 165, 174, and 208 µg L<sup>-1</sup>, respectively, against HCT116, whereas 135, 157, and 187  $\mu$ g L<sup>-1</sup>, respectively, against the A549 carcinoma cell lines. These stable  $SnO<sub>2</sub>$  NPs were recommended as a potent therapeutic agent against cancerous cell lines (Tammina et al. [2017\)](#page-12-20).

#### *11.3.2 Plant-Assisted Template Synthesis of SnO<sub>2</sub>*

Different forms of NPs such as nanotubes, nanospheres, and motifs have been fabricated to enhance their convenient applications in areas of energy storage and gas sensing (Song et al. [2012](#page-12-4); Ahamed Fazil et al. [2015](#page-10-1); Sinha et al. [2017](#page-12-9)). Sun et al.  $(2005)$  $(2005)$  developed a method to synthesize the biomorphic  $SnO<sub>2</sub>$  microtubules, using cotton fibers as templates. The fibers were infiltrated with tin alkoxide solution and subsequently sintered at high temperatures to produce the final  $SnO<sub>2</sub>$  microtubules of 5–15 μm diameter. The BET (Brunauer–Emmett–Teller) surface area and the pore volume of the biomorphic  $SnO<sub>2</sub>$  microtubules were reported to be highest  $(S_{\text{BET}} = 24.2 \text{ m}^2 \text{ g}^{-1}, V_{\text{mic}} = 0.075 \text{ mL g}^{-1})$  at 700 °C based on the N<sub>2</sub>-adsorption isotherms. The fabricated porous  $SnO<sub>2</sub>$  NPs were recommended for gas-sensing applications (Sun et al. [2005](#page-12-3)).

 $SnO<sub>2</sub>$  nanotubular materials were also fabricated using a sonochemical route with the assistance of cotton fibers to obtain a desirable and porous morphology for enhanced sensing response. The nanotubules so produced consisted of nanocrystals of 14.2 nm size when calcined at 700  $^{\circ}$ C. The SnO<sub>2</sub> nanotubules exhibited a good selectivity for acetone at a working temperature of 350  $\degree$ C, with the sensitivity to 20 ppm acetone recorded as 6.4, and a rapid response and recovery (around 9–10 s) (Zhu et al. [2010\)](#page-12-18).

He et al. [\(2011](#page-11-17)) prepared a biotemplate, using ramie fibers for the fabrication of  $SnO<sub>2</sub>/C$  biomorphic materials. In order to study the effect of the finishing processes on the material fabricated, the ramie fibers were given different treatments such as water washing, NaOH soaking, and oxidative bleaching. Ramie fibers and Sn(OH)<sub>4</sub> were used as the carbon and the  $SnO<sub>2</sub>$  precursors, respectively, for each treatment process. The crystallite size of  $SnO<sub>2</sub>$  in the  $SnO<sub>2</sub>/C$  biomorphic materials was recorded to be 2.0–5.0 nm, 2.5–6.3 nm, and 2.6–4.7 nm for each template, viz., original ramie fiber, NaOH-treated ramie fiber, and degummed ramie fiber, respectively. The morphology and properties of the materials produced were reported to vary and could be effectively controlled with different finishing processes (He et al.  $2011$ ). The biomorphic SnO<sub>2</sub>/C composites were also fabricated using the natural cotton as the structure template and the bio-carbon as the precursor (Li et al. [2014\)](#page-12-19). These composites were made of the nano-sized small particles of about 20 nm. The carbon content in the composites obtained had a great impact on their electrochemical performances and could be adjusted by altering the sintering temperature. The composites prepared at 300 °C were reported to exhibit a reversible capacity of 530 mAh g<sup>-1</sup> after 100 cycles at a current density of 100 mA g<sup>-1</sup>. These were recommended for energy storage application such as anode materials in the lithium-ion batteries (Li et al. [2014\)](#page-12-19).

Song et al.  $(2012)$  $(2012)$  described a method of SnO<sub>2</sub> synthesis with morphology that mimics the bioreactors' scaffolds of pollen grains. The technique consists of a facile two-step soakage process (the NP was mobilized on the pollen grain) followed by calcinations to reconstruct the microreactors of pollen grains (*Brassica campestris*) with the  $SnO<sub>2</sub>$  nanoparticle as the gas-sensing materials. The resulting microreactors of  $SnO<sub>2</sub>$  NPs exhibited superior gas-sensing capabilities to  $NO<sub>2</sub>$  in terms of response value and recovery rate, compared with other  $SnO<sub>2</sub>$ -based gas sensors (Song et al. [2012\)](#page-12-4). The reported performance of other  $SnO<sub>2</sub>$  sensors includes the sprayed SnO<sub>2</sub> thin films (Leo et al. [1999](#page-12-21)), SnO<sub>2</sub> and WO<sub>x</sub>−SnO<sub>2</sub> thick films (Chiorino et al.  $2001$ ),  $SnO<sub>2</sub>$  nanowires (Kim et al.  $2011$ ), nanowire-structured SnO<sub>x</sub>−SWNT composites (Hoa et al. [2009](#page-11-20)), and ordered mesoporous SnO<sub>2</sub> (Hyodo et al. [2003\)](#page-11-21), as shown in Table [11.2](#page-9-0).

Ahamed Fazil and associates adopted a plant-assisted template during the synthesis of crystalline SnO2 motifs with porous structure using the *Peltophorum pterocarpum* pollen grains. The motifs were reported to be made up of  $SnO<sub>2</sub>$  NPs of the size of 16–25 nm with a high BET surface area of 82.72 m<sup>2</sup>  $g^{-1}$  recorded when annealed at 600 °C for 2 h. Since a larger surface area of the  $SnO<sub>2</sub>$  motifs would aid the surface reaction with gases better, the resulting porous morphology proved to be useful for gas-sensing applications (Ahamed Fazil et al. [2015\)](#page-10-1).

		Concentration	Response	Recovery	Temp.	
No.	$SnO2$ -based gas sensor	(ppm)	time $t_1(s)$	time $t_2(s)$	$(^{\circ}C)$	Reference
1	Sprayed SnO <sub>2</sub> thin films	$\sim$ 15–50	360	300	350	Leo et al. (1999)
$\mathfrak{D}$	$SnO2$ and $WO3 - SnO2$ thick films	$\sim$ 2 and $\sim 5 - 10$	>300	>300	250	Chiorino et al. (2001)
3	SnO <sub>2</sub> nanowires	$<30-10$	$20 - 60$	>300	300	Kim et al. $(2011)$
$\overline{4}$	Nanowire-structured $SnO_y-SWNT$ composites	$\sim$ 25–60	$\sim 50$	211	200	Hoa et al. (2009)
5	Ordered mesoporous SnO <sub>2</sub>	$<150-100$			300	Hyodo et al. (2003)
6	SnO <sub>2</sub> microreactors	$219.5 - 50$	5	111	330	Song et al. (2012)

<span id="page-9-0"></span>**Table 11.2** Comparison of some SnO<sub>2</sub>-based gas sensors

## 11.3.3 *Doped, Coupled, and Decorated SnO<sub>2</sub> Nanostructure Synthesis*

In order to overcome the challenge of large bandgap and high recombination rate in  $SnO<sub>2</sub>$ , such nanostructures as decorated, doped, and coupled  $SnO<sub>2</sub>$  hetero-structures have been fabricated with enhanced characteristics. Only few reports have appeared so far on the synthesis of these  $SnO<sub>2</sub>$  nanostructures using plant tissues and extracts (Sudhaparimala and Vaishnavi [2016](#page-12-10); Sinha et al. [2017\)](#page-12-9). Sinha and coworkers have reported a phytosynthetic technique for the fabrication of sphere-shaped  $\text{Ag-SnO}_2$ nanocomposite of average particle size of 9 nm, employing the stem extracts of *Saccharum officinarum*. The study reveals the nanocomposite efficacy as being antioxidant and antibacterial due to its action against *Pseudomonas aeruginosa*, *Escherichia coli*, and *Bacillus subtilis*. Also, the Ag-SnO<sub>2</sub> nanocomposite was found to be a good photocatalyst, and its removal efficiency for the abatement of different industrially emerging pollutants such as methylene blue, rose Bengal, methyl violet 6B, and 4-nitrophenol was recorded (Sinha et al. [2017\)](#page-12-9). Further, tin (II) chloride and zinc acetate were used as the precursors and the gel of *Aloe vera* plant as the medium to fabricate the coupled nanocomposite of tin  $(IV)$  oxide and zinc oxide  $(SnO<sub>2</sub>/ZnO)$ . The average crystallite size was 22.27 nm, while application studies recorded the degradation of organic dyes, such as methyl orange, under the visible light irradiation. Moreover, the nanocomposite was effective against the growth of *Staphylococcus aureus* and *E. coli* at the microgram level (Sudhaparimala and Vaishnavi [2016\)](#page-12-10).

#### **11.4 Future Perspectives**

 $SnO<sub>2</sub>$  NPs have been widely researched for many important applications such as energy storage, gas sensing, and photocatalytic degradation. The synthesis route determines how safely they could be adopted in biological and biomedical exercises (as nanofluids, anticancer, antioxidants, and antibacterial materials). The plantassisted (green) synthesis method is a promising and viable technique to fabricate  $SnO<sub>2</sub>$  nanostructures without using harmful chemicals. With the growing acceptability of NMs in biology and medical science, new windows have opened for potential research on green synthesis routes of SnO<sub>2</sub> NPs, in order to render the NPs nonhazardous. Nonetheless, the complex mechanism of phytosynthesis of nanomaterials, such as  $SnO<sub>2</sub>$  nanostructures, is yet to be completely understood. The step reactions involved and the identification of important isolates among the components of plant extracts require in-depth studies to be taken up to adequately understand, improve, and control the reactions for the desired NM synthesis. The efficacy of different  $SnO<sub>2</sub>$  nanostructures as a photocatalyst in pollution control would be better appreciated if future researches on photodegradation use samples of mixed pollutants from different locations for critical analysis. These studies can facilitate an efficient and feasible field application of these photocatalysts to remove the various environmental pollutants.

In the near future, many forms of  $SnO<sub>2</sub>$  nanostructures with enhanced capabilities and efficiencies are likely to be phytosynthesized through doping (metal and nonmetal), co-doping, decorating, and coupling with other metals, metal oxides, chalcogenides, etc. without using the harmful chemicals. Many potential researches would also adopt plant tissues as template for synthesizing the  $SnO<sub>2</sub>$  nanostructures to improve their morphology and porosity and achieve increased surface area for an enhanced surface reaction, which would be suitable for such applications as gas sensing, self-cleaning, catalysis, and photocatalysis, among others.

#### **11.5 Conclusion**

By adopting the green (plant-assisted) synthesis methods, the commonly used hazardous chemicals could be avoided, and the NPs synthesized would be safe for different applications. Since there are only few reports on progress with the plant-assisted synthesis of  $SnO<sub>2</sub>$  nanostructures, this review has summarized the efforts hitherto made with reference to the phytosynthesis of undoped, doped, and template-assisted  $SnO<sub>2</sub>$ nanostructures as well as their performance and applications.

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