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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–TiO₂). The dopant targeted compositions were ten mol percent and based on elemental analysis, many of the M–TiO₂ 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 TiO₂ was observed in all cases. The M–TiO₂ 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–TiO₂ 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 nonthermodynamic reaction strategy for dopant incorporation into a wide range of oxide and non-oxides. © 2015 Elsevier Inc. All rights reserved.

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 TiO₂) is an extensively studied UV absorbing oxide with utility in both organic dye photocatalytic oxidation and water splitting reactions. TiO₂ 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 $(E_g=3.2 \text{ eV})$ and rutile $(E_g=3.0 \text{ eV})$. Typical solution precursor condensation routes to TiO₂ 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 TiO₂ 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 TiO₂ 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 is appears to be synergistic electronic effects between anatase and rutile particles [5].

In addition to being composed of earth-abundant low toxicity elements, TiO_2 shows high UV photocatalytic activity and chemical stability in acidic and basic environments. Renewed interest in TiO_2 photoactivity stems from its ability to produce hydrogen gas fuel from renewable resources, particularly by providing photogenerated electrons to a platinum co-catalyst that produces H_2 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 Ti⁴⁺ 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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and Mn, often leading to colored titanias [23,24]. Most titania doping methods begin with solution reaction/precipitation or ionimplantation followed by thermal annealing or crystallization. Typically, dopant additions to TiO₂ are at low $\sim 1\%$ 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 TiO₂, such dopants may also act as recombination centers for photogenerated electron and holes [25,26]. Apart from photocatalytic activity, transition-metal doped TiO₂ 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 MX₂ (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 TiB₂) [39–42].

Relevant to the current work, solid-state oxygen source reagents (e.g., Na₂O, Na₂O₂, Li₂O) have been used for SSM growth of transition-metal oxides, including complex AM_xO_y structures [33,43–45]. A rapid SSM reaction was also utilized to produce cubic stabilized ZrO₂ by doping zirconia with Ca, Y, or Ce (~5% to 10%) during the SSM process [46].

In previous work, we produced crystalline rutile TiO_2 microparticles using a rapid and exothermic SSM reaction between $TiCl_3$ and Na_2O_2 (Eq. (1)) [47].

$$TiCl_3 + 1.5Na_2O_2 \rightarrow TiO_2 + 3NaCl + 0.5O_2$$
(1)

Rutile TiO₂ 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 TiO₂ 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 TiO₂. 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: TiCl₃ (Aldrich, 99%), CrCl₃ (Alfa Aesar, 98%), MnCl₂ (Specialty Inorganics, 99.5%), FeCl₃ (Alfa Aesar, 98%), CoCl₂ (Alfa Aesar, 99.7%), NiCl₂ (Alfa Aesar, 99%), CuCl₂ (Alfa Aesar, 98%), Na₂O₂ (Sigma Aldrich, 97%). Distilled

deionized water (18 M Ω) and 1 M HCl (Fisher Scientific, diluted) was used for wash processes. P25-TiO₂ (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 TiO₂

First-row 3d transition metals were incorporated into the TiO₂ structure using multiple metal halides precursors in a solid state metathesis (SSM) reaction based on our prior work with SSM TiO₂ synthesis [47]. All reagent manipulations were performed in a Vacuum Atmospheres argon filled glove box. Each anhydrous metal chloride (MCl₂ or MCl₃) was used in an amount to produce a 1 M to 9 Ti molar ratio for products (e.g., M_{0.1}Ti_{0.9}O₂ target) or 10 at% M with respect to total metal amount. Typically, 2.00 g (13.0 mmol) of ground TiCl₃ was mixed and ground in a mortar and pestle with the dopant metal halide. Specifically, dopant amounts used were: CrCl₃ (0.228 g, 1.44 mmol), MnCl₂ (0.182 g, 1.45 mmol), FeCl₃ (0.236 g, 1.45 mmol), CoCl₂ (0.188 g, 1.45), NiCl₂ (0.184 g, 1.42 mmol), and CuCl₂ (0.193 g, 1.44 mmol). The mixed metal halide powder was then mixed with ground Na₂O₂ powder. For the MCl₂ and MCl₃ reactions, respectively, 1.63 g (20.9 mmol) or 1.69 g (21.7 mmol) of Na₂O₂ 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 (\sim 500 °C) using a setting of \sim 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.

observed by wisps of fine powder or smoke exiting the non-sealed edges of the reactor lid and reactions were usually complete within a few seconds leaving the reactor exterior walls warm to the touch. The inside of the reactor was usually covered with a thin coating of yellowish, off-white material, and a large amount of a darker glassy product was in the crucible. In order to purify the crude products and remove sodium containing impurities, metal doped titania samples were washed with 100 ml 1 M HCl for \sim 30 min at room temperature under constant stirring. The acid-washed samples were then rinsed several times with distilled water until the pH of the rinse was neutral. All solid products were dried in air at room temperature. Selected samples were also annealed for one day at 1000 °C in air in a box furnace at a heating at a rate of \sim 100 °C/hr. The samples were cooled naturally to room temperature.

2.3. Product characterization

Phase identification was conducted using Siemens D5000 or Bruker D8 DaVinci powder X-ray diffraction (XRD) systems that analyzed ground powders affixed to glass slides with either vacuum grease or using an acetone slurry. Morphologies and semiquantitative elemental analysis was obtained by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using a Hitachi S4800 or S3400 system. Samples were ground to fine powders and some were lightly pressed into thin pellets for EDS with an IR pellet hand press then affixed onto aluminum stubs with carbon tape. Samples were carbon coated to minimize charging. Quantitative analysis by ICP-OE spectrometry (Varian 720-ES) was performed on acid dissolved samples. Approximately 5 mg of each sample was dissolved in an acid mixture of 5 ml of concentrated H₂SO₄ and 1 ml of concentrated HNO₃, which was heated to \sim 385 °C for 1 h. The cooled solutions were diluted to the 1-100 ppm range depending on the metal concentration. Calibration standard curves were used to determine weight percent content for dopant metals and titanium. Magnetic susceptibility measurements were performed on solid powders at room temperature using a Johnson-Matthey MSB (Evans) magnetic susceptibility balance. Strongly magnetic samples were diluted in NaCl prior to analysis. All molar susceptibility results were corrected for sample core diamagnetism for TiO₂ of 2.9×10^{-5} cm³/mol or M-TiO₂ of 2.98×10^{-5} cm³/mol. Spin-only magnetic moments were calculated from molar susceptibility per mole of dopant metal using $\mu_{\rm B}=2.83(\chi_{\rm m}\times T)^{1/2}$. Scaled molar susceptibility was calculated by subtracting χ_m from undoped SSM-TiO₂ and dividing by the relative molar amount of M determined by ICP M_xTi_{1-x}O₂ structure. Solid diffuse reflectance UVvis measurements were made with a LabSphere RSA accessory on an HP 8453 UV-vis spectrometer. The powders were physically embedded onto filter paper supports sandwiched between glass microscope slides. Each sample's diffuse reflectance (R) data was converted to Kubelka–Munk (K–M) units and plots of F(R) = (1 - 1) $(R)^{2}/2R$ versus energy used to estimate absorption energy onsets or band gaps. The absorption onset data is derived from extrapolation of linear region of absorption rise down to baseline spectral region. Single baselines were used except for the Co- and Mn-TiO₂ data where different baselines better represented onset starting points of different regions. FT-IR spectra were obtained for each sample using KBr pellets in a Nicolet Nexus 760 spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained on a Kratos Axis Ultra Imaging spectrometer using monochromatic Al K_{α} radiation. Powders were embedded in indium foil for analysis. Survey spectra were obtained for acid washed samples (nominally 10 at% M doped TiO₂) and regional area spectra were obtained for Ti2p, O1s, as well as M2p (M=Cr, Fe, Mn, Co, Ni, Cu). Peak positions are reported relative to the C1s peak at 284.5 eV. Semiquantitative surface compositions and peak deconvolutions were performed using CasaXPS software package (www.casaxps.com) with a KratosAxis specific element library (KratosAxis-F1s.lib) and the following RSF factors: Ti2p (2.0), Cr 2p (2.43), Mn2p (2.66), Fe2p (2.96), Co2p (3.59), Ni (4.04), Cu (5.32). Relative atomic surface compositions were measured from survey scans.

2.4. Photocatalytic oxidative degradation of dyes

Photocatalytic oxidative degradation of methylene blue (MB) and methyl orange (MO) in air was performed using an Ace-Hanovia medium pressure 450 W mercury lamp in a water cooled Pyrex jacket. Approximately 10 mg of doped and undoped titanias were loaded into 20 ml pre-cleaned glass scintillation vials with 10 ml of a 3.00×10^{-5} M MB solution or 6.11×10^{-5} M MO solution and a stir bar. A dye sample with no powder was run as a blank. SSM synthesized undoped rutile TiO₂ and Degussa P25 TiO₂ $(\sim 80\%$ anatase) samples were also used for comparison. The sample vials were placed on a large stir plate about 25 cm away from the mercury lamp, all of which were contained in a closed photochemical reactor cabinet. The samples were allowed to stir in the dark for 30 min to allow surface equilibration or adsorption of the MB or MO dye. UV irradiation was in regular intervals of 5 min or longer. Between each interval, the samples were centrifuged and UV-vis measurements were taken on the solution. The analyzed solutions were returned to the original vial and the irradiation was repeated. A similar set of experiments were performed using 420 nm cut off filters (Edmund Optics) to limit the UV lamp output to visible light wavelengths. According to our testing, these cut off filters have a stop band limit or 0.001% T point at 430 nm. Linear regression of $-\ln(C/Co)$ versus time data for 4 data points in the first 20 min of UV irradiation (initial 40 min for visible) was used to estimate initial rate constants for MB dye degradation.

3. Results and discussion

3.1. Synthesis of metal-doped titania via rapid SSM reactions

Rapid and exothermic self-propagating SSM methods for the synthesis of inorganic metal oxide and non-oxide materials have broad flexibility to produce binary solids and more complex structures containing intimately mixed multiple metal and nonmetal components. In the current study, we take advantage of the rapid and non-equilibrium exothermic processes of SSM reactions to incorporate moderate amounts of a second transition-metal into the rutile TiO₂ structure. Typical thermodynamically driven methods for doping transition-metals into titania use sol-gel or solution precipitation methods followed by thermal processing, which leads to low metal dopant levels (\sim 1%) in titania. Given the rapid heating/crystallization afforded by SSM reactions, there is potential for kinetically stabilized higher dopant level incorporation, thus we "overloaded" the reaction system with 10 at% levels of dopant metals. Such additions, should impart visible optical absorption properties to the UV absorbing titania. The ideal SSM reactions for MCl₂ dopants (Mn, Co, Ni, Cu,) and MCl₃ (Cr, Fe) are shown below in Eqs. (2) and (3).

 $0.9 \text{ TiCl}_3 + 0.1 \text{ MCl}_2 + 1.45 \text{ Na}_2\text{O}_2 \rightarrow M_{0.1}\text{Ti}_{0.9}\text{O}_2 + 0.45 \text{ O}_2 + 2.9 \text{ NaCl}$ (2)

0.9 TiCl₃+0.1 MCl₃+1.5 Na₂O₂ \rightarrow M_{0.1}Ti_{0.9}O₂+0.5 O₂+3 NaCl (3)

In all cases, the SSM reactions were easily initiated in a selfpropagating mode using a heated filament in the steel SSM reactor. The doped titania products (generally referred to as $M-TiO_2$) after water and acid workup were visibly colored, with colors

Table 1

Experimental conditions and results for acid-washed transition-metal doped titanias from rapid exothermic SSM reactions between $MCl_x/TiCl_3$ and Na_2O_2 targeting $M_{0.1}Ti_{0.9}O_2$.

M-TiO ₂	MCl _x	XRD ^a	Product color, percent yield	ICP (EDS) analysis Ti:M molar ratio
Cr-TiO ₂	CrCl ₃	Rutile TiO ₂	Yellow, 71%	$\begin{array}{l} 1.0:0.037 \ (1.0:0.046) \\ 1.0:0.104 \ (1.0:0.174) \\ 1.0:0.063 \ (1.0:0.061) \\ 1.0:0.102 \ (1.0:0.115) \\ 1.0:0.042 \ (1.0:0.090) \\ 1.0:0.069 \ (1.0:0.115) \end{array}$
Mn-TiO ₂	MnCl ₂	Rutile TiO ₂	Brown, 86%	
Fe-TiO ₂	FeCl ₃	Rutile TiO ₂	It brown, 73%	
Co-TiO ₂	CoCl ₂	Rutile TiO ₂	Green, 68%	
Ni-TiO ₂	NiCl ₂	Rutile TiO ₂	Gray, 67%	
Cu-TiO ₂	CuCl ₂	Rutile TiO ₂	It brown, 58%	

^a Minor crystalline secondary phases were sometimes observed (see text for details).

generally consistent with the dopant metal in an oxide environment. Table 1 lists several qualitative and quantitative results obtained for these SSM M–TiO₂ products with some of these results highlighted below. The isolated yields for the acid washed materials (assuming ideal $M_{0,1}Ti_{0,9}O_2$ compositions) were generally in the ~60% to 80% range. These yields likely reflect some TiCl₃ loss via its decomposition to volatile TiCl₄ during the highly exothermic SSM reaction.

XRD data showed the presence of Na-Ti-O phases (e.g., $Na_2Ti_6O_{13}$), consistent with our earlier SSM TiO_2 work [47]. An acid wash step removed most detectable NaTi_xO_y impurities. EDS data from water versus acid washed samples show that the acid wash significantly decreases sodium content along with removing some dopant metal. Powder XRD data in Fig. 2 demonstrates that acidwashed metal-doped titanias are primarily crystalline rutile TiO₂ (PDF #21-1276). The rutile TiO₂ phase is expected as these SSM reactions can reach transient temperatures over 1300 °C and so it would be difficult to produce the low-temperature anatase TiO₂ phase under such conditions. Some acid washed samples still show evidence of Na₂Ti₉O₁₉ (PDF #78-1590) and Na₂Ti₆O₁₃ (PDF #37-0951) impurities. The Ni-TiO₂ sample shows two small peaks consistent with NiO and the Co-TiO₂ sample has small peaks that may be Co_2TiO_4 (PDF #39-1410), though some of these small peaks overlap with Na-Ti-O phases.

Selected acid-washed samples were annealed in air at 1000 °C to examine whether metal dopant segregation was observed. Given the high dopant levels in these M–TiO₂ materials, it is not surprising that crystalline metal titanate or Na–M–Ti–O phases are observed after prolonged high temperature annealing. In most annealed products, the major phase remains rutile TiO₂ (except for Co where Na₂CoTi₇O₁₆ is dominant) with new minor phases seen for Cr (Na₂Cr₂Ti₆O₁₆), Mn (Na₂Mn₂Ti₆O₁₆), Fe (Na₂Fe₃Ti₆O₁₆), Ni (NiTiO₃, Na_{0.23}TiO₂, NiO), and Cu (Na_{0.86}Cu_{0.43}Ti_{3.57}O₈, NaCu_{2.5}Ti_{4.5}O₁₂). This provides further support that the rapid SSM reactions trap dopants in non-thermodynamic compositions and structures that will convert to thermodynamically preferred structures upon annealing.

3.2. Compositional analysis of SSM synthesized metal-doped titanias

In contrast to typically low ~1% metal dopant levels found in solution methods to metal doped titanias, the ICP results show the SSM synthesized M–TiO₂ materials have a much higher bulk dopant metal content (Table 1). The transition-metal dopant levels range near the targeted Ti:M ratio for $M_{0.1}Ti_{0.9}O_2$ of 1:0.11 down ~1:0.05. Both ICP and EDS data for these acid-washed SSM reaction products show that they retain significant amounts of dopant metal. Some of the semiquantitative EDS results show higher dopant content than the more quantitative standardized ICP measurements, which may indicate some higher dopant



Fig. 2. Powder XRD data for acid-washed M–TiO₂ samples produced by SSM reactions where M=(a) Cr, (b) Mn, (c) Fe, (d) Co, (e) Ni, (f) Cu. The standard peak positions for crystalline rutile TiO₂ are shown in (g). The * marks Na₂Ti₉O₁₉, • marks Co₂TiO₄, + marks Na₂Ti₆O₁₃, and • marks NiO.

Table 2Summary of XPS analysis on M-TiO2 powders.

Compound	Surface Ti:M (rel. molar ratio)	Ti2p _{3/2} transition (eV)	M2p _{3/2} transitions (eV) ^a
Cr-TiO ₂	1:0.384	458.3	576.8 , 579.4
Mn-TiO ₂	1:0.599	458.0	641.3, 642.7
Fe-TiO ₂	1:0.064	458.4	710.7, 712.7
Co-TiO ₂	1:0.109	458.2	780.1, 782.0,
			784.6, 786.5
Ni-TiO ₂	1:0.100	458.2	855.3 , 861.4
Cu-TiO ₂	1:0.089	457.2	931.4, 932.8, 933.7,
			939.8, 942.3

^a Major transition(s) from peak deconvolution are **bolded**.

concentrations on the particle surface.

The acid-washed M–TiO₂ powders were analyzed by XPS to examine relative composition of metals on the surface and chemical states of the surface species. Table 2 summarizes survey and regional scan data for the metal doped titania powders. In most cases, the semiquantitative surface compositions (Ti:M ratios) for the powders is comparable to the bulk analysis results described earlier, with a few notable exceptions. While the bulk and most of the surface analysis results support that the achieved dopant levels are generally less than the targeted $M_{0,1}Ti_{0,9}O_2$ product, both the Cr and Mn doped samples show very high surface metal dopant amounts relative to their bulk compositions. This result was verified on several different products. The high dopant surface content may impact molecular dye adsorption discussed later in this paper. In comparing ICP with EDS or XPS data in Tables 1 and 2, it appears that the high dopant contents targeted in these shortlived SSM reactions lead to dopant rich near surface regions even if not detected by XRD analysis, specifically observed for Cr, Mn, and Ni doped titanias.

Degussa P25-TiO₂ yields a Ti $2p_{3/2}$ XPS peak at 458.3 eV and undoped SSM–TiO₂ has a peak at 458.2 eV, which are very near literature titania values [49]. The Ti $2p_{3/2}$ binding energies for metal-doped TiO₂ in Table 2 are generally close to the pure TiO₂ values, but several are shifted to lower energies that may indicate some reduced Ti³⁺ on the surface. The commercial P25-TiO₂ and SSM–TiO₂ have one major oxygen O1s chemical environment at ~529.5 eV, which is also the major oxygen surface environment found in the M–TiO₂ samples, in addition smaller peak intensity in the ~530 to 532 eV region for oxide environments due to the metal dopants. The metal dopant's $2p_{3/2}$ peak positions listed in Table 2 are consistent with binary oxide metal oxidation states, for example (lit. value, eV) Cr³⁺ (576.9), Mn⁴⁺ (642.1), Fe³⁺ (710.8), Co²⁺ (780.6) and Ni²⁺ (855.6), and Cu²⁺ (933.6) [50–55]. There may be some Cu⁺ present in the Cu–TiO₂.

3.3. Morphologies of SSM synthesized metal-doped titanias

SEM analysis of M–TiO₂ samples shows a range of particle sizes and shapes, consistent with that expected from a rapid exothermic reaction where powder products reside in a molten NaCl salt flux for a very short time. Fig. 3 shows representative images for the M–TiO₂ powders that were lightly pressed into pellets (additional loose powder images are in Supporting information Fig. S1). The samples are fairly heterogeneous in size and shape, with distinct facets visible on some crystallites faces. Particles with roughly spherical shapes and aggregates are visible as are larger faceted and elongated rod-like structures. The particles roughly range from ~500 nm to 5 µm, though much larger 10–30 µm crystallites are also visible. The well-defined crystallite structures and relative large particles observed from this SSM reaction may be a direct result of the initial powder forming in a byproduct molten salt flux that would aid in product crystallization and growth.

3.4. Magnetic and optical properties of metal-doped titanias

The room-temperature magnetic susceptibilities of the $M-TiO_2$ samples are listed in Table 3. Undoped SSM-TiO₂ shows a small paramagnetic response likely due to either some low level Ti³⁺ or



Fig. 3. Representative SEM images for M-TiO₂ materials with M=Cr (A), Mn (B), Fe (C), Co (D), Ni (E), and Cu (F).

Table 3

Room-temperature magnetic and optical results on $M\mathchar`-TiO_2$ powders from SSM reactions.

M-TiO ₂	Mass (χ_g , cm ³ /g) and molar (χ_m , cm ³ /mol) magnetic susceptibility	Magnetic moment per mol M (BM) ^a	UV-vis ab- sorbance in nm (type, <i>E</i> in eV) ^b	Absorption energy on- sets (eV) from K–M analysis
TiO ₂ (P25)	$\chi_{\rm g} = -0.0098 \times 10^{-6}$ $\chi_{\rm m} = +0.298 \times 10^{-4}$	0.27	408 (o, 3.04)	3.05
TiO ₂ (SSM)	$\chi_{\rm g} = +0.609 \times 10^{-6}$ $\chi_{\rm m} = +0.775 \times 10^{-4}$	0.43	415 (o, 2.99)	3.00
Cr-TiO ₂	$\chi_{g} = +6.34 \times 10^{-6}$ $\chi_{m} = +5.39 \times 10^{-4}$	5.7	570 (o, 2.18), 700 (p, 1.77), 800 (o, 1.55)	2.15, 1.50
Mn-TiO ₂	$\chi_g = +7.55 \times 10^{-6}$ $\chi_m = +6.38 \times 10^{-4}$	3.8	670 (o, 1.85), 710 (p, 1.75), 920 (o, 1.35)	1.80, 1.35
Fe-TiO ₂	$\chi_g = +17.1 \times 10^{-6}$ $\chi_m = +14.1 \times 10^{-4}$	7.5	480 (o, 2.59), 490 (p, 2.53), 580 (o, 2.53)	2.45, 2.10
Co-TiO ₂	$\chi_{\rm g} = +11.2 \times 10^{-6}$ $\chi_{\rm m} = +9.35 \times 10^{-4}$	4.7	510 (o, 2.43), 580 (p, 2.14), 660 (p, 1.88), 800 (o, 1.55)	2.40, 1.60
Ni-TiO ₂	$\chi_{g} = +7.54 \times 10^{-6}$ $\chi_{m} = +6.40 \times 10^{-4}$	6.0	500 (o, 2.48), 740 (p, 1.68), 810 (o, 1.53)	2.55, 1.55
Cu-TiO ₂	$\chi_g = +4.20 \times 10^{-6}$ $\chi_m = +3.72 \times 10^{-4}$	3.4	490 (o, 2.53), 740 (p, 1.68)	2.55

^a Estimated spin-only magnetic moment at 298 K for M–TiO₂ samples calculated from χ_m due to metal dopant (total $\chi_m - \chi_m$ for undoped SSM TiO₂) and scaled per mol M–TiO₂ based on ICP composition. Degussa P25-TiO₂ and SSM–TiO₂ moments are per mole of TiO₂.

^b p=Broad absorption peak, o=onset of absorption event.

other magnetic metal content from either steel reactor or nichrome wire. The paramagnetic responses from metal-doped titanias are all much larger than that for undoped TiO₂ and should be due to the dopant metal. The paramagnetic response from acidwashed M–TiO₂ samples is generally larger for more heavily doped materials. A estimate of magnetic moment per mole of dopant metal is listed in Table 3 (~3.4 to 7.5 BM) and most values fall in a range expected for spin-only paramagnetic metal ions with several unpaired d electrons (n=1–5 unpaired electrons with 1.7–5.9 BM). If one assumes that dopant ions are ideal spin-only paramagnets, then the values in Table 3 roughly correspond to Cr²⁺, Mn⁴⁺, Fe³⁺, Co³⁺, with the Ni and Cu values exceeding that expected for Ni²⁺ or Cu²⁺. The magnetic measurements along with XPS show that metal ions are in oxidized states and possibly clustered together leading to enhanced magnetic behavior.

The solid-state optical absorption properties of the SSM-synthesized M-TiO₂ materials were examined by diffuse reflectance UV-vis spectroscopy. In contrast to white commercial P25 TiO₂, the metal-doped titanias are all visibly colored powders (see Table 1) and show a range of visible light absorption. Undoped SSM rutile TiO₂ has a visible off-white beige color even after acid washing, possibly due to some Ti³⁺ content, but shows little detectable visible absorption versus the M-TiO₂ materials. Table 3 lists approximate absorption wavelengths and energies for the M-TiO₂ products. The extrapolated onset absorption energy for commercial P25 TiO₂ and SSM-TiO₂ samples is near 3 eV, while the M-TiO₂ samples show red-shifted lower energy absorptions $(\sim 1.8 \text{ to } 2.6 \text{ eV})$ and several show with additional absorption further in the visible region around 500–750 nm (\sim 1.7 to 2.5 eV). Optical absorption properties are consistent with transition-metal ions present in the titania. An examination of low energy valence band region of the XPS spectra for M-TiO₂ samples indicates that dopants may raise the valence band energy level that would lead



Fig. 4. Absorption and UV photodegradation of methylene blue (MB) by M-TiO₂ powders. The first half hour is equilibration of dye solution in the dark (surface adsorption) and light was turned on at time=0 h.

to smaller band gaps, however uncertainty and low intensity of the data, makes this a qualitative observation.

3.5. Adsorption and photooxidative degradation of organic dyes on SSM M-TiO₂ powders

Finely ground M-TiO₂ powders suspended in aqueous methylene blue (MB) dye solutions were irradiated with broad spectrum UV illumination with periodic analysis of dye remaining in solution using UV-vis spectroscopy. The MB dye contains a heterocyclic ring with N/S atoms that is oxidatively degradable by oxygen on a catalyst surface. For comparison purposes, undoped rutile SSM-TiO₂ (SSM-TiO₂) and a commercial anatase standard powder $(\sim 50 \text{ nm particles Degussa P25-TiO}_2)$ were analyzed along with the M-TiO₂ samples. The results are shown in Fig. 4. On notable difference for many M-TiO₂ samples versus P25-TiO₂ was observed moderate or large degree (\sim 40% to 90%) of dye surface adsorption that occurred during the 30 min dark equilibration step. This is a fairly reversible process as the Mn-TiO₂ after dark dye equilibration will easily release its adsorbed dye when placed in methanol. After several hours of UV irradiation, SSM-TiO₂ and the M–TiO₂ samples (except the chromium and cobalt samples) retain a bluish color consistent with some adsorbed intact MB dye and leaving very pale colored blue solutions.

For comparison, highly active commercial anatase-rich P25 TiO_2 is more photoactive than these rutile samples and clears dye

Table 4 Summary of methylene blue dye absorption and photodegradation on M-TiO₂.

Compound	Total MB % loss after 2 h UV (% loss from dark absorb)	Rate con- stant k (h^{-1}) for UV MB degrad.	Total MB % loss after 4 h vis (% loss from dark absorb)	Rate constant k (h^{-1}) for vis MB degrad.
MB alone P25-TiO ₂	23 (n/a) 98 [7] (after 0.5 h)	0.14(1) 13.7(5)	23 (n/a) 79 [22] an- nealed: 45 [5]	0.11(2) 0.42(5) annealed: 0.26(3)
SSM-TiO ₂	99 [55]	2.2(3)	79 [43]	0.29(7)
Cr-TiO ₂	63 [46]	0.8(4)	67 [50]	no MB loss
Mn-TiO ₂	99 [95]	3.2(3)	97 [62]	1.7(4)
Fe-TiO ₂	88 [63]	2.2(8)	90 [81]	1.9(8)
Co-TiO ₂	68 [36]	0.54(4)	78 [46]	0.35(7)
Ni-TiO ₂	91 [63]	0.5(1)	69 [45]	0.12(9)
Cu-TiO ₂	97 [53]	3.3(4)	86 [48]	0.8(4)



Fig. 5. Visible light methylene blue photodegradation by $M-TiO_2$ powders. The first half hour is equilibration of dye solution in the dark (surface adsorption) and light was turned on at time = 0 h.

from the solution after \sim 30 min of UV exposure. (Supporting information Fig. S2). Table 4 shows dark absorption and total dye degradation amounts after subsequent 2 h UV irradiation where the most photoactive samples reach high dye degradation values. The initial degradation data was used to calculate approximate first order rate constants from the data (Supporting information Fig. S3). As shown in Table 4, in addition to high dark dye

adsorption, Mn, Fe, and Cu doped samples show respectable dye degradation comparable to the undoped TiO₂ sample.

Similar UV experiments were performed with a methyl orange (MO) dye, which has an azo nitrogen double bond linking two heterocyclic rings. The rutile M-TiO₂ samples absorb little MO dye during dark equilibration and were less photocatalytically active leaving 80–95% MO dye in solution after 4 h of UV irradiation. For comparison, anatase P25-TiO₂ UV photodegrades ~100% of the MO dye after 2.5 h leaving a clear, colorless solution and a white solid. Thus either the rutile structure or interference from metal dopant makes them less effective for MO dye degradation.

Given the visible absorption properties of M–TiO₂ powders, the visible light photocatalytic degradation of MB dye was investigated with filtered UV (> 420 nm). Dark equilibrium dye absorption is again significant for most M–TiO₂ samples, though magnitudes vary from earlier UV studies, suggesting surface charge of M–TiO₂ samples may impact degree of MB absorption. Upon visible light irradiation, several M–TiO₂ samples showed photodegradation activity towards MB, but at reduced rates versus the UV experiments (Fig. 5). Due to UV filtering, both P25-TiO₂ and annealed P25-TiO₂ (rutile phase) samples showed significantly lower dye degradation. Table 4 shows comparison of MB photodegradation after 4 h visible light versus 2 h of UV illumination. While significant visible light assisted MB removal is seen for most samples, only Mn and Fe samples cause dye elimination of 90% or greater.

4. Conclusions

Rapid SSM reactions are capable of incorporating relatively large amounts of dopant metals into titania during the short-lived exothermic reaction. The targeted Ti:M bulk molar ratio was 1:0.11 with actual analyzed values being generally at or below the target value. The nature of the rapid SSM reaction that involves rapid cooling from a molten salt may impact the degree of metal dopant incorporation and observed sodium titanate components. The washed doped rutile TiO₂ materials show optical, magnetic, and structural properties consistent with dopant primarily residing in the oxide structure, though some samples show surface enrichment of dopant content. Several of the M-TiO₂ products show both UV and visible photodegradation activity for a methylene blue dye. In the case of visible light experiments, several M-TiO₂ samples more effectively used the incoming light for photodegradation than the P25 anatase titania standard. All M-TiO₂ samples demonstrated significant dark dye adsorption that may aid in bringing the dye near oxygen and photogenerated electron/ hole pairs that perform the dye oxidation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2015.09.028.

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