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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.7b04032 • Publication Date (Web): 21 Feb 2018

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# Heterogeneous Dual Photoredox-Lewis Acid Catalysis using a Single Bifunctional Nanomaterial

Gregory K. Hodgson and Juan C. Scaiano\*

Department of Chemistry and Biomolecular Sciences, Centre for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, K1N 6N5, Canada.

Email: jscaiano@uottawa.ca

# Abstract:

We report the heterogeneous dual photoredox-Lewis acid catalysis using a versatile and efficient nanocomposite; samarium oxide nanoparticle-decorated titanium dioxide. This emerging class of nanomaterials harnesses the Lewis acidity of the lanthanide, eliminates product contamination by the catalyst and can be excited with visible light. Useful intermolecular and intramolecular net reductive and net neutral photoredox cyclization reactions are presented as examples of the general efficacy of this reusable heterogeneous nanocatalyst in synthetically relevant organic transformations.

Keywords: heterogeneous catalysis, photoredox, Lewis acid, nanomaterials, cyclizations,

samarium, lanthanides

### Introduction

Heterogeneous and homogeneous catalysis are two sides of the same coin; they inherently offer different advantages to the modern chemist. Often the best option is not immediately evident, and ultimately the most suitable choice comes down to the specific requirements of the application. The steady rise in popularity of homogeneous catalysis is primarily attributable to

the relative ease with which both regio- and stereoselectivity can be attained. Such control is indeed a strong asset in pharmaceutical research and natural product synthesis. However, the chemical industry has historically relied heavily upon heterogeneous catalysis for an abundance of important organic transformations owing to the high efficiency stemming from phase separation and catalyst reusability. While heterogeneous catalysts generally suffer from the propensity to yield wider product distributions, the continuing push toward more environmentally sustainable routes to synthetic building blocks and value-added chemicals has seen a resurgence in the field of heterogeneous catalysis. Ideally it would be possible to combine the advantages of homogeneous and heterogeneous catalysis into a single reusable system.

In recent decades, photoredox catalysis has emerged as a powerful tool in synthetic organic chemistry, providing practical strategies for the preparation of a myriad of fine chemicals under mild conditions.<sup>1</sup> Merging photoredox catalysis with transition metal catalysis in dual- or tri-catalytic cycles has become a popular strategy for extending the utility of photoredox catalysts,<sup>2</sup> and pioneering work by Yoon and co-workers has opened a new frontier in the form of cooperative photoredox-Lewis acid homogeneous dual catalysis.<sup>3</sup> Despite these developments, few successful attempts have been made at heterogenizing dual photoredox-transition metal or photoredox-Lewis acid catalysis. In light of this, we identified an opportunity to combine our expertise in nanomaterials science, catalysis and photochemistry to devise novel heterogeneous analogues of dual catalytic systems with the goal of mirroring established product yields and regioselectivities while improving overall efficiency by designing readily separable, reusable, bifunctional heterogeneous nanostructured catalysts.

Lewis acids (LAs) often play critical, yet sometimes understated, roles in synthetic organic chemistry and photochemistry. They can serve to activate heteroatom-containing

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substrates by increasing their electrophilicity and shifting their reduction potentials to more positive values,<sup>4</sup> rendering them more susceptible both to nucleophilic attack and to photoreduction, respectively.<sup>2b,3,5</sup> Several reports have also documented the ability of LAs to impact reaction kinetics by stabilizing key photogenerated radical anion intermediates, leading to alternative reaction mechanisms not observed in non-photochemical counterparts to these catalytic systems.<sup>2b,3,6</sup> Samarium and other lanthanides are well-known to form LA complexes and some, such as SmI<sub>2</sub>, can become powerful reducing agents under appropriate conditions.<sup>7</sup> Other Lewis acidic lanthanide complexes have also been shown to function as catalysts for Friedel-Crafts acylation, the Diels-Alder reaction, alcohol esterification and the Mukaiyama aldol addition reaction.<sup>8</sup> Notably, lanthanide triflates, including Sm(OTf)<sub>3</sub>, have demonstrated exceptional performance as LA catalysts, cocatalysts and as the basis for chiral additives in a variety of homogeneous catalytic and photocatalytic reactions ranging from nucleophilic photoreductive cyclizations<sup>5b,6c</sup> additions<sup>9</sup> to to stereoselective [3+2] and [2+2]photocycloadditions.4b,6d,6e,6g,6h

Photochemical cyclization reactions are ubiquitous in synthetic organic chemistry; they provide access to an array of valuable synthetic precursors and complex molecular scaffolds by enabling otherwise challenging bond-formations.<sup>10</sup> Intermolecular and intramolecular variations of this class of reactions have given rise to a wealth of mechanistic knowledge and a multitude of practical synthetic routes to the preparation of polycyclic systems, four-membered ring motifs and key intermediates in natural product synthesis.<sup>10a,10b,11</sup> In particular, the development of photoreductive cyclizations and especially [2+2] photocycloadditions are regarded by some as among the most significant contributions to the advancement of applied photochemistry in organic synthesis.<sup>10a,11</sup> Heterogenizing this class of catalytic reactions would therefore be a

practical and worthwhile step forward for the academic and industrial chemistry communities (Scheme 1).

**Scheme 1.** Homogeneous and heterogeneous dual catalytic strategies for photoreductive cyclizations and [2+2] photocycloadditions.

Homogeneous Dual Photoredox Lewis Acid Catalysis



With all of these factors in mind, we set out to develop a multifunctional heterogeneous catalyst comprising a nanostructured semi-conductor support decorated with Lewis acidic nanoparticles (NP) that would allow for highly efficient preparation of a suite of useful photocyclization products by way of heterogeneous dual photoredox-LA catalysis. We reasoned that combining the known single electron transfer (SET) properties of semi-conducting oxides such as ceria (CeO<sub>2</sub>) and titania (TiO<sub>2</sub>) with the acidic properties and redox activity of samarium oxide nanoparticles, on which we have previously reported,<sup>12</sup> might induce a synergistic effect that

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would instill Lewis acidity into the nanocomposite material or enhance that of the support, slow down counterproductive electron-hole recombination and potentially extend the absorbance of the catalyst into the visible region. In this work, we describe the first example of purely heterogeneous dual photoredox-LA catalysis, using a single versatile nanocomposite comprised of titanium dioxide decorated with samarium oxide NP ( $Sm_xO_y@TiO_2$ ). This new heterogeneous nanocatalyst is readily recoverable and fully reusable for intermolecular and intramolecular photoreductive cyclizations and [2+2] photocycloaddition chemistry, eliminates product contamination by the catalyst, paving the way for progress in the development of more efficient heterogeneous analogues to homogeneous systems employing cooperative Lewis acid and photoredox catalysis for organic synthesis.

# **Results and Discussion**

We elected to begin our investigation into heterogeneous dual photoredox-LA catalysis with the photoreductive cyclization of chalcones (Table 1). This family of molecules are biologically and pharmaceutically relevant and are also of interest in synthetic organic chemistry.<sup>5b,13</sup> For example, the cyclopentanol derivatives of chalcones can be accessed via a LA-mediated homogeneous photocatalytic cyclization that forms new C-C bonds in the process. The reaction can be initiated by SET from an excited photocatalyst to the starting material to form a radical anion intermediate stabilized by an appropriate LA. Dimerization gives rise to a dienolate which then undergoes monoprotonation followed by a LA-mediated intramolecular aldol addition to form the final cyclized product in a net reductive photoredox mechanism.<sup>1a,2b,5b</sup> In the reported homogeneous system, the LA additive was further responsible for activating the substrate toward SET from the homogeneous photocatalyst Ru(bpy)<sub>3</sub><sup>2+</sup> ( $E_{red} -1.33$  V vs. SCE) by shifting its reduction potential<sup>14</sup> from -1.49 V vs. SCE to a more positive value.

We envisaged a scenario in which a nanostructured, samarium-decorated semi-conductor oxide might be capable of catalyzing this reaction heterogeneously. We began by photochemically preparing two candidate nanocatalysts comprising samarium oxide NP supported on titania (P25) and ceria, henceforth referred to as  $Sm_xO_y(a)TiO_2$  and  $Sm_xO_y(a)CeO_2$ , based on logical modifications to our previously reported work with larger, polydisperse, colloidal samarium oxide nanoparticles  $(Sm_2O_3NP)$ .<sup>12a</sup> In the present work, NP 1.2 ± 0.2 nm in diameter were observed on titania but none could be identified on ceria microparticles by TEM, likely due to a combination of small size, low Sm loading and the relatively large size ( $< 5 \mu m$ ) and thickness of the CeO<sub>2</sub> microparticles (Figures S1-S3). Characterization of these two novel nanomaterials by EDS (Figures S7-S8) detected samarium and XPS revealed the primary oxidation state to be Sm(III) but could not definitively rule out the presence of SmO or metallic samarium, hence the  $Sm_xO_v$  label selected for the materials (Figures S11-12 and associated discussion). Intriguingly, ICP-MS determined that although both materials were prepared with an optimal loading of 5 mol% Sm, the final nanocomposites contained vastly different amounts of samarium (4.7 and 0.29 wt% for TiO<sub>2</sub> and CeO<sub>2</sub>, respectively, Table S1).

Until now, literature reports describing samarium-semiconductor hybrid materials have been limited to the use of ionic samarium(III) as a dopant or co-dopant in TiO<sub>2</sub>,<sup>15</sup> Gd<sub>2</sub>O<sub>3</sub>,<sup>16</sup> and BiFeO<sub>3</sub>.<sup>17</sup> These studies have been mostly concerned with the degradation of organic dyes under aerobic conditions; none involve Sm-related Lewis acidity or employ inert atmosphere and importantly, none of the materials contain samarium-based NP. Indeed, Sm<sub>x</sub>O<sub>y</sub>@TiO<sub>2</sub> exhibited exceptional performance in the photoreductive cyclization of chalcone **1a** relative to Sm<sub>x</sub>O<sub>y</sub>@CeO<sub>2</sub> (Table 1 entries 1 and 2) and to the homogeneous catalytic system (62%, 3 h)<sup>5b</sup> under comparable optimized conditions (Scheme 1). Diffuse reflectance (DR) measurements

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showed that of the two nanomaterials, the absorbance of  $Sm_xO_y@TiO_2$  extends further into the visible region and has a much better overlap with the emission of the 400 nm LED used for photoexcitation of the catalyst (Figure S15). Increasing the optimal loading of samarium on CeO<sub>2</sub> two-fold only resulted in a small increase in the actual Sm loading (0.42 wt%), and the yield of **2a** was actually negatively impacted, decreasing to roughly 50% of that obtained using unmodified commercial CeO<sub>2</sub> with a particle size < 5 µm (Table 1 entries 3-4 and Figures S4, S9, S13). We attempted to increase the samarium loading further by switching to a commercial ceria nanopowder with a particle size (< 25 nm) more comparable to that of TiO<sub>2</sub>. The presence of Sm<sub>x</sub>O<sub>y</sub> NP 0.92 ± 0.2 nm in diameter was confirmed by a combination of TEM, EDS and XPS analyses (Figures S5-S6, S10, S14). The nanoscale CeO<sub>2</sub> did perform marginally better than the micron-range CeO<sub>2</sub> but although we were able to achieve a 3.3 wt% loading of samarium, the material could not match the superior catalytic activity of Sm<sub>x</sub>O<sub>y</sub>@TiO<sub>2</sub> (Table 1 entries 5 and 6).

# Table 1. Heterogeneous dual catalytic photoreductive cyclization of *trans*-chalcone.<sup>a</sup>

° I		nanostructured photocatalyst	( Ph.	Ph	Ph-	Рh	
		<i>i</i> -Pr <sub>2</sub> NEt (5 equiv) MeCN, Ar, 3 h	Phu	Ph	+ +	Ph Ph	
	1a	400 nm LED	FII	2a		3	
			(major	product)	(min	or product)	
Entry		Catalyst		Yield <sup><math>b</math></sup> 2	a (%)	Yield <sup>b</sup> <b>3</b> (%)	
1	Sm <sub>x</sub> O <sub>y</sub> @7	ГіО <sub>2</sub> (4.7 wt % Sr	n)	70		15	
2	Sm <sub>x</sub> O <sub>y</sub> @CeO <sub>2</sub>	$(\leq 5\mu m) (0.29 \text{ wt}^{\circ})$	% Sm)	40		10	
3	Sm <sub>x</sub> O <sub>y</sub> @CeO <sub>2</sub>	$(\leq 5\mu m) (0.42 \text{ wt}^{\circ})$	% Sm)	15		4	
4 <sup><i>c</i></sup>	$CeO_2 (\leq 5 \ \mu m)$		31		8		
5 <sup><i>c</i></sup>	CeO <sub>2</sub> (< 25 nm)		37		9		
6 <sup><i>c</i></sup>	Sm <sub>x</sub> O <sub>y</sub> @CeO <sub>2</sub> (< 25 nm) (3.3 wt% Sm)			31		8	
7		TiO <sub>2</sub>		41		15	
$8^{c,d}$	$TiO_2 + S$	Sm(OTf) <sub>3</sub> additive		37		9	

<sup>*a*</sup>Reaction conditions: chalcone (1 mmol), catalyst (60 mg), *i*-Pr<sub>2</sub>NEt (5 mmol), 15 mL dry MeCN, degassed with argon 20 min, irradiated with a 400 nm LED (90 W); irradiation time was optimized for 100% conversion in entry 1 and coincidentally matched the optimal irradiation time in ref. 5b despite the different light sources used. Longer irradiation times did not result in significantly higher conversion to **2a** using either Sm<sub>x</sub>O<sub>y</sub>@TiO<sub>2</sub> or TiO<sub>2</sub> alone.

<sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy using an internal standard. <sup>c</sup>The [2+2] cycloaddition product was detected in  $\leq 5\%$  yield. <sup>d</sup>Reaction conducted in the presence of 1.2 mM (0.0185 mmol, 11.0 mg) Sm(OTf)<sub>3</sub>, corresponding to the molar amount of samarium present in entry 1. In all cases no linear dimer was detected.

These results are consistent with DR spectra, which illustrate that although the  $CeO_2$ -based materials do possess slightly smaller band gaps than TiO<sub>2</sub> ( $E_{bg} = 3.2$  eV vs. SCE),<sup>18</sup> Sm<sub>x</sub>O<sub>v</sub>@TiO<sub>2</sub> was the only samarium oxide-decorated nanocomposite to exhibit a change in the spectral line profile with respect to the unmodified support (Figures S16-17). The addition of samarium (4.7 wt%, 2.5 mol%) resulted in the appearance of a clear band from 400-450 nm which resembles the known absorbance of colloidal Sm<sub>2</sub>O<sub>3</sub>NP (Figure S18).<sup>12b</sup> This effect has also been observed when titania is doped with 0.05-1.5 mol% ionic Sm(III) using microwaveassisted or auto-combustion sol-gel procedures.<sup>15a,15c</sup> Whether as a result of metal ion doping or the formation of heterojunctions in semi-conductor nanocomposites, red-shifted absorbance is a manifestation of a decrease to the band gap energy of the new overall material.<sup>15c,17,19</sup> The DR of 3.3 wt% Sm<sub>x</sub>O<sub>v</sub>@CeO<sub>2</sub> (< 25 nm) is higher than that of Sm<sub>x</sub>O<sub>v</sub>@TiO<sub>2</sub> and extends comparably far into the visible region (Figure S17); however, lower catalytic activity (Table 1 entry 6) and a lack of the aforementioned spectral feature in the 400-450 nm region suggest that only in  $Sm_xO_y$  (a) TiO<sub>2</sub> was the band gap of the nanocomposite successfully modified with respect to the support (Figures S18-19).

For lanthanide-titania hybrid materials, smaller band gaps arise from the presence of intra-band gap electronic states corresponding to the 4*f* manifold, with the filled states near the valence edge of TiO<sub>2</sub> effectively forming the new highest occupied band of the nanocomposite material.<sup>15a,15b,20</sup> Similar effects on band gap energy have been reported for nanocomposites comprising TiO<sub>2</sub> decorated with various precious metal NP (e.g. Pt, Pd, Ir, Au)<sup>18b,21</sup> as well as first-row transition metal elements like Cu,<sup>22</sup> and have been accredited to equilibration between

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the Fermi levels of the TiO<sub>2</sub> conduction band and the NP on its surface.<sup>21c</sup> An important distinction from the work reported herein is that samarium is more abundant than precious metals and plays an additional role as a LA (Figure 1). In some materials, as DR suggests to be the case for  $Sm_xO_y@TiO_2$ , visible light absorbance and charge transfer can be facilitated by the minor constituent of the nanocomposite ( $Sm_xO_y$  here) and charge separation managed by the native semi-conductor component of the hybrid material.<sup>19b</sup> An additional benefit of nanocomposite catalysts is that hole-scavenging oxygen vacancies generated at heterojunctions (or at metal ion doping sites in other hybrid materials) can increase charge separation and slow down electronhole recombination, making SET from the charge-separated photocatalyst to the substrate more efficient.<sup>15a,19a,19b,23</sup> When  $Sm_xO_y@TiO_2$  was irradiated using solely visible (465 nm) or UV (365 nm) light, conversion of the starting material did eventually near completion, but yields of **2a** were lower in both cases (Table S2). From a practical perspective it is clear that decorating TiO<sub>2</sub> with  $Sm_xO_y$  NP allows the nanocomposite photocatalyst to perform efficient SET after excitation by visible light, and that 400 nm represents an optimal excitation wavelength.



**Figure 1.** Proposed mechanism for the heterogeneous net reductive photoredox-Lewis acid catalytic reductive cyclization of *trans*-chalcones.

The net reductive heterogeneous photocatalytic mechanism proposed in Figure 1 closely resembles the previously-described homogeneous catalytic mechanism,<sup>2b,5b</sup> but likely begins with coordination of two molecules of substrate to a single  $Sm_xO_y$  nanoparticle on the catalyst surface such that the two reactants come into close proximity. As in the homogeneous analogue, photoexcitation of the catalyst and two SET events are followed by radical-radical coupling to form a new carbon-carbon bond. Subsequent monoprotonation of the dienolate followed by intramolecular aldol addition furnishes the substituted cyclopentanol product. Interestingly, the LA samarium triflate has been proposed to take on multiple roles in the homogeneous catalytic version of this system. In addition to stabilizing the radical anion intermediate, it has been reported that a single Sm(III) atom facilitates the ring-closing final step by coordinating to both the enol and carbonyl functionalities of the dienolate, rendering the reaction highly selective

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toward the thermodynamically favoured stereoisomer **2a**. This is not necessarily the case in the heterogeneous mechanism, as the surface of each  $Sm_xO_y$  nanoparticle contains many closely-spaced, non-diffusing Sm(III) atoms available for coordination. Contrary to homogeneous catalysis in solution, when a solid-phase catalyst such as nanostructured  $TiO_2$  or  $Sm_xO_y@TiO_2$  is used, the involvement of multiple LA sites would be less sterically hindered than coordination to a single atom. Nonetheless, the dienolate being anchored to a single NP rather than a single atom prior to cyclization appears to have had the same effect. The diastereoselectivity of the heterogeneously catalyzed reaction equaled that of the homogeneous system and was preserved regardless of whether  $Sm_xO_y@TiO_2$  or the relatively weak LA  $TiO_2$  was used (*vide infra*). It therefore seems reasonable that the enhanced activity exhibited by  $Sm_xO_y@TiO_2$  may be the result of a combination of stronger Lewis acidity as well as a higher number or density of LA sites relative to the unmodified support.

We attribute the slightly higher catalytic activity of CeO<sub>2</sub> (< 25 nm) relative to CeO<sub>2</sub> (< 5  $\mu$ m) to a difference in surface area to mass ratio, a well-known phenomenon in nanocatalysis. This may also contribute to the low samarium loadings achieved using ceria microparticles as supports, but based on the 3.3 wt% Sm achieved with the smaller ceria nanopowder versus 4.7 wt% with the comparably-sized TiO<sub>2</sub>, a more general explanation could be that samarium simply has a greater affinity for titania over ceria. The latter is intrinsically a more reducible support than TiO<sub>2</sub> and therefore might reasonably be expected to act as a stronger LA, yet even as the surface area to mass ratio of ceria was increased toward that of TiO<sub>2</sub> its reactivity only approached but still did not match that of TiO<sub>2</sub> (Table 1 entries 4, 5 and 7). This could be due to faster electron-hole recombination. However, for Sm<sub>x</sub>O<sub>y</sub>@CeO<sub>2</sub> we speculate that the combination of Ce(IV), Sm(III) and Sm(II) might give rise to an internal pathway for non-

radiative energy decay in which photoexcitation of  $Sm_xO_y$  could foreseeably initiate a charge transfer transition loop and impede SET to the substrate (Scheme 2).

**Scheme 2**. Possible charge transfer transition loop in samarium-decorated ceria, explaining the non-radiative dissipation of energy after light excitation.

$Sm_xO_y + hv \longrightarrow Sm_xO_y^*$	(1)
Sm(II)* + Ce(IV) → Sm(III) + Ce(III)	(2)
Sm(III)* + Ce(III) → Sm(II) + Ce(IV)	(3)
Sm(III) + Ce(III) - Sm(II) + Ce(IV)	(4)

According to reported ground state reduction potentials of Sm(III) ( $E_{red}^{III/II} \approx -1.6$  V) and Ce(IV) ( $E_{red}^{IV/III} \approx -1.8$  V),<sup>20a</sup> Scheme 2 may be feasible. Additionally, polydisperse colloidal Sm<sub>2</sub>O<sub>3</sub>NP are thought to exist as a dynamic mixed oxides of primarily Sm<sub>2</sub>O<sub>3</sub> with localized surface regions of the less stable SmO,<sup>12a,12c</sup> and when irradiated, at certain loadings their presence may impact the ability of ceria to cycle between CeO<sub>2</sub> and the less stable Ce<sub>2</sub>O<sub>3</sub> state.

It is important to note that ICP-MS showed that  $Sm_xO_y@TiO_2$  does not leach samarium and therefore that the nanomaterial functions as a purely heterogeneous catalyst (Table S1 and associated calculation). In all cases minor amounts of pinacol coupling of **1a** were observed and in some instances traces of the [2+2] photocycloaddition product were also detected. The reaction did not proceed significantly in the absence of the amine, the catalyst or in the dark at 35°C (the temperature reached by the reaction mixture under irradiation; see Table S2 and associated discussion). As is typical in heterogeneous photocatalysis using TiO<sub>2</sub>-based materials, the role of the amine is primarily to turn over the photocatalyst by acting as a sacrificial electron donor to holes ( $h^+$ ) trapped on the catalyst surface. However, the  $\alpha$ -aminoalkyl radical formed after amine oxidation and rapid deprotonation ( $E_{red} -1.12$  V vs. SCE)<sup>24</sup> could also have contributed to reduction of **1a** ( $E_{red} -1.49$  V) once the latter was activated by the LA samarium.

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In any event,  $Sm_xO_y@TiO_2$  outperformed  $Sm_xO_y@CeO_2$  and unmodified  $TiO_2$  even when titania was used together with  $Sm(OTf)_3$  in an equivalent molar quantity of samarium (Table 1 entries 1, 7 and 8). Based on these encouraging results,  $Sm_xO_y@TiO_2$  was selected for further exploration of its potential as a heterogeneous photoredox-LA catalyst.

We next investigated the scope of the reaction (Table 2). To our satisfaction,  $Sm_xO_y@TiO_2$  was able to catalyze the photoreductive cyclization of a series of mono- and disubstituted chalcone derivatives bearing electron-donating and electron-withdrawing substituents in a similar fashion to  $Ru(bpy)_3^{2+,5b}$  Compared to the homogeneously catalyzed system, our heterogeneous dual catalytic strategy produced significantly higher yields of the photoreductive coupling product for the parent chalcone as well as for substrates bearing either an electron-withdrawing group (EWG) at the 4'-position or an electron-donating group (EDG) at the 4'- or at the 4-position (**1a-c** and **1f**, Table 2 entries 1-3 and 6). In a similar trend to that observed in the homogeneously catalyzed reaction,  $Sm_xO_y@TiO_2$  is less tolerant of EWGs at the 4-position but unlike the system described by Xia and coworkers, here the yield remains low even when EWGs are simultaneously present at both the 4'- and the 4-positions (**1d-e**, Table 2 entries 4 and 5).

Entry	Substrate	Product	Time (h)	$\operatorname{Yield}^{b}(\%)$	dr
		$R^2$ $O$ $R^1$ $R^1$ $R^2$ $OH$ $R^1$			
1	$1a, R^1 = Ph, R^2 = Ph$	2a	3	70 (62)	>10:1
2	$\mathbf{1b}, \mathbf{R}^1 = 4\text{-MeO-Ph}, \mathbf{R}^2 = \mathbf{Ph}$	2b	5	67 (47)	>10:1
3	<b>1c</b> , $R^1 = 4$ -Cl-Ph, $R^2 = Ph$	2c	3	90 (84)	>10:1
4	<b>1d</b> , $R^1 = 4$ -Cl-Ph, $R^2 = 4$ -F-Ph	2d	3	27 (78)	>10:1
5	<b>1e</b> , $R^1 = Ph$ , $R^2 = 4$ -F-Ph	2e	3	32 (59)	>10:1
6	<b>1f</b> , $R^1 = Ph$ , $R^2 = 4$ -MeO-Ph	2f	3	65 (54)	>10:1
$7^c$	$\mathbf{1a}, \mathbf{R}^1 = \mathbf{Ph}, \mathbf{R}^2 = \mathbf{Ph}$	2a	3	41 (62)	>10:1

**Table 2.** Substrate scope for the heterogeneous photoreductive cyclization of chalcones **1a-f** catalyzed by  $\text{Sm}_x O_v @ \text{Ti}O_2.^a$ 

<sup>*a*</sup>Reaction conditions: *trans*-chalcone (1 mmol),  $Sm_xO_y@TiO_2$  (60 mg), *i*-Pr<sub>2</sub>NEt (5 mmol), 15 mL dry MeCN, degassed with argon 20 min, irradiated with a 400 nm LED (90 W). <sup>*b*</sup>Determined by <sup>1</sup>H NMR spectroscopy using an internal standard. Yields in parenthesis refer to the analogous homogeneous system from ref. 5b. <sup>*c*</sup>Control reaction using unmodified TiO<sub>2</sub> as the catalyst.

In addition to the convenience of easy separation of our heterogeneous catalyst from the reaction mixture by simple centrifugation, avoidance of product contamination by the catalyst and the absence of any additional additives to remove, another major advantage of heterogeneous catalysis is the potential for catalyst reusability. We were pleased to observe that  $Sm_xO_y@TiO_2$  can be recovered and used to catalyze the photoreductive cyclization of **1a** for at least five cycles at the same laboratory bench scale (1 mmol starting material) without showing any evidence of diminished catalytic activity. In cycles two through five the reaction still reached completion after three hours of irradiation, suggesting that reusing the catalyst had no obvious impact upon the reaction kinetics (Figure 2). This high level of reusability goes a long way to demonstrating the advantages offered by heterogeneous catalysis. Aside from the obvious environmental benefit of reducing dependence on precious metals, from a purely economic perspective the increased cost-effectiveness of replacing a system comprising commercially available  $Ru(bpy)_3^{2+}$  and  $Sm(OTf)_3$  (as in ref. 5b) with  $Sm_xO_x@TiO_2$  on an equivalent scale is over 90-fold for just the

first use of the readily recoverable catalyst, including the cost of the samarium precursor lost during the preparation of the nanocatalyst (Table S3 and associated discussion).



Figure 2. Reusability study of  $Sm_xO_y@TiO_2$  in the heterogeneous photoreductive coupling of chalcone 1a to form the cyclopentanol derivative 2a. Reaction conditions were identical to those summarized in Table 1 and Table 2, including reaction time and scale, and the recovered catalyst was used without any additional pre-treatment.

Turnover number (TON), the number of moles of substrate converted to product per mole of active sites prior to catalyst deactivation, and similarly turnover frequency (TOF), are important metrics routinely used to characterize and compare the efficacies of different catalysts. However, obtaining reliable values for TON and TOF can be difficult for many nanostructured heterogeneous catalysts, including  $Sm_xO_y@TiO_2$ , due to the presence of an unknown number of active sites. NPs might possess multiple active sites and their catalytic activities could differ greatly as a result of non-uniform size or spatial distributions on the support. In addition, many of the atoms making up each NP do not represent potential active sites because they are not located on the NP surface. In the case of  $Sm_xO_y@TiO_2$  the problem is compounded further because the precise stoichiometry of the samarium oxide nanoparticle surface is uncertain. Therefore, commenting on turnover as a function of moles of samarium atoms or numbers of

NPs does not allow for an easy and direct comparison to the known TONs or TOFs of other catalysts. For nanocomposites catalysts such as  $Sm_xO_y@TiO_2$ , where the support possesses some degree of catalytic activity on its own, the presence of additional or cooperative active sites on the support must also be considered. Even the accurate molecular weight of the nanocomposite catalyst is an elusive quantity, and so incorporating moles of catalyst into TON and TOF calculations is not an option. Estimates of TON and TOF should therefore be made and interpreted with caution so as to avoid unreasonable comparisons with other heterogeneous or homogeneous catalysts. Based upon these considerations, estimating TON and TOF of heterogeneous catalysts as functions of substrate and catalyst mass may become a useful convention.<sup>25</sup> By this method, TON was 187 with respect to mass of samarium and 9 with respect to total mass of the nanocomposite. However, both values should be regarded as low estimates because they are based upon just the first five cycles of use rather than until complete catalyst deactivation. Similarly, TOF was 12 h<sup>-1</sup> and 0.6 h<sup>-1</sup> as a function of mass of samarium or total catalyst mass, respectively (calculations available in the Supporting Information).

We expanded our investigation into the photocatalytic activity of  $Sm_xO_y@TiO_2$  to include the intramolecular [2+2] photocycloaddition of bis(enones) **4a-c** and found that  $Sm_xO_y@TiO_2$  is indeed a versatile heterogeneous catalyst. The [2+2] cycloaddition of unsaturated enones is often employed as a key step in natural product synthesis and is an important tool in the construction of synthetic building blocks.<sup>10a,10b,11</sup> Elegant strategies for the homogeneous photocatalytic version of this reaction using Ru(bpy)<sub>3</sub><sup>2+</sup> have been studied extensively by Yoon,<sup>6c-e</sup> and non-photochemical routes have been investigated by Krische<sup>10d,26</sup> and Bauld.<sup>27</sup> We have also reported in the past that the reaction can be photocatalyzed heterogeneously, by platinized titania (Pt@TiO<sub>2</sub>).<sup>18b</sup>

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Utilizing the Lewis acidity of  $Sm_xO_y@TiO_2$  allowed us to make substantial improvements to the efficiency of the heterogeneously catalyzed reaction (Table 3). We obtained higher yields of the [2+2] cycloadducts **5a** and **5b** in a much shorter reaction time (71% **5a** and 72% **5b** in 1 h here vs. 51% **5a** and 42% **5b** in 15 h using Pt@TiO\_2 in ref. 18b), under conditions that are now on par with the homogeneous catalytic system reported by Yoon (Scheme 1). Compared to Pt@TiO\_2, we were also able to increase the selectivity for the desirable [2+2] cycloadduct to 78% for **5a** and 81% for **5b**, and greatly improve the catalyst reusability up to at least three cycles without significant loss of activity (Figure S20). Using the previously described method, TON (based on 3 cycles) and TOF were 117 and 39 h<sup>-1</sup> by mass of samarium and were 6 and 2 h<sup>-1</sup> by total nanocomposite mass, respectively.

Table 3. Heterogeneous intramolecula	r [2+2] cycloaddition	of bis(enones) 4a-c. <sup>a</sup>
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R	4	Sm <sub>x</sub> O <sub>y</sub> @TiO <sub>2</sub> DABCO (5 equiv) MeCN, Ar, 1 h 400 nm LED		R + 0 R + 7 K	R + $R$	-0 0 H R 7
Entry	Substrate	Catalyst & Conversion <sup>b</sup> (%)	Product	Selectivity (%)	$\operatorname{Yield}^{b}(\%)$	dr
1a	<b>4a</b>	Sm O @TiO	5a	78	71	1.2:1
1b	$X = CH_2$	$\operatorname{Sin}_{\mathbf{x}}\operatorname{O}_{\mathbf{y}}(\underline{w}) \operatorname{IO}_{2}$	6a	10	9	>10:1
1c	R = Ph	71	7a	12	11	>10:1
2a	<b>4a</b>	TiO	5a	57	47	1.3:1
2b	$X = CH_2$	83	6a	22	18	>10:1
2c	R = Ph	05	7a	17	14	>10:1
3a	4b	Sm O @TiO	5b	81	72	1.8:1
3b	$X = CH_2$	$\operatorname{Sin}_{\mathbf{x}}\operatorname{O}_{\mathbf{y}}(\underline{w}) \operatorname{IO}_{2}$	6b	4	4	>10:1
3c	R = 4-Cl-Ph	09	7b	15	13	>10:1
4a <sup>c</sup>	4c	Sm O @TiO	5c	0	$0^d$	-
$4b^c$	$\mathbf{X}=\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{2}$	$\operatorname{Sin}_{x}\operatorname{O}_{y}(\underline{w}) \operatorname{IO}_{2}$	6c	18	13 <sup>e</sup>	1.2:1
$4c^{c}$	R = Ph	/3	7c	74	54	1.4:1

<sup>*a*</sup>Reaction conditions: substrate (0.17 mmol), catalyst (20 mg), DABCO (5 equiv), 5 mL dry MeCN, degassed with argon 20 min, irradiated with a 400 nm LED (90 W). Longer irradiation times did not result in significantly higher conversion to the [2+2] cycloadduct using either  $Sm_xO_y@TiO_2$  or  $TiO_2$  alone. <sup>*b*</sup>Determined by <sup>1</sup>H NMR spectroscopy using an internal standard unless otherwise noted. <sup>*c*</sup>Irradiation time not optimized for conversion. <sup>*d*</sup>Isolated yields. <sup>*e*</sup>Yield determined by <sup>1</sup>H NMR spectroscopy performed on an impure fraction of the crude product mixture obtained after flash chromatography. DABCO = 1,4-diazabicyclo[2.2.2]octane.

Similar to the photoreductive cyclization of chalcones,  $Sm_xO_y@TiO_2$  significantly outperformed unmodified TiO<sub>2</sub> in terms of yield but also in selectivity for **5a** (Table 3 entries 1a and 2a). Higher yield and selectivity for the [2+2] cycloadduct over the reductive coupling and [4+2] hetero-Diels-Alder products (**6a** and **7a**, respectively) relative to both TiO<sub>2</sub> and Pt@TiO<sub>2</sub> is most likely due to coordination to samarium, mirroring results observed by Yoon upon addition of a LA.<sup>6c,6e</sup> Diastereoselectivity was again unaffected by modification of the TiO<sub>2</sub> support with samarium, and remained high for **6a-b** and **7a-b**, matching results reported using Pt@TiO<sub>2</sub> or the homogeneous catalyst Ru(bpy)<sub>3</sub><sup>2+</sup> in the presence of a LA additive. However, here the diastereometric ratio was much lower for the [2+2] cycloadducts (Table 3). Conversion of a symmetric bis(enone) with identical aryl substituents possessing an EDG at the 4-position (R = 4-MeO-Ph) was less effective and not quantified.

Interestingly, Yoon reported that bis(enone) **4c**, bearing an additional methylene unit in the carbon tether, exclusively underwent the [4+2] hetero-Diels-Alder cycloaddition to form **7c**.<sup>6g</sup> While we also did not detect any trace of the [2+2] cycloadduct **5c** in our analogous heterogeneously catalyzed system, we did isolate the reductive coupling product **6c** with 18% selectivity (Table 3 entries 4a-c). Yoon suggested that **6c** could be the result of over-reduction and reductive cleavage of **7c** at longer irradiation times (>24 h). Although the quantities of reagents were only given in equivalents in that report, our system was irradiated for much less time (1 h), albeit with a different light source (90 W 400 nm LED at 2 mm vs. 200 W tungsten filament bulb at 30 cm in ref. 6g). In the homogeneously catalyzed system the addition of 10 equivalents of H<sub>2</sub>O resulted in a dramatic increase in the yield and selectivity for **7c**, and the time required to reach complete conversion decreased from 9.5 to 1 h.<sup>6g</sup> We instead observed an opposing trend, with 10 equivalents of H<sub>2</sub>O resulting in a decrease in conversion from 73% to

 less than 60% in 1 h. These differences in reactivity do much to highlight the inherent divide between homogeneous and heterogeneous catalytic systems, but could be viewed as an advantage or disadvantage depending upon the specific application.



**Figure 3.** Proposed mechanism for the heterogeneous net neutral photoredox-LA dual catalytic intramolecular [2+2] photocycloaddition of symmetric aryl bis(enones).

A mechanism for the heterogeneous catalytic intramolecular [2+2] photocycloaddition of symmetric bis(enones) is proposed in Figure 3. Similar to the photoreductive cyclization of chalcones, the proposed heterogeneous catalytic mechanism for the major product closely follows that of the homogeneous catalytic system.<sup>1a,2b</sup> SET from the photoexcited nanocomposite catalyst to the LA-activated substrate forms the key radical anion intermediate stabilized by the LA  $Sm_xO_y$  NP. Subsequent intramolecular Michael addition leads to closing of the five-membered ring followed by cyclobutanation to afford the samarium-coordinated ketyl radical, which then gives up an electron to yield the cycloadduct **5** (one diastereomer shown for clarity).

Unlike the photoreductive cyclization of chalcones then, the intramolecular [2+2] photocycloaddition of bis(enones) is a net neutral redox process and the possibility of a chain component in the overall mechanism should not be ignored. In principle, oxidation of the ketyl radical in the final step of the mechanism could proceed via SET to quench  $h^+$  in the photocatalyst, or by reduction of another molecule of substrate to propagate a chain reaction. Since heterogeneous catalytic reaction mechanisms are often difficult to study and to know with certainty, Figure 3 focuses instead on what is likely to be the dominant pathway to the major [2+2] photocycloaddition product. Further work to elucidate the precise nature of the mechanism, extend the scope of the reaction and improve diastereoselectivity is currently underway in our laboratory and may be the subject of a future report.

# Conclusion

In summary, we have described the efficacy and versatility of the first member of a new class of bifunctional nanomaterials,  $Sm_xO_y@TiO_2$ , in the first two examples of heterogeneous dual photoredox-Lewis acid catalysis. The nanocomposite material utilizes visible light to perform both net reductive and net neutral photoredox processes requiring LAs. It efficiently catalyzes the intermolecular photoreductive cyclization of a series of chalcones as well as the intramolecular [2+2] photocycloaddition of bis(enones), two classes of substrates and cyclization reactions with proven track records of high synthetic utility. Further,  $Sm_xO_y@TiO_2$  is easily recovered, reusable for several cycles, functions as a purely heterogeneous catalyst without leaching, and may yet possess even more general applicability for heterogeneous dual photoredox-LA catalysis. This work demonstrates the potential for realizing systems that combine all the benefits of homogeneous and heterogeneous catalysis, and should set in motion a

wide range of new collaborative efforts across synthetic organic, industrial and catalysis research.

# **Associated Content**

Supporting Information

Experimental details, instrumentation, characterization of materials and organic compounds (PDF)

# Acknowledgement

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada,

the Canada Foundation for Innovation, and the Canada Research Chairs program for generous

financial support, including a Doctoral Post Graduate Scholarship for G. K. Hodgson. Thanks are

due to M. Grenier, Y. Liu, S. Curtis and S. Mommers for their relevant technical expertise.

Special thanks to S. Impellizzeri for valuable insights and a special thanks as well to S. Pitre for

productive discussions.

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