Anion doped binary oxides, SnO$_2$, TiO$_2$ and ZnO: Fabrication procedures, fascinating properties and future prospects

R Nagarajan*, Vinod Kumar & Shahzad Ahmad
Materials Chemistry Group, Department of Chemistry, University of Delhi, Delhi 110 007, India
Email: rnagarajan@chemistry.du.ac.in

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Doping the oxygen in the three technologically important binary oxides SnO$_2$, TiO$_2$, and ZnO, with other anions such as nitrogen, carbon, fluorine, sulfur and chlorine by various synthetic procedures are described. The crystal structures of these oxides along with their electronic structures are summarized. The evolution of many useful properties, such as efficient photocatalysis, high electrical conductivity with high optical transparency on doping with some of these anions, is discussed. An important milestone achieved by our research group for the synthesis of F-doped SnO$_2$ and ZnO powders is highlighted. Heavily F-doped SnO$_2$, obtained by the safe, simple, reliable and reproducible synthetic approach developed by us is the first example among oxide semiconductors to show Moss-Burstein effect, and consequently the defect states are produced in the system on injection of extra charge carriers. These trapped defect states give rise to glow curves in the thermoluminescence spectrum. This observation suggests the use of SnO$_2$:F as a thermal UV sensors in high radiation environments. In the concluding part, the need for the investigation into the interesting structural, electronic and optical properties, especially in the heavily doped regime, are portrayed as part of the future directions of research in these oxides.

Keywords: Oxides, Binary oxides, Doping, Anion doping, Tin dioxide, Titania, Zinc oxide, Photocatalysis, Sensors, Electrical conductivity

Intentional doping into a crystal with impurity atoms has revolutionized the semiconductor industry due to their wide spread applications in electronic and electro-optic components$^1$. Though cationic doping into the lattice for tailoring the band gap of materials for the desired applications has been studied extensively and is reasonably understood, the mechanism of the evolution of many interesting properties arising from the anionic doping is debatable and requires more studies to achieve clarity. However, in both the scenario, many interesting electronic and optical properties, under the heavily doped regime, are yet to be fully explored and understood. When employing dopants to change the optical response of a material, it is desirable to maintain the integrity of the crystal structure of the host material while changing its electronic structure. The crystal structure of a material is directly related to the ratio of cation and anion size in the crystal lattice$^2$. It appears to be relatively easier to achieve cationic substitution in a controlled fashion than to substitute one anion for the other due to the difference in the charge states and ionic radii.

One of the main reasons for fewer studies on anion doped semiconductors is due to their synthetic challenge. This review focuses on the status of an important and experimentally challenging area of the synthesis/fabrication of anion doped binary oxides SnO$_2$, TiO$_2$ and ZnO. The choice of these three oxides is based on the very high consumer demand projected due to their ecofriendly nature with applications in various fields, such as photovoltaics, photocatalysis, self-cleaning coatings and flat panel display devices$^{3-14}$. There exists an obvious heterogeneity in the method of synthesis and hence, the results from the reports vary. They differ greatly in the methods to introduce the dopant, which range from chemical methods such as sol-gel reactions, electrochemical doping, and oxidation of nitride (in the case of titanium) to physical methods, such as magnetron co-sputtering and ion implantation. Therefore, a review of the current status describing the synthesis and properties and the unsolved issues regarding the anion doping in the oxides, SnO$_2$, TiO$_2$ and ZnO is essential. This review is organized in the following way. Fabricating the anion doped SnO$_2$, TiO$_2$ and ZnO by different synthetic methodologies is given primary emphasis, followed by the description of fascinating properties exhibited by the anion doped systems. Finally, the challenges faced by the scientists, especially synthetic chemists in particular, are highlighted to provide an incentive to other scientists to study the effect of doping on the structure and the properties further.
Crystal Structures and Electronic Properties of SnO₂, TiO₂, and ZnO

SnO₂ and TiO₂ crystallize in rutile structure, but TiO₂ is also found in anatase form²; their structures obtained using Diamond software is shown in Fig. 1(a & b). Rutile structure of SnO₂ and TiO₂ possess tetragonal symmetry, space group: \(P4_2/mnm\), with \(a = 4.755 \text{ Å}, c = 3.199 \text{ Å} \) (SnO₂) and \(a = 4.592 \text{ Å}, c = 2.957 \text{ Å} \) (TiO₂)². The anatase form of TiO₂ also possesses tetragonal symmetry, but crystallizes in a different space group of \(I4_1/amd\) with \(a = 3.782 \text{ Å}, c = 9.502 \text{ Å}\). In the crystal structure of SnO₂ and TiO₂, slightly distorted octahedral coordination around the central metal ion by the six oxygen ions is present. In anatase, the corner-sharing octahedra form (001) planes the edges of which are connected with the plane of octahedral units below. In both type of structures, the stacking of the octahedral units, result in threefold coordinated oxygen atoms. The wurtzite structure of ZnO has a hexagonal unit cell with \(c/a = 1.633\) crystallizing in \(P6_3mc\) space group². (Fig. 1c). The structure is composed of two interpenetrating hexagonal close packed (hcp) sub lattices, each of which consists of one type of atom displaced with respect to each other along the threefold \(c\)-axis in fractional coordinates.

As a direct band gap \(n\)-type semiconductor \(\left( E_g = 3.6 \text{ eV}, \right)\) SnO₂ is a promising material for a variety of applications. The valence bands of the stoichiometric SnO₂ originate mainly from the O 2\(p\) state with mixing of Sn 5\(s\) and 5\(p\) states and these levels are responsible for the cohesion, while the conduction band contains mainly 5\(s\) orbitals. The origin of the \(n\)-type behavior is the native non-stoichiometry caused by the oxygen vacancies. The electronic structure of TiO₂ \(\left( E_g = 3.2 \text{ eV}, \right)\) is governed by a strong hybridization between the Ti 3\(d\) and the O 2\(p\) states around the Fermi level. The upper valence band is dominated by O 2\(p\) levels and the lower conduction band is formed mainly by Ti 3\(d\) states. ZnO is a direct energy band gap (3.37 eV) semiconductor in which the conduction band derives mainly from the zinc orbitals¹³.

Fabrication Procedures and Properties of Anion Doped SnO₂, TiO₂, and ZnO

Anion doping in SnO₂

Fluoride appears to be the most favored dopant and substituent in SnO₂ due to the following: (a) its ionic size \(\left( F^-: 0.133 \text{ nm} \right)\) very closely matches with that of the oxide ion \(\left( O^{2-}: 0.132 \text{ nm}\right)\), (b) the energy of the Sn–F bond \(\left( \sim 31.05 \text{ D}^0/\text{kJ mol}^{-1}\right)\), and, (c) since the charge on the fluoride ion is only half that of the charge on the oxide ion, the Coulomb forces that bind the lattice together are reduced. Among the transparent conducting oxides (TCO), F-doped SnO₂ (FTO) tops the list due to their high chemical stability, mechanical strength, and thermal resistance, as well as their low cost⁴. Their favorable visible transmittance and infrared reflectance in that of the Sn–O bond \(\left( \sim 31.05 \text{ D}^0/\text{kJ mol}^{-1}\right)\), and, (c) since the charge on the fluoride ion is only half that of the charge on the oxide ion, the Coulomb forces that bind the lattice together are reduced. Among the transparent conducting oxides (TCO), F-doped SnO₂ (FTO) tops the list due to their high chemical stability, mechanical strength, and thermal resistance, as well as their low cost⁴. Their favorable visible transmittance and infrared reflectance in…

Fig. 1 – Structural arrangement of (a) rutile SnO₂, (b) anatase TiO₂, and (c) wurtzite ZnO.
comparison with tin oxide films doped with other impurities make them ideal candidates for preparing low emissivity coating glass (Low-E glass). FTO has been proposed to be an alternative to ITO due to its cost effective value in the fabrication of organic photovoltaic devices.

F-doping in SnO$_2$ in the powder and thin film forms has been achieved by many synthetic techniques and are summarized in Table 1, along with the significant outcome of such methods. FTO films have been fabricated by chemical vapor deposition techniques, dip coating technique, spray pyrolysis, ultrasonic spray pyrolysis, reactive RF sputtering, and pulsed laser deposition methods. Bae et al. grow SnO$_2$:F films using a low-pressure metalorganic chemical vapor deposition (LP-MOCVD) with tetramethyltin. FTO films were also obtained using the organo-tin precursor tert-ammyloxyfluorodipentan-2,4-dionatotin (IV) complex.

By the atmospheric pressure chemical vapor deposition (APCVD) procedure, Zhao et al. deposited FTO films with monobutyl tin trichloride (C$_4$H$_9$SnCl$_3$) and trifluoroacetic acid (CF$_3$COOH) as the sources of tin and fluorine. Similarly, highly conducting FTO films were prepared by Talaty et al. employing the single-source precursor (SSP), [SnCl$_4$(OC(H)OC$_2$H$_5$)$_2$] in an APCVD system. Pyrosol method followed by ultrasonication has been applied to fabricate FTO films. In dual-source CVD procedures, a tin precursor (e.g. Me$_2$Sn, SnCl$_4$) along with either F$_2$, NH$_4$F, HF, BrCF$_3$, CF$_3$COOH or other fluorocarbons, as the fluorine sources were used to achieve F-doped SnO$_2$. Fabrication of SnO$_2$:F films from a soluble and volatile SSP were less common since compounds/complexes with a direct Sn–F bond were found to be insufficiently volatile, as such species commonly generated bridged oligomers/polyomers through F: $\rightarrow$ Sn interactions, e.g. Ph$_3$SnF.

This aspect was overcome using Sn(O$_2$CCF$_3$)$_2$ and Bu$_2$Sn(O$_2$CCF$_3$)$_2$. Purely inorganic complexes Sn[OCH(CF$_3$)$_2$]:2(HMMe$_2$) and Sn[OCH(CF$_3$)$_2$]:L (L=HMMe$_2$, C$_5$H$_5$N) were also employed successfully for making FTO films. The Sn(IV) containing species, when used for making films, generated FTO with good optical transparency (>85 %) but high resistivity (2.1 × 10$^{-3}$ ohm cm), while the divalent tin analogue, Sn[OCH(CF$_3$)$_2$]:HMMe$_2$ afforded non-conductive SnO$_{0.9-1.3}$F$_{0.1-0.4}$, suggesting that hydrolysis, rather than oxidation, was driving the film deposition; both processes required LPCVD due to limited precursor volatility. Organotin fluoroalkoxides perform poorly in comparison with organotin fluoroalkyls (R$_3$SnRf) as precursors for SnO$_2$:F synthesis. Noteworthy is the use of organotin fluoroalkoxylates (R$_3$SnO$_2$Rf), as they are air stable, cheap and easy to handle.

<table>
<thead>
<tr>
<th>Source employed</th>
<th>Methodology</th>
<th>Dopant</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_4$H$_2$F$_6$O$_2$/CF$_3$COOH/ SF$_6$/Bu$_3$SnORf/ E$_3$SnO$_2$CC$_2$F$_3$</td>
<td>APCVD (thin films)</td>
<td>1.02-4.80 at.%</td>
<td>Intricate synthesis set-up, poisonous gaseous and presence of carbon as impurities</td>
<td>15, 24, 28, 35, 34</td>
</tr>
<tr>
<td>HF</td>
<td>CVD (thin films)</td>
<td>4.5 at.%</td>
<td>Low sheet resistance and high optical transparency</td>
<td>16, 26</td>
</tr>
<tr>
<td>NH$_4$F</td>
<td>SP (thin films)</td>
<td>~30 wt.%</td>
<td>Low resistivity</td>
<td>21, 22, 29</td>
</tr>
<tr>
<td>SnO$_2$+SnF$_2$</td>
<td>Laser deposition (thin film)</td>
<td>5–20 %</td>
<td>Optical transmittance of 87 %</td>
<td>25</td>
</tr>
<tr>
<td>DFM (CH$_2$F$_2$)</td>
<td>Vapor phase synthesis (powder)</td>
<td>27.1 at.%</td>
<td>Sn(CH$_3$)$_4$ as a precursor and hazardous F source</td>
<td>38</td>
</tr>
<tr>
<td>SnF$_2$(R’COCHCOR’)/(C$_4$H$_9$-C=C)$_3$-SnRF/ SnF(O’Am)(acac)$_2$</td>
<td>Sol-gel and calcination (powder)</td>
<td>3.0-8.0 at.%</td>
<td>Much lower resistivity than ITO, carbon as impurities</td>
<td>39, 40</td>
</tr>
<tr>
<td>HF</td>
<td>Thermal decomposition (powder)</td>
<td>&lt;10 mol%</td>
<td>Use of organic Sn precursor, Sn$_2$(C$_6$O$_7$H$_4$).H$_2$O</td>
<td>41</td>
</tr>
<tr>
<td>N(CH$_3$)$_4$F.4H$_2$O</td>
<td>Microwave polyol approach (powder)</td>
<td>1-10 mol%.</td>
<td>Defect sites studied by solid state NMR</td>
<td>42</td>
</tr>
<tr>
<td>KSnF$_3$</td>
<td>Oxidation (powder)</td>
<td>21.23 % (63.81 at.%)</td>
<td>Air stable single source inorganic precursor, heavily doped, high surface area &amp; photocatalytic, thermoluminescence</td>
<td>43</td>
</tr>
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</table>
For the preparation of the SnO$_2$:F powders, the sol-gel method (employing organometallic precursors) and spray pyrolysis techniques are reported. Ha et al. obtained SnO$_2$:F by the slow hydrolysis of the single molecular precursor, fluoro-(2-methylbutan-2-oxy)dipentan-2, 4-dionato)-tin complex. The sol-gel process was coupled with the hydrothermal treatment to obtain SnO$_2$:F nanocrystals by Wu et al. Han and co-workers prepared FTO nano-powders by combining the sol-gel and the combustion methods with acetylene black as fuel. Suffner et al. doped fluorine in SnO$_2$ by passing difluoromethane (DFM) over SnO$_2$. Toupane and co-workers applied sol-gel routes derived from organo-tin complexes containing fluoride and by which ~3 mol % fluoride was found to be doped in SnO$_2$. A similar approach was also used by Han and co-workers. Esteves et al. prepared F-doped SnO$_2$ powders by Pechini’s process using tin citrate, Sn$_2$(C$_6$O$_7$H$_4$)$_2$, H$_2$O and ethylene glycol. SnO$_2$:F nanoparticles were also fabricated by a microwave assisted polyol approach from SnCl$_4$ and N(CH$_3$)$_3$F.

Synthetic procedures that are known to yield F-doped SnO$_2$ powders employed a tin source (SnCl$_2$ or SnCl$_4$) and the fluoroine source (NH$_4$F, CH$_2$F$_2$, SF$_6$ and HF). Whenever organotin complexes were used as SSP, heat treatment after the reactions to get rid of the volatile organic impurities and to improve crystalline nature of the final product was found to be essential. Total elimination of carbon impurities was difficult, thus making it hard to understand the effect of F-doping on the properties of SnO$_2$. In any case, doping higher concentration of fluoride ions in SnO$_2$ was not easily achievable in the powder form; in many instances, it was either restricted by the fluoride concentration in the precursor or the contamination of the final product due to the incomplete removal of the fluorinating agents.

We have reported the successful synthesis of fluoride-doped SnO$_2$ by a novel oxidation procedure in which the inorganic fluoride complex of Sn$^{2+}$, KSnF$_3$, was employed as the SSP. KSnF$_3$ is air stable, easy to prepare and easy to handle. Its controlled oxidation with H$_2$O$_2$ was carried out at 100 ºC to obtain F-doped SnO$_2$. The choice of this precursor was based on the fact that the mixed metal complex fluorides are highly hydroxyphilic due to same size of the fluoride and hydroxide ions. Also, SnO$_2$ could very easily be obtained from the hydroxides of tin. More importantly, the reactions were conducted at low temperatures which did not require any intricate set up or handling of hazardous fluorinating agents. The use of inorganic precursor prevented inclusion of carbon in the product, which is usually the contaminant starting with an organotin precursor. Core level X-ray photoelectron spectroscopy (XPS) measurements provided conclusive evidence for the heavy doping of fluorine in SnO$_2$ (21.3 %), the highest concentration achieved in powders till now. SnO$_2$:F nanocrystals, obtained by our method, showed greater thermal stability up to 300ºC (without the evolution of the hazardous HF) as revealed by the hyphenated TG-MS techniques. These results will find greater applications for the fabrication of large scale coatings of heavily F-doped SnO$_2$ by spray pyrolysis and dip coating or electrophoretic thin film deposition procedures.

Enormous blue shift in the band gap was observed in our F-doped SnO$_2$ sample which was related to the heavily doped situation due to the Moss-Burstein effect with increase in the carrier concentration. This is the first time that this effect has been demonstrated in an oxide semiconductor. Evaluation of SnO$_2$:F as a photo catalyst for the degradation of aqueous Rhodamine B (Rh B) dye solution showed efficiency matching with the commercial Degussa P-25. Without external irradiation, the heavily F-doped SnO$_2$ nano crystals showed a broad glow curve at 454 K in the thermoluminescence spectrum, signifying the presence of F-centres (Fig. 2). On irradiating the SnO$_2$:F samples with UV light, the glow curve resolved into two, one centred at 440 K and the other at 520 K (Inset of Fig. 2). The results from this study indicated its use as potential thermal and UV sensors.

![Fig. 2 – Thermoluminescence glow curve of (a) SnO$_2$:F obtained by the low temperature oxidation of KSnF$_3$ and (b) undoped SnO$_2$. Inset shows TL glow curve of SnO$_2$:F recorded at 3 K/s after irradiating with UV light for 10 minutes.](image-url)
Though considerable literature on the effects of other dopants such as N and S in SnO$_2$ exist, very few reports are available on the possible N-doping of SnO$_2$. Undoped SnO$_2$ is an $n$-type semiconductor (due to the existence of intrinsic defects) while $p$-type SnO$_2$ films have been reported by Al or In doping \cite{45}. Yan et al. \cite{46} suggested that $p$-type SnO$_2$ can also be achieved by nitrogen doping. Pan et al. \cite{47} have grown nitrogen-incorporated SnO$_2$ thin films on Si (100) and quartz substrates by reactive sputtering of a Sn target in gaseous mixture of N$_2$–O$_2$.

**Anion doping in TiO$_2$**

First reports of anion-doped TiO$_2$ began to appear in the early 1990s \cite{48}, but the study of Asahi and co-workers \cite{49} in 2001 on the N-doped TiO$_2$ exhibiting excellent visible light photocatalytic activity turned the researchers’ attention towards anion doping as a prelude to produce second generation materials that would increase the photocatalytic activity of TiO$_2$ over the UV and much of the visible-light region. Subsequently, many studies appeared on the preparation of N-doped, C-doped, S-doped, F-doped TiO$_2$ and N and C co-doped TiO$_2$ materials and their evaluation as visible light catalysts. The use of N$^{3-}$, C$^{4-}$, S$^{2-}$, or halides (F, Cl, Br, I) as doping agents, in TiO$_2$, have been subjected to intense research and are summarized in several review articles \cite{50}. The application of this oxide in water electrolysis, heterojunction solar cells and gas sensing in addition to photocatalysis adds to the list of its fascinating properties which are described in detail in many reviews \cite{51,52}. The various method of obtaining the anion doped TiO$_2$ are presented in Table 2.

Solution phase methods such as the sol-gel and solvothermal process are low-cost, convenient and robust approaches to prepare anion doped TiO$_2$. By a simple wet process in which the hydrolysis product of Ti(SO$_4$)$_2$ with ammonia was calcined using an ordinary electric furnace in dry air at 400 °C, tracely nitrogen-doped TiO$_2$ powders (yellow in color) were prepared \cite{52}. The nitrogen-doped titania were also obtained by hydrolysis of titanium tetrachloride with a nitrogen-containing base such as ammonia, ammonium carbonate, or ammonium bicarbonate, followed by the calcination in air at 400 °C, yielding a dopant concentration of 0.08 ± 0.13 wt% of nitrogen \cite{53}. In solution phase synthesis, additives such as urea and alkyl ammonium salts were used as dopant sources to prepare N-doped TiO$_2$. These nitrogen precursors were either added during TiO$_2$ synthesis or used to treat TiO$_2$ powders in order to accomplish anion doping \cite{54}. Belver and coworkers \cite{55} synthesized a series of N-containing titanium precursors by modifying titanium tetraisopropoxide with different amine type ligands. By reacting TiCl$_4$ with 2, 2’-bipyridine, Sano and coworkers \cite{56} obtained N-doped TiO$_2$ through Ti$^{4+}$-bipyridine complex. Anion doped TiO$_2$ was synthesized by a simple solvothermal method \cite{57} starting with a molecular titanium precursor containing nitrogen and carbon, viz., titanium tri-thanolaminato isopropoxide. Nitrogen concentration in the TiO$_2$ was enhanced up to 8 % by the direct amination of the 6-10 nm sized titania particles \cite{58}. The nitrogen doped titanium dioxide (TiO$_2$) nanocrystals were also prepared by heating TiN at 450, 550 and 650 °C for 2 h in air yielding a mixture of anatase and rutile phases \cite{59}. The incorporation of nitrogen ions in TiO$_2$ single crystals was also achieved by sputtering with N$_2$+$/Ar+$ mixtures and subsequent annealing to 900 K under ultrahigh vacuum conditions \cite{60}.

The evolution of N-doped TiO$_2$ occurred on thermal treatment of amorphous ammonium titanium oxychloride precursor, synthesized using varying Ti/Cl ratios \cite{61}. Nitrogen and sulfur co-doped and

<table>
<thead>
<tr>
<th>Source employed</th>
<th>Methodology</th>
<th>Remarks</th>
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</tr>
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<tbody>
<tr>
<td>Ammonia</td>
<td>Hydrolysis of Ti(SO$_4$)$_2$ followed by heating</td>
<td>Trace quantity of nitrogen doped</td>
<td>52</td>
</tr>
<tr>
<td>Ammonium carbonate &amp; bicarbonate</td>
<td>Hydrolysis of TiCl$_4$ followed by heating at moderate temp.</td>
<td>Less than 0.01 % nitrogen doped</td>
<td>53</td>
</tr>
<tr>
<td>TiC</td>
<td>Oxidative annealing</td>
<td>0.32 % of carbon doped with respect to oxygen in TiO$_2$</td>
<td>54</td>
</tr>
<tr>
<td>Titanium isopropoxide modified with different amine type ligands</td>
<td>Sol-gel method, single source precursor</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>Amines</td>
<td>Direct reaction with TiO$_2$ nanoparticles</td>
<td>8 %</td>
<td>58</td>
</tr>
<tr>
<td>HF</td>
<td>Sol-gel method</td>
<td>F doped TiO$_2$</td>
<td>67</td>
</tr>
<tr>
<td>TiN</td>
<td>Controlled oxidation by heating at 450, 550 and 650°C</td>
<td>Mixture of rutile and anatase</td>
<td>71</td>
</tr>
</tbody>
</table>

Table 2 – Summary of the different type of dopants and the synthetic methodology used to dope in TiO$_2$
N-doped TiO₂ anatase were obtained by manual grinding with urea and thiourea, respectively and annealing at 400 °C. During the hydrolysis of titanium tetraisopropoxide, urea-water-alcohol mixture was added to effect anion doped TiO₂. Electrochemical methods were employed to exactly control anion doping of N and F-ions taking electrolyte solutions of titanium salt and ammonium ions, nitrate ions and fluoride ions. F-doping in to TiO₂ is found to be effective for enhancing the photocatalytic activity, as in the case of nitrogen and carbon doped systems.

While in the products from the wet chemical methods, substantial portion of the doped nitrogen is not directly bound to Ti, in the N, F co-doped TiO₂ powders obtained by the spray pyrolysis, the N-atoms form a localized energy state above the valence band of TiO₂ suggesting bonding between the dopants and Ti. F-doping in TiO₂ had no influence on the band structure. Band structure calculations carried out for the F-doped TiO₂ indicate that the F-2p levels do not mix with the existing bands and hence, are not expected to contribute to the optical absorption spectra. F-doping modifies the DOS near the conduction band minimum so that the resulting effect is similar to the creation of oxygen vacancies.

Yellow colored carbon-doped anatase TiO₂ powders were fabricated by oxidative annealing of TiC. The amount of carbon doped by this method was 0.32 % with respect to oxygen. Carbon-doped TiO₂ showed photocatalytic activities for the decomposition of IPA (isopropyl alcohol) to CO₂ via acetone under visible-light (400–530 nm) irradiation.

Presently, the question of whether anionic doping by nitrogen and/or carbon resulting in band gap narrowing in TiO₂, the extent of such narrowing, and the utility of the resultant materials, is a matter of much debate in the scientific literature. On the other hand, so far as the photoelectrochemical response by the anionic doped TiO₂ is concerned, the improvement is at best modest in majority of the research reports.

**Anion doping in ZnO**

Table 3 summarizes the dopant sources and the synthetic methodology employed for the fluoride ion doping in ZnO. F-doping in ZnO films and powders was achieved by CVD method, sputtering procedures, spray pyrolysis and precipitation methods. Liang & Gordon fabricated ZnO:F films by the APCVD procedure using tetramethylethlenediamine adduct of diethyl zinc. This process had the advantage of using a stable chelated precursor, paving way for a better control over doping and reproducible growth of uniform films. Tsai et al. made ZnO:F films from ZnF₂ followed by post-annealing under vacuum. Kim & co-workers used a mixture of Ar and CF₄ to achieve F-doped ZnO thin films from ZnO target.

Spray pyrolysis method presents some noticeable advantages, such as a wide possibility of varying the films properties by changing the composition of the starting solution and also that of low cost when large-scale production is needed. Many reports are available for the spray pyrolysis method of making F-doped ZnO films. Kumar et al. deposited ZnO:F thin films using Zn(OOCCH₃)₂ and NH₄F by spray pyrolysis technique. A similar procedure was adopted by Martinez et al. with the modification of ZnCl₂ and trifluoroacetic acid.

Yakuphanoglu et al. prepared fluoride doped ZnO thin films by spin coating method using a gel obtained from Zn(OOCCH₃)₂ and NH₄F with monoethanolamine as stabilizer. Fujihara et al. fabricated ZnO:F films by the APCVD procedure using tetramethylethlenediamine adduct of diethyl zinc. This process had the advantage of using a stable chelated precursor, paving way for a better control over doping and reproducible growth of uniform films. Tsai et al. made ZnO:F films from ZnF₂ followed by post-annealing under vacuum. Kim & co-workers used a mixture of Ar and CF₄ to achieve F-doped ZnO thin films from ZnO target.

**Table 3 – Summary of the synthetic conditions and methodology adopted for the successful F-doping in ZnO**

<table>
<thead>
<tr>
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<th>Dopant</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoyl fluoride</td>
<td>CVD (thin film)</td>
<td>~ 0.2 %</td>
<td>Film growth rate decreased with fluoride</td>
<td>73</td>
</tr>
<tr>
<td>ZnF₂</td>
<td>RF magnetron sputtering (thin film)</td>
<td>1-10 %</td>
<td>Single Source precursor</td>
<td>74, 75</td>
</tr>
<tr>
<td>NH₄F</td>
<td>Spray pyrolysis (thin film)</td>
<td>1-5 %</td>
<td>Film thickness controlled procedure</td>
<td>76-80</td>
</tr>
<tr>
<td>NH₄F/ZnF₂</td>
<td>Sol gel (thin film)</td>
<td>5-15 %</td>
<td>Low equipment cost</td>
<td>81, 82</td>
</tr>
<tr>
<td>NH₄F</td>
<td>Precipitation method (powder)</td>
<td>5 %</td>
<td>Time and energy saving</td>
<td>83</td>
</tr>
<tr>
<td>KZnF₃</td>
<td>Decomposition via oxidation (powder)</td>
<td>~ 6 %</td>
<td>Air stable inorganic precursor, No handling of harmful HF or fluorine gas generation, readily scalable, reproducible</td>
<td>84</td>
</tr>
</tbody>
</table>
employed ZnF₂ precursor for the synthesis of ZnO:F by the hydrolysis procedure similar to the one employed for sol-gel synthesis. Martinez & co-workers⁸³ obtained F-doped ZnO by heating the mixture of oxalic acid, zinc acetate solutions in ethanol and NH₄F.

Our research group successfully synthesized the ZnO:F nanocrystals by a novel synthetic approach in which the fluoride-doped zinc peroxide was first obtained followed by its decomposition⁸⁴. ZnO₂:F was obtained by a simple low-temperature oxidation of the cubic perovskite, KZnF₃, with H₂O₂. The following mechanism involving the sequences of chemical reactions could be conceived for the formation of inherently F⁻ doped ZnO:

\[
\text{KZnF}_3 + \text{H}_2\text{O}_2 \rightarrow \text{KZnF}_{3-x}(\text{OH})_x
\]

\[
\text{KZnF}_{3-x}(\text{OH})_x \rightarrow \text{Zn(OH)}_2 + \text{HF} + \text{KOH}
\]

\[
\text{Zn(OH)}_2 + \text{HF} \rightarrow \text{ZnO}_2: \text{F}
\]

\[
\text{ZnO}_2: \text{F} \rightarrow \text{ZnO}: \text{F}
\]

With H₂O₂ as the oxidizing agent, KZnF₃ was believed to be dissociated resulting in Zn(OH)₂ and KOH. Zinc hydroxide on refluxing at 120 °C, under highly alkaline conditions provided by the generated KOH, could possibly have resulted in ZnO₂. The highly reactive HF, presumed to be generated in situ, might have replaced some of the hydroxyl groups, thus resulting in ZnO₂:F. Yellow colored ZnO:F nanocrystals were obtained by just simple thermal decomposition of ZnO₂:F at 450 °C.

We extensively studied the structure, optical, and photocatalytic properties of the ZnO:F nanocrystals. Core level XPS measurements provided conclusive evidence for the doping of fluorine (6.1 %) in ZnO. A red shift in the excitonic absorption and photoluminescence spectrum were observed on F doping in ZnO. The presence of higher oxygen vacancies in ZnO:F was inferred from the Raman spectroscopic analysis. The band gap value of ZnO:F, estimated from the diffuse reflectance spectrum, was 3.0 eV, and showed broad visible emission. As a consequence of higher oxygen vacancies, ZnO:F exhibited efficient photocatalytic activity under visible irradiation for the degradation of aqueous MB dye solution.

The low electrical resistivity of the ZnO:F films has been attributed to the high electron mobility caused by the fluorine doping in oxygen sites, perturbing mainly the valence band, thereby leaving the conduction band relatively free of scattering. Recently, Xu et al.⁸⁶ reported fluoride doped ZnO films with low electrical resistivity and good optical transparency. The refractive index of the ZnO:F films were found to vary with increase in the fluorine concentration⁷⁶. Fluorine doped ZnO thin films were demonstrated to exhibit cathodoluminescence characteristics.⁸⁵ A giant linear electro-optic (Pockels) effect was observed in the ZnO:F films due to substantial non-centrosymmetric charge density distribution between the wurtzite ZnO films and the additional charge density polarization caused by fluoride doping⁷⁶. Kumar et al.⁷⁹ showed that fluoride doping leads to considerable reduction in electrical resistivity, enhancement of optical transmission and reduction in photosensitivity. Fluoride doping in ZnO presents the advantage of improving the transport properties; however, it adversely affects the growth, setting a compromise between these two facts, which limits the performance of F-doped ZnO as a transparent electrode.

The p-type doping in ZnO may be possible by substituting either group-I elements (Li, Na, K) for Zn sites or group-V elements (N, P, As) for the O sites. Theoretically, nitrogen is the best dopant for p-type doping, since it has nearly the same radius as oxygen, low ionization energy, ease of handling, low material toxicity, and source abundance and is the shallowest acceptor in ZnO. The p-type ZnO films were deposited by magnetron sputtering⁹⁸, chemical vapour deposition⁹⁹, pulsed laser deposition⁹⁰ and molecular beam epitaxy⁹¹ techniques. The N incorporated into ZnO was found to be compensated severely by both intrinsic and extrinsic defects, such as oxygen vacancies⁹², hydrogen impurities⁹³ and nitrogen molecules⁹⁴, making N-doped ZnO to remain as n-type. Several nitrogen-doping sources, e.g. N₂, NH₄NO₃, NO, NH₃, CH₃COONH₄ and N₂O⁸⁸-⁹⁴, were examined to fabricate p-type ZnO samples. Although nitrogen is not very soluble in ZnO, its solubility can be greatly enhanced by forming NO–H complexes in ZnO co-doped with H impurities⁹⁵. Two acceptor states, N-on-O substitution (Nₐₙ) and zinc vacancy (V₇z) were identified in N doped ZnO, which may have contributed towards the observed p-type conductivity⁹⁶.

Though oxygen has many physical and chemical properties similar to those of sulfur, due to a similar structure of the electronic shell, S has rarely been doped in ZnO due to problems in fabrication owing to
the stability of sulfur at the ZnO film growth temperature. The fabrication of ZnO film usually carried out at growth temperatures above 400 °C. On the other hand, sulfur is stable only at a low temperature, and vaporizes readily at 100 °C to an appreciable amount and its vapor pressure reaches 1 atm at 447 °C. Moreover, sulfur is highly reactive in the presence of oxygen to form intermediate phases such as a ZnSO₄ easily. These appear to be some of the reasons for the non-availability of many studies. Bae et al. used a two-step catalyst assisted chemical vapor deposition process to get S-doped ZnO nanowires. Yoo and co-workers obtained S-doped ZnO thin film by the laser ablation of ZnS target. In an ecofriendly and novel procedure, S-doped ZnO was obtained by simple mechanochemical synthesis followed by thermal decomposition of bithiourea zinc oxalate powders.

Conclusions and Future Prospects

It is evident from this review that the wet chemical routes for the anion doped SnO₂, TiO₂ and ZnO are superior to other methods as they produce anion doped specimens reproducibly and eliminate the secondary impurity phase formation. Doping the anions from single source precursors appears to yield homogeneously doped products as compared to heating the oxide with the volatile and gaseous dopant sources. However, the control of the anion concentration in the lattice and designing new precursors for the auto doping of these anions are the indispensable challenges to the synthetic chemists. Critical and additional investigation in to band gap narrowing taking in to account the actual composition of the samples, especially when heavily doped, the growth of high quality anion doped single crystals and their structural determinations to establish the exact positions of the dopant atoms in the lattice, viz., substitutional versus interstitials are some of the other key issues that remain open. Since all the three oxides discussed in this review show extensive applications based on their efficient use under the solar spectrum, issues related to their photostability must also be addressed.

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