



# Rapid solid-state metathesis route to transition-metal doped titanias



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## ABSTRACT

Rapid solid-state metathesis (SSM) reactions are often short-lived highly exothermic reactions that yield a molten alkali halide salt that aids in product growth and crystallization. SSM reactions may also produce kinetically stabilized structures due to the short (seconds) reaction times. This report describes the investigation of rapid SSM reactions in the synthesis of transition-metal doped titanias (M-TiO<sub>2</sub>). The dopant targeted compositions were ten mol percent and based on elemental analysis, many of the M-TiO<sub>2</sub> samples were close to this targeted level. Based on surface analysis, some samples showed large enrichment in surface dopant content, particularly chromium and manganese doped samples. Due to the highly exothermic nature of these reactions, rutile structured TiO<sub>2</sub> was observed in all cases. The M-TiO<sub>2</sub> samples are visible colored and show magnetic and optical properties consistent with the dopant in an oxide environment. UV and visible photocatalytic experiments with these visibly colored rutile M-TiO<sub>2</sub> powders showed that many of them are strongly absorbent for methylene blue dye and degrade the dye under both UV and visible light illumination. This work may open up SSM reactions as an alternate non-thermodynamic reaction strategy for dopant incorporation into a wide range of oxide and non-oxides.

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## 1. Introduction

Metal oxide coatings and particles have been utilized in a wide range of materials applications including energy storage and catalysis for energy or fuel production. In the photocatalytic arena, titanium dioxide (titania or TiO<sub>2</sub>) is an extensively studied UV absorbing oxide with utility in both organic dye photocatalytic oxidation and water splitting reactions. TiO<sub>2</sub> photocatalysis has been utilized for self-cleaning window coatings [1,2]. Titania exists in primarily two synthetically accessible forms with UV band gap ( $E_g$ ) energies: anatase ( $E_g=3.2$  eV) and rutile ( $E_g=3.0$  eV). Typical solution precursor condensation routes to TiO<sub>2</sub> involve heating amorphous titanium hydroxide precipitates near  $\sim 500$  °C to produce the more catalytically active anatase form. Anatase irreversibly transforms to the thermodynamically stable rutile form upon heating to higher temperatures near 600 °C, with the transition temperature influenced by precursor used and presence of trace impurities or dopants in the amorphous structure [3]. While bulk crystalline rutile TiO<sub>2</sub> is less UV photocatalytically active than anatase, likely due to recombination of photogenerated electrons and holes, rutile nanoparticles have shown significant photo-assisted oxidation properties [4]. Commercial TiO<sub>2</sub> that is a mixture of anatase: rutile in  $\sim 4:1$  ratio (e.g., Degussa P25) shows notably high photocatalytic activity. The nature of this activity appears

to be synergistic electronic effects between anatase and rutile particles [5].

In addition to being composed of earth-abundant low toxicity elements, TiO<sub>2</sub> shows high UV photocatalytic activity and chemical stability in acidic and basic environments. Renewed interest in TiO<sub>2</sub> photoactivity stems from its ability to produce hydrogen gas fuel from renewable resources, particularly by providing photo-generated electrons to a platinum co-catalyst that produces H<sub>2</sub> from water under UV illumination [6]. Both gold and platinum metal particles deposited on titania show photocatalytic utility [7,8]. Synthetic efforts in recent years have focused on modifying titania light absorption properties into the desirable visible light solar spectrum. For example, organic dyes placed on its surface allow anatase titania nanoparticles to act as photovoltaic light to energy conversion (solar cell) materials [9].

Alternate methods to improve titania visible light absorption take advantage of metal and non-metal dopant incorporation into the titania structure. The dopant species can either substitute for Ti or O ions in the lattice or to occupy interstitial sites in the structure or form oxyanions embedded in the lattice. Anion doping by main-group elements (e.g., C, N, S, halogens) [10] onto the oxygen site or into interstitials can potentially raise valence band or lower the conduction band energy levels or introduce new dopant levels within the band gap for visible light absorption [11–16]. Ionic radii of many common oxidation states of transition metal of  $\sim 70$  to 90 pm are similar to the Ti<sup>4+</sup> ionic radius or 75 pm [17]. Cation doping of titania with transition-metal and main-group metals includes Fe [18,19], Co [20], Cr [21], Ni [22],

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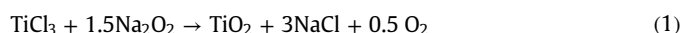
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and Mn, often leading to colored titanias [23,24]. Most titania doping methods begin with solution reaction/precipitation or ion-implantation followed by thermal annealing or crystallization. Typically, dopant additions to TiO<sub>2</sub> are at low ~1% to 5% levels to limit thermodynamically preferred second phases that will form during high temperature annealing. While transition-metal dopants may impart visible light absorption properties to TiO<sub>2</sub>, such dopants may also act as recombination centers for photogenerated electron and holes [25,26]. Apart from photocatalytic activity, transition-metal doped TiO<sub>2</sub> can also exhibit interesting dilute magnetic semiconductor (DMS) properties when doped with magnetic ions [27–29]. Metal doped titanias have also found application in hydrogen evolution catalysis and lithium ion batteries [30–32].

This paper describes a solvent-free single-step reaction to rapidly produce metal-doped titanias using a solid state metathesis (SSM) reaction strategy that takes advantage of precursor thermochemical exothermicity to produce crystalline products in seconds in self-propagating reactions that often require little or no external energy input. Rapid SSM reactions are an alternate strategy to solution phase reactions and can rapidly produce crystalline metal oxide and non-oxide materials using highly exothermic ion exchange reactions without the need for subsequent annealing. The SSM reactions extend back to the early 1900's, but were actively developed as a rapid materials growth strategy over the past couple of decades. Work in the early 1990's by Kaner and Parkin demonstrated the utility of rapid self-propagating SSM reactions to produce a wide range of inorganic materials in seconds using initiation methods including hot wires, ampoules placed in heated furnaces, and by external flames [33–35]. Crystalline products rapidly formed by SSM reactions include layered MX<sub>2</sub> (M=Mo, W, X=S, Se) [36], GaE (E=N, P, As) [37,38], transition-metal and lanthanide nitrides, phosphides, and borides (e.g. ZrN, GdN, ZrP, and TiB<sub>2</sub>) [39–42].

Relevant to the current work, solid-state oxygen source reagents (e.g., Na<sub>2</sub>O, Na<sub>2</sub>O<sub>2</sub>, Li<sub>2</sub>O) have been used for SSM growth of transition-metal oxides, including complex AM<sub>x</sub>O<sub>y</sub> structures [33,43–45]. A rapid SSM reaction was also utilized to produce cubic stabilized ZrO<sub>2</sub> by doping zirconia with Ca, Y, or Ce (~5% to 10%) during the SSM process [46].

In previous work, we produced crystalline rutile TiO<sub>2</sub> micro-particles using a rapid and exothermic SSM reaction between TiCl<sub>3</sub> and Na<sub>2</sub>O<sub>2</sub> (Eq. (1)) [47].



Rutile TiO<sub>2</sub> is synthesized in seconds using this exothermic exchange reaction that transiently reaches temperatures as high as the NaCl boiling point of ~1400 °C. We also synthesized anatase TiO<sub>2</sub> nanoparticles using similar exchange reactions under solvothermally heated conditions [48]. In the current study, we examine the ability of rapid SSM reactions to introduce moderate (~10 at%) levels of transition-metals into rutile TiO<sub>2</sub>. The structural and physical properties of these SSM-synthesized metal-doped titanias and their utility in UV and visible organic dye adsorption and oxidation photocatalysis are described.

## 2. Experimental section

### 2.1. Reagents

All starting materials were used as received: TiCl<sub>3</sub> (Aldrich, 99%), CrCl<sub>3</sub> (Alfa Aesar, 98%), MnCl<sub>2</sub> (Specialty Inorganics, 99.5%), FeCl<sub>3</sub> (Alfa Aesar, 98%), CoCl<sub>2</sub> (Alfa Aesar, 99.7%), NiCl<sub>2</sub> (Alfa Aesar, 99%), CuCl<sub>2</sub> (Alfa Aesar, 98%), Na<sub>2</sub>O<sub>2</sub> (Sigma Aldrich, 97%). Distilled

deionized water (18 MΩ) and 1 M HCl (Fisher Scientific, diluted) was used for wash processes. P25-TiO<sub>2</sub> (Degussa Corp.) and methylene blue (high purity, Alfa Aesar) or methyl orange (85% dye content, Sigma Aldrich) dyes were used in photocatalysis studies.

### 2.2. Synthesis of transition-metal doped TiO<sub>2</sub>

First-row 3d transition metals were incorporated into the TiO<sub>2</sub> structure using multiple metal halides precursors in a solid state metathesis (SSM) reaction based on our prior work with SSM TiO<sub>2</sub> synthesis [47]. All reagent manipulations were performed in a Vacuum Atmospheres argon filled glove box. Each anhydrous metal chloride (MCl<sub>2</sub> or MCl<sub>3</sub>) was used in an amount to produce a 1 M to 9 Ti molar ratio for products (e.g., M<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>2</sub> target) or 10 at% M with respect to total metal amount. Typically, 2.00 g (13.0 mmol) of ground TiCl<sub>3</sub> was mixed and ground in a mortar and pestle with the dopant metal halide. Specifically, dopant amounts used were: CrCl<sub>3</sub> (0.228 g, 1.44 mmol), MnCl<sub>2</sub> (0.182 g, 1.45 mmol), FeCl<sub>3</sub> (0.236 g, 1.45 mmol), CoCl<sub>2</sub> (0.188 g, 1.45), NiCl<sub>2</sub> (0.184 g, 1.42 mmol), and CuCl<sub>2</sub> (0.193 g, 1.44 mmol). The mixed metal halide powder was then mixed with ground Na<sub>2</sub>O<sub>2</sub> powder. For the MCl<sub>2</sub> and MCl<sub>3</sub> reactions, respectively, 1.63 g (20.9 mmol) or 1.69 g (21.7 mmol) of Na<sub>2</sub>O<sub>2</sub> was used to properly balance NaCl salt elimination from the SSM reaction. The intimately ground powders were placed inside a stainless steel crucible that was then placed inside a custom-made thick wall steel SSM ignition reactor that resembles a non-sealed bomb calorimeter (Fig. 1). Ceramic and quartz crucibles were initially used for these SSM reactions, however, due to the violent nature or rapid thermal changes that occur in these reactions, such crucibles frequently fractured after only a few uses so a stainless steel crucible was generally used. After placing the steel crucible in the reactor, a 0.64 mm diameter nichrome wire was attached to two electrical posts on the reactor lid and was buried in the precursor powder. The closed reactor was removed from the glove box and the wire was resistively heated to a red hot level (~500 °C) using a setting of ~10 V on a Variac, which initiated the SSM reaction. Reaction initiation was

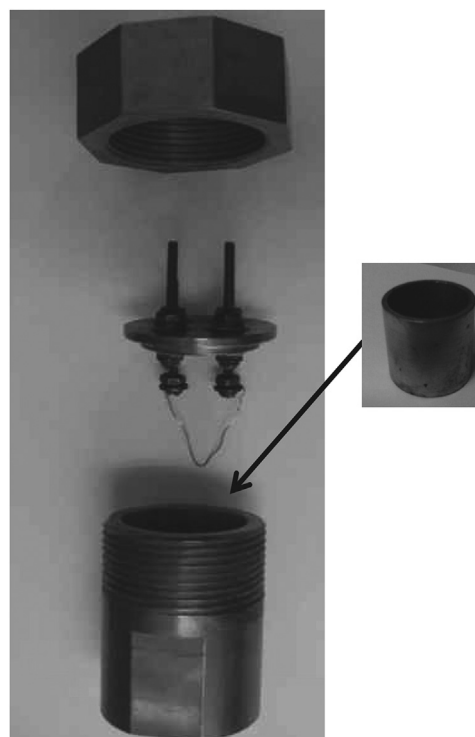


Fig. 1. Exploded view image of a home-built steel SSM reactor.

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