Structural diversity in transition metal-doped titanium oxo-alkoxy complexes: Potential sol-gel intermediates for doped titania nanoparticles and complex titanates

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Abstract
Since the discovery of its photocatalytic properties, titanium dioxide has remained one of the most popular and widely used metal oxide photocatalysts. Its major drawback, however, lies in the narrow region (UV) of sunlight necessary to produce reactive oxygen species. This have been countered by sensitizing with organic dyes to red-shift the absorption spectrum but also with doping of other metals and non-metals. Volume doping or surface modification have demonstrated improved photocatalytic efficiency, mainly via red-shifted absorption by introduction of intermediate energy states between the valence band (VB) and conduction band (CB) and increased number of surface hydroxyl groups (which can form reactive hydroxyl radicals) from charge compensation, and in some cases by improved surface-adsorption of organic molecules. Doped titania and complex titanates have traditionally been produced via, for instance, co-precipitation of mixed metal salts or via solid-state synthesis. While these methods usually are simple, they offer limited control over size, shape, and phase composition. An alternative is the use of single-source precursors (SSPs), i.e., molecules already containing the desired metal ratio in a homogenous distribution. The last one or two decades have seen an increased number of reported transition metal-doped titanium oxo-alkoxides (TOA), particularly for the first-row transition metals as potential single-source precursors (SSP) for doped titania and complex titanates. This review aims at providing an overview of TM-doped TOAs, focusing on first and second row TM elements, with special emphasis on their synthesis, photochemical properties, and their applications as SSPs.

Graphical abstract

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Highlights

- The synthesis and structures of transition metal-doped titanium oxo-alkoxy complexes are reviewed.
- Their applications as precursors for complex oxide materials are reported with focus on photo(electrochemical) applications.
- An extensive set of references is provided.

1 Introduction

Titanium(IV) dioxide (TiO₂, titania) has been in the spotlight for photochemical reactions since Honda and Fujishima reported the ability of titania to photochemically split water in 1972 [1]. Many comprehensive reviews on the synthesis and applications of titania nanoparticles have been published over the years (e.g., refs. [2-8]). It is also employed as anode material in dye-sensitized solar cells [9]. The two major allotropes of titania, anatase and rutile, possess different photocatalytic activities, where anatase despite its wider band gap (ca. 3.2 eV) is considered more effective than rutile (ca. 3.0 eV). This has been explained, for instance, by lower charge carrier recombination rates and higher density of surface hydroxyl groups for the former phase [10, 11]. The photoexcitation of titania results in an electron-hole pair where the excited electron can react with oxygen to form the super oxide radical or with terminal hydroxide groups to surface hydroxyl radicals, and the hole can reduce water to hydroxyl radicals. These radical species have potential to completely mineralize organic pollutants [12].

Below ca. 14 nm, anatase is the most stable phase [13], but over this size rutile becomes the thermodynamically most stable phase. Pure anatase will irreversibly transform into rutile between 500 °C and 600 °C. The transformation is initiated from the particle surface [14]. Hence, surface functionalization, i.e., dopants, have the ability to stabilize the surface and increase the onset temperature of rutile transformation and also hinders aggregation into larger particles with reduction of active surface area. Additionally, the incorporation of surface lanthanides (oxides) on titania have facilitated photocatalytic degradation via improved surface adsorption of organic pollutants (Lewis acid-base complex formation) and formation of intermediate energy levels between VB and CB [15]. Conventional wet chemical methods to surface modify/dope titania with TM compounds include precipitation of metal salts on pre-formed nanoparticles [16], sol-gel synthesis [17-20], and hydro/solvothermal processing [21-23].

Several successful efforts to synthesize single-source precursors for bimetallic titanates have been reported including cobalt titanate [24], titanium molybdate [25], and zirconium titanate [26]. Furthermore, additional organic ligands in the SSPs can facilitate formation of highly porous materials due to gas evolution during combustion/calcination [27] and also increase volatility for application in chemical vapor deposition (CVD) of complex oxides [28]. Organosoluble metal doped TOAs have additionally been proposed as “molecular photocatalysts” in synthetic organic chemistry, thus their absorption in the visible region is of interest [29]. Metal-doped and complex titanates are likely to find advanced applications in (photo)catalysis and biomedicine, and their controlled synthesis via carefully designed single-source precursors remains attractive.

The last twenty years have seen an increased interest in TOAs doped with transition metals, particularly the first and second row elements. The purpose of this review is to provide an overview of the synthetic strategies employed to produce TM-doped TOAs, types of structures obtained, and their applications which special emphasis on photochemistry and the use as SSPs. The scope is limited to complexes containing Ti-O(R)-M linkages (M = first or second row transition metal, R = alkoxide, or bridging ligand) and where titanium(IV) alkoxides have been used as the titanium precursor to keep it relevant to the sol-gel process and formation of doped titania and titanates. Herein the term titanium oxo-alkoxy coordination complex (or simply complex) is used and “cluster” is reserved to compounds with metal-metal bonds as originally proposed by F. A. Cotton [30].

2 Formation of titania nanoparticles

For sol-gel reactions in organic medium, titanium(IV) alkoxides are the most common precursors. Titanium alkoxides with less bulky side-groups tend to be oligomeric, e.g., [Ti(OEt)₄]₄ and [Ti(OMe)₄]₄ [31, 32] while [Ti(OPr)₄] tends to be monomeric in non-polar solvents [33]. As a result of the lower electronegativity of titanium compared to silicon and coordination unsaturation, titanium alkoxides react more rapidly with water than the silicon alkoxides [34-36]. It is well-known that addition of water to pure titanium alkoxides immediately results in a white precipitate, which is usually not the case for titanium alkoxides modified with chelating ligands. This have been interpreted as stabilization...
against of hydrolysis by, e.g., blocking of coordination sites from H$_2$O and by stabilization from ligands not easily hydrolysable [37, 38]. However, strongly complexing ligands have been demonstrated less hydrolysable compared to alkoxy groups and can thus provide both protection against aggregation and to control the size of primary titania nanoparticles [39, 40]. Studies of acetate-modified titanium (IV) butoxide by Doeuff et al. [41] demonstrated the bridging acetate to be more easily hydrolyzed compared to the chelating acetate, where the latter one needed thermal treatment for removal. The strongly chelating acetate increased gelation time, favoring gels rather than colloidal particles.

Extensive efforts have been devoted on the functionalization of titanium oxo-alkoxy compounds with different organic ligands which is an attractive way to introduce new functions and create organic-inorganic hybrid materials. This has been covered in several comprehensive reviews [35, 42–44]. Hydrolysis of ligand-modified TOAs has been used to obtain titania of complex morphologies [45, 46].

More recent studies by Kessler and co-workers [34], however, have actually demonstrated the increased reactivity of different metal alkoxides modified with chelating ligands, based on increased M–O bond lengths and calorimetric measurements. A series of studies have reported the hydrolysis of heteroleptic titanium oxo-alkoxide complexes modified with chelating and bridging ligands in contact with water to form crystalline nano-anatase [45, 47]. Due to the high reactivity of HO-Ti-OR, these species are never observed as a product of hydrolysis analogous to HO-Si-OR, but instead oligonuclear titanium oxo-alkoxy complexes with hexacoordinated titanium centers are formed as discrete Ti$_x$O$_y$(OR)$_z$L$_d$ species in a simultaneous hydrolysis-condensation reaction [48]. This has recently been supported by in situ studies by Kanaev’s group [49, 50]. These oxo-species will act as nuclei for the formation of primary metal oxide particles via aggregation and condensation in a process referred to as micelles templated by self-assembly of ligands (MTSAL) (Fig. 1). The ligands from the oxo-complexes are transferred to the particle surface and provide solution stability, forming a colloid. The strength and kinetics of the nanoparticle-ligand interactions can be studied employing diffusion ordered nuclear magnetic resonance spectroscopy [51], as well as distinguish between distinct chemical species in solution [52, 53]. The formation of an “invisible” colloid stabilized by chelating and/or bridging ligands presumably supported the idea of inhibited hydrolysis by modification with chelating ligands.

Nano-anatase can form directly from single crystals of a titanium oxo-alkoxide via thermolysis or (thermal) hydrolysis. For example, immersing crystals of [Ti(OCH$_3$)$_4$]$_4$ in boiling water resulted in fully crystalline anatase nanoparticles after 30 min. Hydrolysis and subsequent formation of nuclei resulted in a contraction and densification of original crystal structure, with formation of lamellar sheets as observed in TEM micrographs. The resulting anatase nanoparticles had a large surface area of 288 m$^2$ g$^{-1}$ [54].

The very same phenomenon was observed for a tetranuclear titanium alkoxide complex modified with tert-butylphosphonic acid and acetylacetonate ligands (Fig. 2) [46]. Hence, thermal hydrolysis of bimetallic single-crystal oxo-alkoxide complexes may provide a route to highly porous complex oxides, which remains to be explored.

The first step in the formation of the oxide phase is the generation of Ti-O-Ti bonds [55], thus, oxo-alkoxides can be considered intermediates for oxide materials from the sol-gel process [56]. Hence, the incorporation of a hetero-metal, M, to form Ti-O-M, in TOAs could provide a route to obtain both doped titania and complex titanates. However, if the ion radius and/or charge of the dopant are too different from Ti$^{4+}$, separate oxide phases can form during hydrolysis/thermolysis of heterometallic complexes [48]. Doeuff et al. [57] used electron paramagnetic resonance (EPR) to study the incorporation of Cr$^{3+}$ into titania, starting from titanium(IV) butoxide and chromium(III) acetylacetonate. Upon heating of the two precursors, several bimetallic intermediates could be distinguished. After hydrolyzing and annealing of the intermediates, EPR indicated both volume and surface doping of Cr$^{3+}$ in the anatase. A recent study on rare-earth element-doped titania employing photoluminescence spectroscopy suggested the
dopants of larger ionic radii (compared to Ti$^{4+}$) can be incorporated in low-crystallinity anatase lattice. However, as the annealing temperature was increased and the crystallinity improved, the dopants appeared to migrate out towards the anatase surface [22].

### 3 First-row transition metals

Of the transition metals, the first-row elements dominate as dopants for TOAs, and in particular Fe, Mn, Co, and Zn. As the nuclearity increases, they tend to adapt a spherical shape and based on the position of the heterometal, two subclasses of the spherical structures can be distinguished; peripherally and internally doped TOAs. In the peripherally doped TOAs the dopant is located on the surface and in the internally doped TOAs the dopant is encapsulated within the titanium-oxygen framework. Complexes containing simultaneously internal and external dopants also exists. It can also be noted that most TOAs containing two or more transition metal dopants commonly contain an additional chelating/bridging ligand attached to the dopant. Examples of synthetic strategies are given in Scheme 1.

#### 3.1 Vanadium

A few titanium-containing polyoxovanadate alkoxy complexes have recently been reported by Matson’s group (Fig. 3) [58, 59]. The Lindqvist type [(TiOCH)$_3$V$_2$O$_6$(OCH$_3$)$_2$]$^-$ was formed by reaction between [Ti(OMe)$_4$]$^4-$ and VO(OCH$_3$)$_3$ in methanol at elevated temperature with [NBu$_4$][BH$_4$] as reductant. They latter extended this work to incorporate a second titanium ion, to obtain [(TiOCH$_3$)$_2$V$_4$O$_5$(OCH$_3$)$_2$]$^-$ by increasing the Ti equivalents and removing the reductant [59]. The substitution of a V for a Ti$^{4+}$ ion demonstrated increased oxidation potential for the vanadyl complex [58].

#### 3.2 Chromium

A small chromium-containing complex, [Ti$_3$O(CrCl)(OEt)$_4$], was reported by Eslava and co-workers [60] from solvothermal reaction between titanium(IV) ethoxide and chromium(II) chloride. The chromium ion connects to the (Ti$_3$O) fragment via three µ$_3$-OR bridges and a µ$_4$-oxygen bridge. It had a rather weak absorption in the visible region. Another, more peculiar, chromium-containing TOA was produced by Yi et al. [61]. They reacted an aqueous solution of...
titanyl sulfate (TiOSO₄) with Na[CpCo(P(O)-(OEt)₂)₃](Cp = cyclopentadiene) and Na₂Cr₂O₇ to obtain, via recrystallization from a dichloromethane: hexane mixture, the trimetallic complex [TiCpCo(P(O)-(OEt)₂)₃]₂[μ- CrO₄]₃. The two Ti⁴⁺ ions are bridged via three tetrahedral CrO₄-ligands and are further bridged to the CoCp unit via three diethyl phosphate molecules. It could catalyze the oxidation of benzyl alcohol to benzaldehyde. Zhang and co-workers [62] reported a larger TOA with high content of chromium in from solvothermal reaction between titanium(IV) isobutoxide with Cr(CH₃COO)₃ (approx. 5:4 ratio) and benzoic acid (HBA) in acetonitrile. A ring-like complex formulated as [Ti₁₂O₁₈Cr₆(BA)₃₀] was obtained. Altering [TiO₆] and (CrO₆) octahedra were linked by µ₂-benzoate and oxo-ligands. The complex displayed an improved visible absorption with a maximum around 610 nm, and the absorption continued into the near infrared region. It was reported to have a hydrogen production rate of 147.86 μmol·g⁻¹·h⁻¹ under simulated solar light. PXRD characterization before and after catalysis suggested operational stability of the electrodes. Examples of Cr-TOAs are shown in Fig. 4.

### 3.3 Manganese

Manganese is one of the most common TM dopants for TOAs and structures representing nuclearities from Ti₁ to Ti₂₈ and containing from one to four manganese ions have been reported, with particular contribution from the groups of Wright and Coppens.

One early structure was synthesized by Sobota’s group [63] by reaction between [Ti(iOPr)₄] and 0.5 eq. [Mn₄(μ₂-Cl)Cl₃(OMe)₄(2-ME)₃]² (2-ME = 2-methoxyethanol) at room temperature which afforded the complex [TiMn₃(μ₃-2-ME)₃]₂[μ₂-2-ME)₃]₃[μ-Cl]Cl₂(iOPr)₂. While it was not intended as a SSP, they investigated the complex as a catalyst for ethylene polymerization with AlEt₂Cl and methylaluminoxane for which it showed some activity. Eslava et al. [64] reacted [Ti(OEt)₄] with MnCl₂ in a solvothermal route with ethanol as solvent to obtain [Ti₄O{Mn₂Cl₃}(OEt)₁₅]. Several [Ti₄O{MCl}(OEt)₁₅] complexes were obtained from the same route (and equivalents) where M = Co, Zn, Fe, and Cu. For Mn, two manganese ions were incorporated into the structure, where the two Mn²⁺ were connected via a μ-Cl bridge, and connected to Ti⁴⁺ centers via bridging ethoxide groups. Unlike the Co, Fe, and Cu analogues, the manganese complex did not absorb in the visible spectrum. Li and co-workers [65] reported a relatively big TOA [Ti₁₈O₉₃Mn{MnPhen}₃(OEt)₂₀] containing four Mn²⁺ ions. This compound was produced via solvothermal treatment of [Ti(OEt)₄]₄ and manganese acetate dihydrate with 1,10-phenanthroline as additive in ethanol as solvent. Following calcination in air at 600 °C it yielded manganese-doped titania, predominantly in the rutile phase with some segregated α-Mn₂O₃ (Fig. 5).

Coppens’ group [66] reported another Mn-TOA, [Ti₁₁O₁₄{MnX}(OPr)₁₇] via reaction between [Ti(iOPr)₄] and MnX₂ (X = Cl, Br, or I) in a solvothermal method. The inclusion of a peripheral Mn²⁺ ion to TOA resulted in some
red-shift of the UV-vis absorption spectrum but considerably less compared to the FeII analogue. Yang and colleagues [67] also utilized a solvothermal method to synthesize $[\text{Ti}_{12}\text{O}_{16}\text{Mn}_2\text{(Cat)}_2\text{(BA)}_4\text{(OEt)}_{22}]$ from $[\text{Ti(OPr)}_4]$ and $\text{Mn(CH}_3\text{COO)}_2$ with catechol (Cat) and benzoic acid (BA) as stabilizing ligands. The manganese ions were integrated into the inorganic oxo-core via $\mu_2$-O, $\mu_3$-O, benzoate, and catecholate bridges. Electrodes of the complex prepared by dip-coated indium tin oxide (ITO) substrates had an improved photocurrent response compared to their reference titanias, but it was substantially lower compared to the cobalt analogue.

Chen et al. [68] used a solvothermal reaction between titanium(IV) ethoxide and manganese(III) acetate, with ammonium bromide as additive, to obtain a large, Keggin-like $[\text{Ti}_{28}\text{O}_{38}\text{Mn(OEt)}_{40}]$ complex with a tetrahedral manganese center. Notable, MnIII was reduced to MnII in the structure, but the complex could not be obtained by using manganese(II) acetate as reagent. The band gap of the $\text{Ti}_{28}\text{Mn}$ complex (2.74 eV) was substantially lower compared to undoped $\text{Ti}_{28}$ complex (3.43 eV), as determined by diffuse-reflectance spectroscopy. In another publication, Lv and co-workers [69] investigated the effect on the band gap by doping a $\text{Ti}_{14}$ complex with $\text{Mn}^{2+}$, $[\text{Ti}_{14}\text{O}_{14}\text{Mn(OEt)}_{28}(\text{OH})_2]$, as it previously had been reported to have a significantly lowered band gap. They did, however, found the actual band gap to be higher than that of anatase-$\text{TiO}_2$, ca. 3.36 eV. For the $\text{Fe}^{2+}$ and $\text{Gd}^{2+}$ analogues, band gaps were determined to 3.22 eV and 3.57 eV respectively, by UV-vis diffuse reflectance spectroscopy. The previously reported 2.65 eV band gap was proposed to be caused by contamination of amorphous Mn-doped titania. Chen et al. [70] reported another Mn-TOA formulated as $[\text{Ti}_{13}\text{O}_{16}\text{Mn}_4(\text{THME})_4\text{Br}_4\text{(OEt)}_{12}]$, obtained via solvothermal reaction between $[\text{Ti(OEt)}_4]$ and $\text{MnBr}_2$ in ethanol with 1,1,1-tris(hydroxymethyl)ethane (THME). It consists of a semi-spherical oxo-core of octahedrally coordinated Ti4+ ions, caped with terminal ethoxide ligands and four $\eta^3$-THME ligands. Four peripheral, octahedrally coordinated manganese ions are present. They form a polymeric network via Mn(µ-Br)2Mn bridges between the individual complexes. Diffuse reflectance spectroscopy determined the band gap to ca. 2.57 eV. Zhang and co-workers [71] synthesized a smaller complex, $[\text{Ti}_6\text{O}_2\text{Mn}_2(\text{PPA})_2(\text{Sal})_6\text{(OEt)}_4(\text{EtOH})_2]$, from reaction between $[\text{Ti(OEt)}_4]$ and an unspecified manganese salt with phenylphosphonic acid (PPA) and salicylic acid (Sal) as additives. It contains two $\text{Ti}_3$O sub-units liked by two $\mu_2$-oxygen and two bridging phenylphosphonate ligands to form a cube-like structure. The PPA ligands acts as bridges connecting the titanium ions while the Sal ligands act both bridging and chelating. Each titanium center has one chelating Sal ligand, which are positioned to form an “ion trap” that can coordinate a metal ion with up to six oxygen bonds. The Mn2+ ion utilizes five of these bonds. Dissolution of this complex in a Triton X-100 solution led to the self-assembly of flower-like nanosheets that appeared to be amorphous from HRTEM imaging (Fig. 6). Photocatalytic degradation of rhodamine B by the flower-like assemblies was investigated and reported to be
about 80% after 30 min after exposure to 280 W xenon lamp. This was considerably higher compared to the zinc and terbium analogues of ca. 25% and 18%, respectively. Examples of Mn-TOAs are given in Fig. 7.

3.4 Iron

Iron represents another popular dopant for TOAs which may stem from the improved photocatalytic performance of iron-modified titania as an effect of red-shifted absorption spectra and improved charge carrier-transport [72, 73]. The first iron-containing complexes, \([\text{Ti}_2\{\text{FeCl}\}(\text{iOPr})_9]\) and \([\text{Ti}_3(\text{OMe})_2(\text{iOPr})_9]\), were reported by Nunes and co-workers [74] in 2002 by reaction between \([\text{Ti}(\text{iOPr})_4]\) and FeCl\(_2\) in a toluene: isopropanol mixture in the presence of KOPr. In a follow-up work, the same group investigated the decomposition products of \([\text{Ti}_2\{\text{FeCl}\}(\text{iOPr})_9]\) under various conditions. PXRD indicated complex mixtures of different iron and titanium oxide phases in all cases [75]. Three additional Fe-TOAs, \([\text{Ti}_{11}\text{O}_{14}\{\text{FeCl}\}(\text{OPr})_{17}]\), \([\text{Ti}_{11}\text{O}_{14}\{\text{FeBr}\}(\text{OPr})_{17}]\), and \([\text{Ti}_{11}\text{O}_{14}\{\text{FeI}\}(\text{OPr})_{17}]\), analogues to \([\text{Ti}_{12}\text{O}_{16}\{\text{OPr}\}_{15}]\), were later prepared by Coppens’ group [66]. [Ti(\text{OPr})\(_4\)] was reacted with FeCl\(_2\), FeBr\(_2\), or Fe(CH\(_3\)COO)\(_2\) + NH\(_3\) in presence of salicylic acid and heated in a sealed glass tube at 150 °C. The three compounds are isostructural, varying only in the anion coordinating to iron center, however, no salicylate ligands were incorporated into the complexes. The three FeTi\(_{11}\) complexes demonstrated improved absorptions in the visible region, with little apparent influence from the halogen anion.

Eslava and colleagues [64] prepared a small Fe-TOA from a solvothermal reaction between \([\text{Ti(OEt)}_{14}]\) and FeCl\(_2\) which afforded \([\text{Ti}_{12}\{\text{FeCl}\}(\text{OEt})_{15}]\). The Fe\(^{2+}\) ion connected to the TOA via three bridging ethoxide groups. The complex had a red-shifted absorbance into the visible region up to ca. 600 nm. The same group latter utilized a post-functionalization route to modify \([\text{Ti}_{17}\text{O}_{28}(\text{OEt})_{20}]\) with FeCl\(_2\) in toluene, which afforded \([\text{Ti}_{17}\text{O}_{24}(\text{FeCl})(\text{OEt})_9]\) [60]. The Fe\(^{2+}\) ion is connected via three bridging ethoxide groups. One Ti\(^{4+}\) ion located three bonds away from the iron dopant had a terminal ethoxide ligand replaced by a chloride ion. An increased absorbance of visible light was observed for the iron-containing complex in UV-vis measurements. A large, peripheral type Fe-TOA complex, \([\text{Ti}_{17}\text{O}_{28}(\text{FePhen})_2(\text{OPr})_{18}]\) was reported by Jarzembska et al. [76] by solvothermal reaction of \([\text{Ti}(\text{OPr})\(_4\)]\) and Fe(CH\(_3\)COO)\(_2\) with 1,10-phenanthroline (Phen) as additive in isopropanol. The structure consisted of a spherical \((\text{Ti}_{17}\text{O}_{28}(\text{OPr})_{10})\) core with two Fe\(^{2+}\) ions in “para-position”, connected via \(\mu_2\)-O and \(\mu_3\)-O bridges. Each Fe\(^{2+}\) center contained one chelating Phen ligand. Exposure of visible light to a thin film of the complex deposited on a fluorine doped tin oxide (FTO) electrode generated a photocurrent between 400 nm and 640 nm. Lv and colleagues [69] synthesized a Keggin-like \([\text{Ti}_{14}\text{O}_{48}\text{Fe}(\text{OEt})_{28}(\text{OH})_2]\) cage compound with the Fe\(^{II}\) ion encapsulated in the structure. The iron ion is connected to
Ti$^{4+}$ solely via $\mu_3$-O bridges in a pseudotetrahedral arrangement. Given the relatively high condensation number (Ti/O = 1), the structure hydrolyzed only slowly at ambient conditions. The band gap was determined to 3.22 eV by diffuse reflectance spectroscopy. A selection of Fe-TOAs is shown in Fig. 8.

### 3.5 Cobalt

An early Co-TOA was reported by Eslava and co-workers [77] when they obtained the complex $[\text{Ti}_7\text{O}_4\text{Cl}(\text{OEt})_{19}]$ when attempting to synthesize $[\text{Ti}_2\text{Cl}(\text{OEt})_{9}]$ from a 1:1 reflux of $[\text{KTi}_2(\text{OEt})_9]$ and CoCl$_2$ in toluene. In an attempt to obtain the complex in better yield they solvothermally reacted $[\text{Ti}(\text{OEt})_4]_4$ with CoCl$_2$ in a 7:1 ratio but instead obtained $[\text{Ti}_2\text{O}(\text{CoCl})(\text{OEt})_{15}]$ as an apparently favorable product since it was afforded over a wide range of synthetic conditions. In a follow up work, the same group successfully synthesized $[\text{Ti}_7\text{O}_4\text{Cl}(\text{OEt})_{19}]$ via post-functionalization of $[\text{Ti}_7\text{O}_4(\text{OEt})_{20}]$ with 1 eq. of CoCl$_2$ in toluene [60]. It had a slightly increased visible absorption in the 500–650 nm range. Lai and co-workers [78, 79] reported two use of two additional Co-doped TOAs, $[\text{Ti}_{12}\text{O}_{15}(\text{iOPr})_{17}]$ and $[\text{Ti}_{11}\text{O}_{14}(\text{CoI})(\text{iOPr})_{17}]$ as SSPs for production of CoTi materials for (photo)electrochemical water oxidation. They were prepared by solvothermal reaction between $[\text{Ti}(\text{iOPr})_4]$ and CoX$_2$ (X = Br or I) in 9:1 ratio. The complexes were dissolved in dichloromethane and drop-casted on FTO-coated glass. The exposure of atmospheric water caused hydrolysis of the complexes which resulted in the entrapment of the cobalt ions in an amorphous titania network (Fig. 9). The authors reported an oxygen production of ca 9.4 µmol h$^{-1}$ and a Faradaic efficiency of 90% from the electrode prepared from $[\text{Ti}_{12}\text{O}_{15}(\text{iOPr})_{17}]$ and $[\text{Ti}_{11}\text{O}_{14}(\text{CoI})(\text{iOPr})_{17}]$. Based on
similar results for the electrode prepared from \([\text{Ti}_{11}\text{O}_{14}\{\text{CoI}\}^4\text{(OPr)}_{17}]\), they concluded that very similar materials were formed during the hydrolysis of the two SSPs.

Wang et al. \cite{80} reported the doubly doped Co-TOA \([\text{Ti}_4\text{O}_4\text{Co}_2(\text{BA})_{12}(\text{CH}_3\text{CN})_2]\) obtained by reaction between \([\text{Ti}(\text{iOPr})_4]\) and \(\text{Co(acac)}_2\) in acetonitrile with benzoic acid (BA) as additive. This compound displayed good absorption over the entire visible spectrum. Density functional theory (DFT) calculations by the authors indicated that a metal-to-core charge transfer from the cobalt dopant contributed to the increased absorption of visible light. Photoelectrodes were prepared by spin-coating ITO glass electrodes with a dichloromethane solution of the complex. A stable photocurrent of 0.9 \(\mu\)A cm\(^{-2}\) was reported. Another larger, doubly doped complex, \([\text{Ti}_{12}\text{O}_{10}\text{Co}_2(\text{Cat})_2(\text{BA})_{4}(\text{OE})_{22}]\) was prepared from the reaction between \([\text{Ti}(\text{iOPr})_4]\) and \(\text{Co(CH}_3\text{COO})_2\) in anhydrous ethanol with benzoic acid (HBA) and catechol (H\(_2\)CA) as additives. An electrode was prepared by dip-coating a TiO\(_2\)/ITO substrate in a dichloromethane solution of the complex. X-ray photoelectron spectroscopy analysis of the electrode indicated some partial hydrolysis, based on the shift of the O1S signal as compared to TiO\(_2\). A stable photocurrent response with a current density of 12.0 \(\mu\)A cm\(^{-2}\) was reported \cite{67}.

A CoTiO\(_3\) SSP was prepared by Ehsan and co-workers \cite{24} by reacting \(\text{Co(CH}_3\text{COO})_2\) and \([\text{Ti}(\text{iOPr})_4]\) (in a 1:2 ratio) in tetrahydrofuran (THF) with excess of trifluoroacetic acid (TFA). This afforded \([\text{Ti}_4\text{O}_6\text{Co}_2(\text{TFA})_{8}(\text{THF})_{6}]\). The complex was dissolved in ethanol and aerosol-assisted CVD on FTO glass with subsequent annealing was employed to produce electrodes. During annealing (500–600 °C) the complex decomposed into a CoTiO\(_3\):TiO\(_2\) composite, consisting of pure ilmenite and rutile phases for CoTiO\(_3\) and TiO\(_2\), respectively (Fig. 10). This composite was evaluated for electrochemical detection of dopamine, and a limit of detection of 0.083 \(\mu\)M was reported. A selection of Cr-TOAs is shown in Fig. 11.
A series of cobalt-doped TOAs were prepared by Lv et al. [81] as models for Co-doped titania; [Ti4O{CoBr}(OEt)15], [Ti7O5{CoBr}(OEt)19], [Ti24O34{CoBr}2(OEt)30], and [Ti20O28{Co2I3}(HPO3)(OEt)23]. They were synthesized by solvothermal reaction between [Ti(OEt)4] and CoBr2 or CoI2. The two larger TOAs, [Ti23O34{CoBr}2(OEt)30] and [Ti20O28{Co2I3}(HPO3)(OEt)23], displayed more red-shifted absorption edges compared to the two smaller TOAs (likely the quantum confinement effect), and absorbed strongly between 600 nm and 750 nm. The two smaller TOAs, [Ti4O{CoBr}(OEt)15] and [Ti7O5{CoBr}(OEt)19], on the other hand, displayed more blue-shifted absorption edge and had very similar absorption spectra to their previously reported [Ti4O{CoCl}(OEt)15]. From DFT calculations of the complexes, they suggested a dipole-induced decrease in band gap caused by the inclusion of the Co2+ dopant. This conclusion was challenged in a latter publication by Coppens [66].

3.6 Nickel

Kessler and co-workers [34] prepared a small Ni-doped TOA, [Ti2Ni2(OEt)4(acac)4], by refluxing Ni(acac)2 and [Ti(OEt)4] in toluene with subsequent crystalization at room temperature. Microhydrolysis of [Ti2Ni2(acac)4(OEt)8] by addition of 99.5% ethanol resulted in formation of a new complex of very different stoichiometry, [TiONi2(acac)2(OEt)8] [82]. The [Ti2Ni2(acac)4(OEt)8] complex was latter used by Tahir et al. [83] as a SSP for producing NiTiO3 by thermal decomposition at 500 °C (Fig. 12). Another small Ni-TOA was prepared by Eslava et al. [64] from reaction of [Ti(OEt)4] with 0.06 eq. NiCl2 ethanol and afforded after recrystallization in toluene the compound [Ti2{NiCl}(OEt)5], which consists of two triangular [Ti2Ni] units linked via μ2-OET and μ2-OEt bridges, and the [Ti2Ni] units are in turn linked via two μ2-Cl bridges. UV-vis measurement in solution (toluene) revealed a strongly blue-shifted absorption edge ascribed to the lack of a titanium-oxo core, but with two small absorption bands in the visible region. A selection of Ni-TOAs is shown in Fig. 13.

Hu et al. [84] reacted [Ti(μOPr)4] with low equivalents of NiX2 (X = Cl, Br, or I) to obtain a series of isostructural Ni-doped TOA, [Ti11O14(NiX)(μOPr)17], differing only in the halide anion. The peripheral Ni2+ is connected to the TOA via three μ3-oxygen bridges, and has one terminal halogen ligand. The authors performed extensive investigation of the photo-responses of the compounds. The inclusion of Ni2+ did extend absorption of the complex into the visible region, as compared to the Ti11 and Ti12 references. Interestingly, a dependence on the halide anion was observed where the absorption edge was red-shifted most in the order Cl > Br > I. No photocurrent could be observed from the complexes under visible light irradiation. It was concluded that the doping with Ni2+ (and the Zn2+ analogue) had a negative impact on the UV-photoactivity.

A linear-type complex, [Ti12O16Ni2(Cat)2(BA)4(OEt)22] were recently reported by reaction between [Ti(OEt)4] and Ni(CH3COO)2 in anhydrous ethanol with two different additives; benzoic acid (HBA) and catechol (H2Cat) [67]. It features two central Ni2+ ions connected via edge-sharing, and μ3-oxygen bridges. The Ni2+ are further connected to the (Ti6) units via bridging catecholate, benzoate, and μ3-oxygen bridges. The photocurrent density of the complex, 1.8 µA cm−2, were smaller compared to that of the Mn and Co analogues, 12.0 and 3.6 µA cm−2, and only moderately higher compared their reference complex, [Ti4O4(Cat)2(BA)4(μOPr)10], of 0.8 µA cm−2 indicating influence from the TM dopant. However, the photocurrent measurements were conducted in an aqueous Na2SO4 solution and no characterization of the electrodes after reaction was reported. A rare example of two co-crystallized Ni-doped TOAs [Ti6O16Ni4(acac)4(C6H5COO)16(CH3CN)2] + [Ti2O2Ni2(acac)2(C6H5COO)10] ([Ti2Ni2 + Ti3Ni2]) were recently reported by Wang and colleagues [85]. They were obtained by solvothermal reaction between [Ti(μOPr)4] and Ni(acac)2 (3:1 Ti:Ni ratio) in acetonitrile with benzoic acid as additive. At 100 °C, the [Ti2Ni2] unit was obtained, and by increasing the temperature to 120 °C, the [Ti3Ni4 + Ti4Ni2] unit was instead afforded. The [Ti3Ni4 + Ti4Ni2] complex exhibited an improved absorption in the visible region, which was ascribed by the authors to be caused by
[Ti₄Ni₂]-to-[Ti₈Ni₄] charge-transfer. Photocurrent responses under a 300 W xenon lamp were determined to ca. 0.6 μA cm⁻² and ca. 0.8 μA cm⁻² for [Ti₄Ni₂] and [Ti₈Ni₄ + Ti₄Ni₂], respectively. PXRD measurements before and after reaction were claimed to indicate stability under the working conditions.

### 3.7 Copper

An early Cu-TOA was reported by Veith and co-workers [86] by a simple metathesis reaction between [KTi₂(iOPr)₉] and CuCl₂ to afford [Ti₂{CuCl}(iOPr)₉]. It appeared monomeric in solution from ¹H and ¹³C NMR analyses. Later, Hamid and colleagues [87] attempted to synthesize a Cu-TOA SSP for producing copper titanate films. By reacting Ti(DMAE)₄ (DMAE = N,N-dimethylaminoethanolate) and Cu(CH₃COO)₂ dihydrate in a 2:3 ratio using toluene as solvent the compound [Ti₄O₆Cu₆(DMAE)₆(OAc)₉(OH)] was obtained. Thermal decomposition at 300 °C resulted in a ca. 0.77:0.23 mixture of Cu₃TiO₄ and TiO₂. Eslava and co-workers [64] prepared a small Cu-doped TOA, [Ti₁O {CuCl}(iOPr)₅] as a potential SSP. While the production of Cu-doped TiO₂ from it was not attempted, UV-vis measurements displayed substantially improved absorption in the 550–800 nm region. Liu et al. [88] prepared a novel complex [Ti₆O₂Cu₂(FSA)₆(CH₃COO)₂(CH₃CN)₂(ℓOPr)₁₀] by solvothermal reaction between [Ti(ℓOPr)₄], and Cu(CH₃COO)₂ in a 3:1 mixture with 3-fluorosaliclylic acid (FSA) as additive and acetonitrile as solvent. The obtained complex consisted of two typical (Ti₃O) units, separated by two (CuIII_O₃) octahedra. Rather extensive photochemical studies were conducted on the compound and their reference complex, [Ti₇O₄(FSA)₄(ℓOPr)₁₂]. The measurements were, however, conducted in aqueous media and no characterization of their compounds after measurements in water were reported. This is very important considering the hydrolytic instability of titanium oxo-alkoxides (even for the ligand-modified ones) [22, 34, 46]. Two additional Cu-TOAs with the general formula [Ti₅O₆Cu₄(OOCR)₁₆] were reported by Artner and co-workers [89] from reaction between [Ti(iOPr)₄] and Cu(CH₃COO)₂ with either methacrylic acid (MA) or propionic acid (PA), in a Ti:Cu ratios 1:2 and 1:1 for MA and PA, respectively. However, in both cases complexes with Ti:Cu ratios of 5:4 were obtained. No application was reported. A similar compound to the ones reported by Artner were synthesized by Wang et al. [80], but methacrylic acid and propionic acid were replaced with benzoic acid. Their complex, [Ti₅O₆Cu₄(C₆H₅COO)₁₆], was deposited on ITO glass from a dichloromethane solution, and photocurrent and hydrogen production under a 300 W xenon lamp were investigated. A stable photocurrent of ca. 0.8 μA cm⁻² and a hydrogen production of 42.02 μmol g⁻¹ h⁻¹ were reported. In agreement with Eslava and colleagues [64], absorption in the 550–800 nm range was improved. The authors concluded the complex was stable under operational conditions based on FTIR and PXRD analyses. A selection of Cu-TOAs is shown in Fig. 14.
3.8 Zinc

Hu and co-workers [84] synthesized a \([\text{Ti}_{11} \text{O}_{14} \text{ZnX}(\text{iOPr})_{17}] (X = \text{Cl or Br})\), a peripheral type complex, as part of an isostructural series of metal-doped TOAs. Photo-current activity turned out to be lower compared to their undoped \([\text{Ti}_{12} \text{O}_{16} (\text{iOPr})_{16}]\) and \([\text{Ti}_{11} \text{O}_{13} (\text{iOPr})_{18}]\) references. Eslava et al. [64] reported a low-nuclear \([\text{Ti}_{4} \text{O} (\text{ZnCl})(\text{OEt})_{15}]\) complex. UV-vis measurements in solution displayed no visible light absorbance and a very blue-shifted UV-absorption.

The structure \([\text{TiZn}(\text{2-ME})(\text{THF})\text{Cp}_2 \text{Cl}_2]\) (2-ME = 2-methoxyethanol) was produced by reacting \([\text{TiCp}_2 \text{Cl}_2]\) with metallic Zn (1:2 Ti:Zn ratio) in a mixture of THF and 2-methoxyethanol at room temperature [90]. The two chloride ions from the titanocene dichloride complex were replaced by a chelating 2-methoxyethanol ligand using the excess Zn(OR)₂ to extract the chloride ions to form Zn(OR)Cl and/or ZnCl₂ [91]. The compound was systematically investigated as a SSP for zinc titanates by thermolysis. After thermal decomposition of the compound by annealing at 800 °C, a mixture of ZnTiO₃, rutile-TiO₂, Zn₂Ti₃O₈, and ZnO were detected by PXRD. At 900 °C, rutile-TiO₂ and Zn₂Ti₃O₈ phases seemed to dominate [90]. Artner and co-workers [92] prepared a Zn-TOA \([\text{Ti}_4 \text{O}_6 \text{Zn}_2 (\text{OMc})_{10} (\text{iOPr})_2]\) (OMc = methacrylic acid) from a room-temperature reaction with stoichiometric amounts of \([\text{Ti}(\text{iOPr})_4]\) and Zn(CH₃COO)₂ with methacrylic acid as additive with a small amount of dichloromethane as solvent. The complex is structurally related to the TOA \([\text{Ti}_6 \text{O}_{4} (\text{OR})_8 (\text{OOCR})_3]\), forming two \([\text{Ti}_2 \text{Zn}]\) subunits sharing a µ3-oxygen bridge and being connected via bridging methacrylate molecules and µ2-oxygen bridges. Two binuclear structures, \([\text{TiZnEt}(\text{H}_3\text{DPTA}) (\text{iOPr})_2]\) and \([\text{TiZnPhen}(\text{H}_3\text{DPTA}) (\text{iOPr})_2]\) (H₃DPTA = diphenolate tetraamine) were prepared by reaction between \([\text{Ti}(\text{iOPr})_4]\) and diethyl zinc or diphenyl zinc in toluene at room temperature. These two complexes were employed as catalysts in various reactions and had moderate activity for ring opening polymerization of ε-caprolactone [93].

A bimetallic zinc-titanium complex for production of ZnTiO₃ via aerosol assisted CVD was reported by Ehsan and co-workers [94]. By reaction \([\text{Ti}(\text{iOPr})_4]\) with Zn(CH₃COO)₂ in a 2:1 ratio with an excess of trifluoroacetic acid (TFA) in THF they obtained \([\text{Ti}_4 \text{O}_6 \text{Zn}_2 (\text{TFA})_8 (\text{THF})_6]\). It consists of a Ti₄-oxo core with two octahedral zinc ions located in “para-position” connected via µ₁-oxygen bridges and bridging TFA ligands. By employing an aerosol-assisted CVD method, they produced a mixed TiO₂:ZnTiO₃ film (Fig. 15). The phase-composition of the film was dependent on the solvent used and was most efficient for an acetonitrile solution of the complex which gave a film consisting of 85% ZnTiO₃, 12% rutile-TiO₂, and 3% anatase TiO₂. A selection of Zn-TOAs are shown in Fig. 16.

4 Second-row transition metals

With the exception of zirconium, much fewer TOAs doped with second-row transition metals have been reported to date. Some of the most relevant examples are summarized below. Contrary to the first-row transition metals, here are more examples of compounds with higher number of dopants, e.g., Ti:TM ratios 2:1, 1:1, and 1:2. The application of additional bridging heteroligands also appears important for these structures. Examples of synthetic strategies are given in Scheme 2.

4.1 Yttrium

The first Y-TOA, \([\text{Ti}_2 \text{Y}(\text{iOPr})_6 \text{Cl}_2]\), was reported by Veith and colleagues in 1997 [86] via a metathesis reaction between \([\text{KTi}_2 (\text{iOPr})_8]\) with YCl₃ in a heated iPrOH:toluene mixture. The yttrium ion is connected via doubly and triply bridging isopropoxide ligands. No applications were reported. An analogous structure, \([\text{Ti}_2 \text{Y}(\text{iOPr})_8 (\text{NO}_3)_2]\), was recently reported from a solvothermal reaction between \([\text{Ti}(\text{iOPr})_6]\) and...
and Y(NO₃)₃·6H₂O in toluene [22]. It was investigated as a potential SSP for yttrium titanate or yttrium-doped titania via hydrolysis. However, anatase-phase titania was the only observed product (Fig. 17). Three additional Y-TOAs were prepared Schubert’s group [95] as part of their investigation of methacrylate-substituted titanium oxo-complexes as precursors for hybrid materials. Despite varying the [Ti(nOPr)₄]:Y(OCH₃)₃ ratio from 2:1 to 18:1, three complexes with the common core {Ti₄Y₂O₄} were obtained, differing only in the composition of coordinating ligands, i.e., methoxide (MeOH), methacrylic acid (McOH), and 2-methoxymethanol (2-ME, the solvent), yielding [Ti₄O₄Y₂(OMc)₁₄(2-ME)₂], [Ti₄O₄Y₂(OMc)₁₄(McOH)₂], and [Ti₄O₄Y₂(OMc)₁₂(2-ME)₂(McOH)₂]. Examples of Y-TOAs are given in Fig. 18.

4.2 Zirconium

There has been a certain interest in heterometallic Zr-Ti complexes as SSPs for zirconium titanates. The first Zr-TOAs were prepared by Caulton and co-workers [96] in a facile reaction between a zirconium pinacolate (Pin) complex [Zr₂(Pin)₂(HPin)₄] and [Ti(OPr)₄] in THF. By using either Zr:Ti ratios 1:1 or 1:2, [TiZr₂(Pin)₄(HPin)₄(OPr)₂] or [Ti₂Zr₂(Pin)₆(OPr)₄], respectively, were obtained. In both structures Ti is pentacoordinated and Zr and Ti are connected via bridging pinacolate ligands. Their initial attempts to produce Zr-TOA from mixtures of homoleptic zirconium and titanium alkoxides were apparently unsuccessful. However, the introduction of chelating and bridging functions from the pinacolate ligands, as well as reduced steric hindrance, was proposed to facilitate the formation of the two Ti-Zr complexes.

Several structures were reported by Kemmitt’s group in the early 2000s [97, 98]. [Ti₂Zr₂(C₃H₇O)₁₂(MDEA)₂] was produced by reacting stoichiometric amounts of [Ti(OPr)₄] and Zr(OPr)₄ with N-methyl diethanolamine (H₂MDEA) in benzene. They latter prepared the dinuclear [TiZr(MDEA)₃(C₃H₇O)₂] simply by doubling the amount of H₂MDEA. Moraru et al. [99] reported four additional Zr-TOAs; [Ti₄O₆Zr₄(OMc)₁₆(OBu)₄], [Ti₂O₄Zr₄(OMc)₁₄(OBu)₂], [Ti₄O₄Zr₂(OMc)₁₀(OBu)₆], and [Ti₂O₆Zr₆(OMc)₂₀] by reaction between [Ti(Obu)₄], [Zr(Obu)₄] or [Zr(OPr)₄] with excess methacrylic acid in butanol. The starting Ti:Zr ratios were well reflected in the structures, except for the Ti₂Zr₆ complex, which co-crystallized with the Ti₄Zr₂ complex. These compounds feature (ZrO₈) units linked in a zigzag pattern and terminated by edge- or corner-sharing (TiO₆) octahedra. A latter study from the same authors investigated the core-stability after functionalization with a variety of organic ligands to produce different hybrid materials, exploiting the
alkene function in methacrylic acid. According to the extended absorption fine structure (EXAFS) analysis, the metal-oxo frameworks were retained after functionalization [100].

Spijksma and co-workers prepared the SSP [(Ti(iOPr)3)2Zr(DEA)3] (DEA = diethanol amine) by a reaction 1:2:3 of [Zr(iOPr)4], [Ti(iOPr)4], and DEA, where the two titanium centers where connected to the nonacoordinated Zr4+ via bridging DEA ligands [101]. In a subsequent publication, this complex was successfully utilized as a SSP for production of essentially pure microporous srilankite (ZrTi2O6) (Fig. 19) by thermal decomposition at 800 °C, much lower compared to the traditional solid-state reaction [26]. A selection of Zr-TOAs is given in Fig. 20.

### 4.3 Niobium

Nb-TOAs are sparse, but one example was recently reported by Yuan and co-workers [102] from the reaction between [Ti(iOPr)4] and NbCl5 in n-propanol with embonic acid (EA) as additive. This afforded the structure H4[Ti2O2Nb2(EA)4(OOPr)2]. The titanium and niobium ions are connected by μ2-oxygen bridges and embonate ligands. The niobium ions further have one terminal n-propoxide ligand each. A band gap of ca. 1.4 eV was reported.

### 4.4 Molybdenum

A Mo-TOAs of the Linqvist-type structure, TBA3[TiO18Mo5(PrO)], was prepared by Errington and colleagues [103] from the reaction between (TBA)2[Ti2O4], (TBA)4[Ti8O26], and [Ti(iOPr)4] in acetonitrile (TBA = tetrabutylammonium) followed by the addition of water (1.5 eq to Ti) and subsequent heating to 100 °C. In a latter publication the same authors used TBA3[TiO18Mo5(OiPr)8]2x as precursor to obtain a series of new complexes; [Ti18Mo5(OPr)6], [Ti18Mo5(OBu)6], [Ti18Mo5(Ome)6], [Ti18Mo5(BuO)6], [Ti18Mo5(4-MeC6H4O)6], [Ti18Mo5(2-CHO-C6H4)6], and the dimer [μ-O(TiO2Mo3)]6, varying only in the set of ligands. No applications were reported.

An interesting example of a Mo-TOA was reported by Eslava et al. [60]. They solvothermally reacted [Ti(OEt)4]4 with MoCl5 in ethanol and obtained ([Ti4O8Mo2(OEt)10]2). It features a central MoO10 framework with the relatively short distance (2.609 Å) between the molybdenum ions that suggests Mo-Mo bonding within the complex. The Mo-core was encapsulated by a layer of titanium atoms, connected via oxo and bridging ethoxide ligands. This complex had an extended absorption of visible light in the 400 nm to 550 nm. Several Mo-TOAs were synthesized by Uchiyama et al. [25] by reacting [Ti(iOPr)4] with MoO(OMe)4 or MoO(iOPr)4 in toluene, which afforded the complexes [Ti2O4Mo2(OMe)4(OOPr)4], [Ti12O22Mo6(iOPr)16(iPrOH)2], and [Mo7O31xTi7x(OiPr)8x(OOPr)8x+2x]. Annealing of the Mo7Ti7 compound at 500 °C afforded TiMoO5 as major phase, with minor impurities of anatase-TiO2, Ti6O11, and MoO3. It showed promising result for use as anode material in Li ion batteries. A selection of Mo-TOAs is shown in Fig. 21.

### 4.5 Cadmium

A variety of Cd-TOAs have been reported, from tri-nuclear Ti2Cd up to the spherical Ti17Cd2. An early Cd-TOA was produced by Veith and co-workers [105] as part of their series of [MTi2(OPr)6] structures. Reacting [KTi2(OPr)6] with CdI2 in toluene yielded [Ti2(CdI)2(OPr)6], though no application was reported. Wu et al. [106] prepared the doubly doped cadmium-containing complex [Ti17O28(Cd8Phen)2(PrO)18] of peripheral type from reaction between [Ti(iOPr)4] and Cd(OAc)2 dihydrate in isopropanol. Electrodes were prepared by coating of ITO...
Fig. 18 Structures of selected Y-TOAs. a \([\text{Ti}_2\text{Y}(\text{iOPr})_4(\text{NO}_3)_2]\). b \([\text{Ti}_2\text{O}_2\text{Y}_2(\text{OMc})_2(2\text{-ME})_2]\). Hydrogen atoms and alkoxide ligands have been removed for clarity. Turquoise is yttrium, green is titanium, red is oxygen, purple is nitrogen, and grey is carbon.

Fig. 19 Composite membrane from a Zr-TOA. a SEM micrograph of ZrTiO$_3$ film deposited on a $\gamma$-Al$_2$O$_3$ substrate and (b) PXRD of \(\text{[Ti}^{\text{OPr}})_{2}\text{Zr}(\text{DEA})_2\text{]}\) treated at different temperatures. The strongest diffraction planes for srilankite are indicated by an asterisk. Copyright (2006) Wiley. Used with permission from ref. [26].

Fig. 20 Structures of selected Zr-TOAs. a \(\text{[Ti}^{\text{OPr}})_{3}\text{Zr}(\text{DEA})_2\text{]}\). b \(\text{[Ti}^{\text{OPr}})_{3}\text{DEA}_3\text{]}\). c \(\text{[Ti}^{\text{OPr}})_{3}\text{Zr}(\text{OMc})_2\text{]}\) and \(\text{[Ti}^{\text{OPr}})_{3}\text{DEA}_2\text{]}\). d \(\text{[Ti}^{\text{OPr}})_{3}\text{Zr}(\text{OMc})_4\text{]}\). Hydrogen atoms and alkoxide ligands have been removed for clarity. Light blue is zirconium, green is titanium, red is oxygen, blue is nitrogen, and grey is carbon.

Glass with dissolved complex and the photocurrent response was investigated. It displayed very poor photocurrent response in comparison to the \[\text{Ti}_{17}\text{O}_{28}\{\text{CoII-Phen}\}_2(\text{iOPr})_18\] analogue, explained by poor redox properties of Cd. Artner and co-workers [92] reported a methacrylate-substituted Cd-TOA from reaction of equimolar amounts of \[\text{Ti}(\text{OPr})_4\] and \[\text{Cd}^{2+}\text{CH}_3\text{COO}_2\] with 10 eq. of methacrylic acid in CH$_2$Cl$_2$. This afforded \[\text{Ti}_2\text{O}_2\text{Cd}_4(\text{CH}_3\text{COO})_2(\text{OMc})_{10}(\text{iPrOH})_2\]. The cadmium octahedra are connected via corner and edge-sharing. The titanium ions are connected via bridging methacrylate ligands and one bridging $\mu_3$-oxygen, connecting one Ti$^{4+}$ to two different Cd$^{2+}$ ions. A similar Cd-TOA, but with inverted core-structure, was prepared by Liu and colleagues [107]. Solvothermal reaction between \[\text{Ti}^{\text{OPr}})_{4}\] and 0.7 eq. Cd(NO$_3$)$_2$ hexahydrate in acetonitrile with excess tert-butylacetic acid (BA) gave $\text{H}_2[\text{Ti}_4\text{O}_8\text{Cd}_2(\text{BA})_{12}(\text{OPr})_2]$. Here, the Cd$^{2+}$ ions are connected to the...
Ti$_4$O$_2$-core via bridging 4BA ligands and μ$_3$-oxygen
groups, connecting one Cd$^{2+}$ with two different titanium ions. The complex did not absorb in the visible region according to solid-state UV-vis measurements. The band gap was determined to 3.39 eV. The authors investigated hydrogen production under a 300 W xenon lamp by dispersing powder of H$_2$[Ti$_4$O$_4$Cd$_2$(4BA)$_{12}$(OPr)$_2$] in water. A hydrogen production of 3.15 μmol h$^{-1}$ was reported. Operational stability was claimed by comparing PXRD patterns before and after reaction. However, the reported PXRD patterns displayed substantial differences. A recent work reported a series of structures based on the (Ti$_{10}$Cd$_2$O$_8$) core functionalized with a series of salicylate derivatives [108] from reaction between [Ti(OPr)$_4$] with Cd(NO$_3$)$_2$·4H$_2$O (Ti:Cd ratio 6.5) in ethanol and heated at 60 °C for a week. All complexes had improved visible absorption up to ca. 600 nm, probably due to the salicylate ligands. Band gaps were reported to vary between 2.07 and 2.32 eV. Photocurrent responses of the Cd-TOAs were mostly improved, up to ca. 3 μA cm$^{-2}$ compared to the undoped reference complex [Ti$_2$O(4-MeSal)$_8$(OEt)$_{16}$], ca. 0.8 μA cm$^{-2}$. Photoelectrodes were prepared by suspending the complexes in a water: ethanol solution containing Nafion followed by ultrasonication, and subsequent drop-casting on ITO electrodes. Complex stabilities were evaluated by recording PXRD patterns before and after soaking crystals in water for 24 h. While some of the complexes retained fairly similar diffraction patterns, others showed distinct changes. A selection of Cd-TOAs is shown in Fig. 22.

5 Summary

To date, an extensive library of heterometallic titanium oxo-alkoxide complexes has been reported. In some cases, isostructural series have been synthesized simply by changing the dopant precursor. These compounds are very interesting for studying decomposition into oxide materials. Based on the doped TOAs reported so far, a few trends may be discerned. First, with a few exceptions (e.g. the polyoxometalate-like Mo-TOAs), most reported TOAs containing two or more transition metal dopants are stabilized by bridging or chelating heteroligands such as carboxylates or β-diketonates. While singly doped TOAs generally can exist as only (oxo)-alkoxy complexes, the dopant transition metal commonly retains one halide ion if a transition metal halide was used as precursor. Secondly, the reported TOA structures modified with second-row transition metals tend to have higher numbers of dopants compared to the first-row transition metals. However, the identity of the modifying ligands may have an influence on this and will require further investigation.
While the doped TOAs generally are considered attractive single-source precursors for complex oxides and doped titania, much fewer studies have actually focused on obtaining the materials. A few successful examples include ZrTi2O6, NiTiO3, CoTiO3, ZnTiO3, and manganese-doped rutile. As synthetic details are available for a large number of potential single source precursors, some focus should be directed toward systematic investigations (e.g., temperature, ligand, solvent effects) on their conversion into oxide materials.

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**Compliance with ethical standards**

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