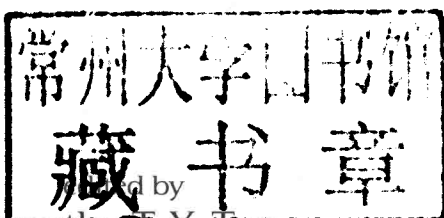


RARE EARTH NANOTECHNOLOGY

edited by
Timothy T. Y. Tan



RARE EARTH NANOTECHNOLOGY



ed by
Timothy F. Y. Tan

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Rare Earth Nanotechnology

Copyright © 2012 by Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4316-30-9 (Hardcover)

ISBN 978-981-4364-20-1 (eBook)

Printed in the USA

*I humbly dedicate this book to my parents,
Mr Tan Boon Chew and Mdm Lee Ah Sioh,
and sister, Ms Tan Foong Yee,
who have provided the foundation and
compassion on which I have been blessed
to rely and build.*

Preface

Rare earth elements (REE) are gaining ubiquitous importance in modern technology and have been touted as the “vitamin of chemistry.” They help technologies perform better and have their own unique characteristics. Many high-technology industries depend heavily on these unique elements for the manufacture of permanent magnets and batteries, which are vital to efficient military and green technologies such as wind turbines and hybrid batteries, as well as in smartphones and laptops.

REE are, in fact, not rare, and most of them are fairly abundant in the earth’s crust. What is rare about REE is their supply. China controls 95% of the world’s REE production, not exactly due to geological luck but more due to economic and scientific strategies. In 2011, REE attracted unprecedented news when China announced a 70% cut in its rare earth production, sending shockwaves through the world as it feared a supply crunch. Since then, various plans to establish rare earth production outside China have been in the pipeline, with Australian mining company Lynas having been successfully granted approval to build one of the largest rare earth refineries in Malaysia.

This book was conceived prior to these events, when the exploration, research, and development of rare earth materials in nanotechnology were burgeoning at the start of the millennia, especially in the fields of nanomedicine and nanophosphors. This book, therefore, focuses on the potential applications of rare earth materials in these areas and their state of the art in these applications. The aim of each chapter is to review and highlight the strategies and insights of the research work in the relevant areas, in a hope to establish continued and long-term research efforts of these amazing materials in nanotechnology.

This book consists of six chapters put together in a cohesive and sequential manner, but they can be read as standalone chapters. As the properties of rare earth elements can be found in many textbooks and journal articles, they have not been included in this book. The book begins with highlighting key strategies in

the design and synthesis of various types and forms of rare earth nanomaterials (Chapter 1), followed by Chapter 2, which discusses various approaches to synthesizing rare earth nanomaterials of different morphologies and their surface modification to render them suitable for their intended applications. Rare earth materials have intriguing optical and magnetic properties. In Chapter 3, recent works on the application of rare earth nanoparticles in fluorescence microscopy are highlighted, with a strong focus on upconversion rare earth nanoparticles as they are most suited as imaging probes for biological specimen. In the pursuit of better imaging contrast to achieve more accurate diagnosis, there has been much interest, and success, in the use of rare earth nanoparticles as “proof-of-principle” magnetic resonance imaging contrast agents. Their state of the art is discussed in Chapter 4. Chapter 5 demonstrates the foresight of researchers for bimodal contrast agents in bioimaging technology, of which the optical and magnetic properties of rare earth nanomaterials are simultaneously exploited to achieve more accurate and sensitive imaging in fluorescence and magnetic resonance imaging. The last chapter presents the advances and promises of rare earth nanomaterials as cheaper and more efficient lighting materials in light-emitting diodes, resonating the global need for green lighting technologies.

Rare earth elements will continue to exert their significant impact in modern technologies in the coming decade. Supply–demand will shift toward equilibrium with the discovery of more mines and the construction of new refineries.

Hopefully, this book will provide the readers, be it researchers, engineers, or policymakers, with bountiful ideas and inspirations to effect a new level of nanotechnological revolution using REE, especially in the much-needed energy and healthcare sectors.

Timothy T.Y. Tan

Contents

<i>Preface</i>	xi
1. Synthesis of Rare Earth Nanomaterials	1
<i>Chun-Hua Yan, Chao Zhang, and Ling-Dong Sun</i>	
1.1 Introduction	1
1.2 Precipitation/Co-Precipitation Route	2
1.3 Sol-Gel Route	7
1.4 Hydrothermal/Solvothermal Route	10
1.5 Thermal Decomposition Route	19
1.6 Microwave Route	27
1.7 Microemulsion Route	28
1.8 Other Routes	29
1.9 Summary	32
2. Structural Control and Surface Modifications of Rare Earth Nanomaterials	43
<i>Gautam Kumar Das and Timothy T.Y. Tan</i>	
2.1 Introduction	43
2.2 Nucleation, Seed, and Crystals	45
2.3 Dimensionally Controlled Rare Earth Nanomaterials	47
2.3.1 Zero-Dimensional (0D) Rare Earth Nanostructures	49
2.3.2 One-Dimensional (1D) Rare Earth Nanostructures	52
2.3.3 Two-Dimensional (2D) Rare Earth Nanostructures	58
2.3.4 Core-Shell Rare Earth Nanostructures	61
2.3.5 Hollow Rare Earth Nanostructures	64
2.3.6 Complex Rare Earth Nanostructures	67
2.3.7 Phase Control of Rare Earth Nanostructures	70
2.4 Modification of the Surface of Rare Earth Nanostructures	72

2.5 Conclusion	75
3. Rare Earth Nanomaterials in Fluorescence Microscopy	83
<i>Muthu Kumara Gnanasammandhan and Yong Zhang</i>	
3.1 Introduction and Overview	83
3.2 Rare Earth Nanoparticles	84
3.2.1 Lanthanide Chelates	86
3.2.2 Lanthanide-Doped Nanoparticles	87
3.2.2.1 Downconversion nanoparticles	88
3.2.2.2 Upconversion nanoparticles	89
3.3 Nanoparticle Synthesis	91
3.4 Surface Functionalization	93
3.5 Applications	94
3.5.1 <i>In vitro</i> Microscopy	95
3.5.2 <i>In vivo</i> Microscopy	98
3.5.3 Multimodal Imaging	100
3.5.4 Multifunctional Nanoparticles	101
3.6 Summary and Outlook	101
4. Rare Earth Nanomaterials in Magnetic Resonance Imaging	107
<i>S. Roux, R. Bazzi, C. Rivière, F. Lux, P. Perriat, and O. Tillement</i>	
4.1 Introduction	107
4.2 Multifunctional Nanostructures Functionalized by Gadolinium Chelates for Multi-Modal Imaging	112
4.2.1 Introduction	112
4.2.2 Fluorescent Silica Nanoparticles and Other Oxide Nanoparticles	114
4.2.3 Mesoporous Nanoparticles	123
4.2.4 Paramagnetic Quantum Dots	126
4.2.5 Paramagnetic Gold Nanoparticles	132
4.3 Gadolinium (III) Containing Crystalline Nanoparticles	136
4.3.1 Introduction	136
4.3.2 Synthesis and Functionalization of Gadolinium Oxide Nanoparticles	137
4.3.3 Synthesis of Gadolinium-Containing Crystalline Nanoparticles	144

4.3.3.1 Fluoride nanoparticles containing gadolinium (III)	144
4.3.3.2 Carbonate particles containing gadolinium (III)	147
4.3.3.3 Gadolinium metal-organic frameworks (Gd-MOFs)	148
4.4 Conclusion and Future Outlook	151
5. Rare Earth Nanomaterials in Integrated Modalities Imaging	161
<i>Y. Zhang and Timothy T.Y. Tan</i>	
5.1 Introduction and Overview	161
5.1.1 Positron Emission Tomography and Single Photon Emission Computed Tomography	164
5.1.2 Magnetic Resonance Imaging	165
5.1.3 Optical Imaging	166
5.1.4 X-Ray Computed Tomography	166
5.1.5 Ultrasonography	167
5.2 Rare Earth Based Multimodal Molecular Imaging Contrast Agents	168
5.2.1 MRI/Optical Imaging Probes and Their Bioapplications	168
5.2.1.1 Gd ³⁺ -based multifunctional nanomaterials	168
5.2.1.2 SPIO-based multimodal imaging agents	188
5.2.1.3 Dy-based multifunctional nanomaterials	192
5.2.2 Other Multimodality Contrast Agents and Their Bioapplications	193
5.3 Conclusions	195
6. Rare Earth Nanophosphors in Light-Emitting Diodes	203
<i>Chin Yun Tee, Gautom Kumar Das, Yan Zhang, and Timothy T.Y. Tan</i>	
6.1 Introduction and Overview	203
6.2 How Does LED Work?	205
6.2.1 Production of White Light from LED	207
6.3 Synthesis of Rare Earth Doped Phosphors	208

6.3.1	Solid-State Synthesis of Bulk YAG:Ce Phosphors	209
6.3.2	Co-Precipitation Synthesis of Rare Earth Phosphors	210
6.3.3	Sol-Gel Synthesis of LED Rare Earth Phosphors	210
6.3.4	Hydrothermal/Solvothermal Synthesis of LED Rare Earth Phosphors	211
6.4	Factors Affecting the Luminescence Properties of Rare Earth Phosphors	212
6.4.1	Yellow-Emitting Phosphors	218
6.4.1.1	Cerium-doped yttrium aluminum garnet phosphors (YAG:Ce)	218
6.4.1.2	Silicate-based phosphor	222
6.4.2	Red-Emitting Phosphors	223
6.4.2.1	Nitride-based phosphors	223
6.4.2.2	Niobate and tantalate	226
6.4.3	Green-Emitting Phosphors	228
6.4.3.1	Silicates	228
6.4.3.2	ZnO	231
6.4.4	Blue-Emitting Phosphors	233
6.4.4.1	Phosphate-based phosphors	233
6.5	Conclusions	235
	<i>Index</i>	245

Chapter 1

Synthesis of Rare Earth Nanomaterials

Chun-Hua Yan, Chao Zhang, and Ling-Dong Sun

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Laboratory in Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing, 100871, China
yan@pku.edu.cn

1.1 Introduction

This chapter discusses the synthesis of rare earth nanomaterials, mainly covering rare earth oxides, sulfides, halides, and oxysalts. Basically, the synthetic routes of rare earth nanomaterials can be sorted into two main categories: the “dry” methods and the “wet” methods. The former refers to the synthetic routes like solid-state reaction, self-propagating synthesis, and several physical routes (e.g., CVD, PLD, and magnetic sputtering). In contrast, the wet methods generally involve solution-based processes, during which various parameters can be finely adjusted (including reaction time, temperature, concentration, pH value, as well as the utilization of coordination reagents, templates, mineralizers, etc.), and thus exhibit particular superiorities in controlling phase purity, chemical homogeneity, size, and morphology of the final products. In addition,

Rare Earth Nanotechnology

Edited by Timothy T.Y. Tan

Copyright © 2012 Pan Stanford Publishing Pte. Ltd.

ISBN 978-981-4316-30-9 (Hardcover), 978-981-4364-20-1 (eBook)

www.panstanford.com

compared to “dry” methods, which commonly resort to rigorous conditions such as high temperature, high pressure, or high vacuum, the “wet” syntheses are usually carried out under relatively mild conditions, which also help to lower energy consumption and total cost. Therefore, the discussion in the following sections will be mainly focused on wet methods, including precipitation, sol-gel, hydrothermal/solvothermal, thermal decomposition, microwave, microemulsion routes, and so on.

1.2 Precipitation/Co-Precipitation Route

The precipitation/co-precipitation route usually affords products with pure phase, and the experimental procedures are relatively simple. The metal ions are first precipitated from solutions as hydroxides, carbonates, and oxalates, which undergo the subsequent calcination treatment to form the products. Binary compounds, such as CeO_2 and RE_2F_3 , can be readily obtained by this method; yet for those complex systems (doped systems and ternary systems, for example), the precipitation procedure requires particular care because the precipitation rates can vary for different metal ions. In such cases, certain coordination reagents may be necessary to adjust the synchronicity in the subtle co-precipitation procedure, so as to obtain homogeneous products with predesigned compositions. Due to the relatively simple operations involved in this route, mass production is easily achieved.

The rare earth compound ceria (CeO_2) is currently under most extensive and intensive investigation. It adopts a cubic fluorite phase in a wide temperature range (from ambient temperature up to its melting point), and the fluorite structure can be preserved to a considerable extent under reductive atmospheres. The reduction from Ce^{4+} ions to Ce^{3+} ions can generate oxygen vacancies, which act as highly reactive sites for plenty of catalysis redox reactions. When the size of ceria is reduced down to the nanometer dimensions, the catalytic activity is much elevated due to the enlarged surface area, enhanced oxygen storage capacity, which caters to the demands of three-way catalysts, fuel cells, and so on. Due to the cubic phase, nanoceria tends to expose low-index crystal surfaces, i.e., {100}, {110}, and {111}, and usually takes the shape of nanocubes, nanooctahedra, nanowires, and nanotubes.

Ceria nanocrystals can be readily prepared by the precipitation method, using either Ce(IV) or Ce(III) soluble salts as Ce source. Nanoceria can be directly obtained in aqueous solution, and in some cases, intermediates like hydroxides or carbonates are obtained first, which form nanoceria through post-heating treatment in air.

Zhang *et al.* reported the synthesis of ceria using $\text{Ce}(\text{NO}_3)_3$ as Ce source and hexamethylenetetramine as the base [1]. Particles in the size range of 3–12 nm were prepared at room temperature, and larger particles were made by calcination at 400–800°C. Han *et al.* obtained ceria nanotubes via two successive stages: precipitation and aging (Fig. 1.1) [2]. Ammonia was used to form precipitates from aqueous solution of $\text{Ce}(\text{NO}_3)_3$ at 100°C, and the precipitates were aged for a long time of 45 days. The formation of the tubular structure was found to be strongly dependent on the precipitation temperature and aging time.

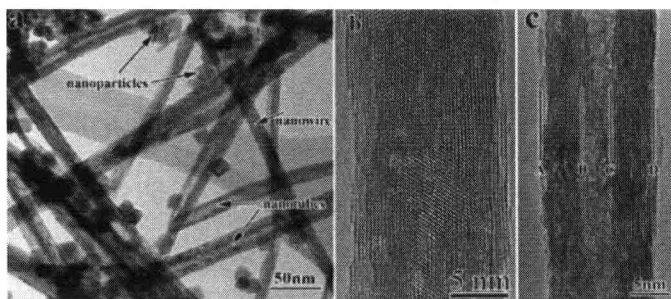


Figure 1.1 (a) Typical morphology of the ceria samples. There are three kinds of nanostructures: nanoparticles, nanowires, and nanotubes as marked in the figure. (b) High-resolution image of a nanowire. (c) High-resolution image of a nanotube.

Du *et al.* prepared ceria nanorods along the [211] or [110] direction by refluxing at 100°C, and pearl-chain-like nanostructures at lower temperatures (70–90°C) (Fig. 1.2) [3]. An oriented attachment mechanism was proposed, claiming that the nanorods and pearl chains are formed by self-organization of truncated octahedral ceria nanocrystals.

Ceria–zirconia solid solution, as a well-known ceria-based material with large oxygen storage capacity, is also extensively studied. Hydroxide co-precipitation synthesis of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ was reported by Deshpande *et al.* [4]. Cerium ammonium nitrate and

zirconyl chloride were used as Ce and Zr source, respectively, and nitric acid as the peptizing agent. They also employed the nanocasting technique to prepare a range of mesoporous $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ beads, using polymeric porous beads as the hard template [5].

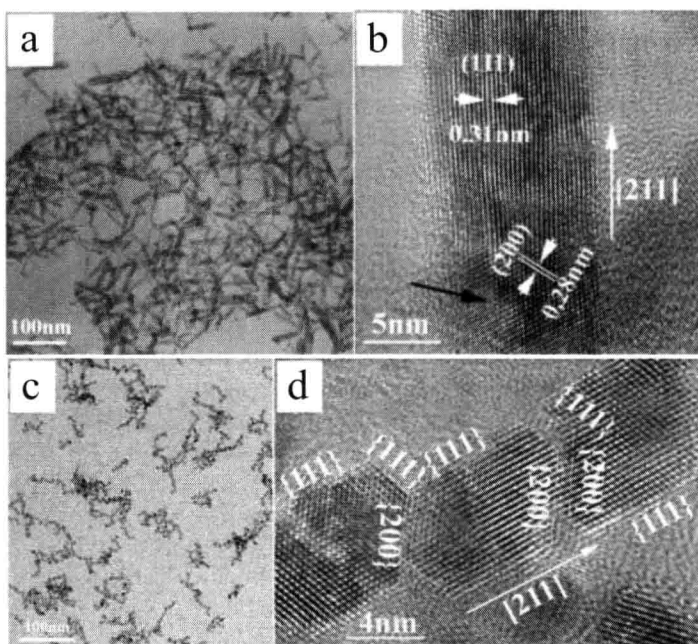


Figure 1.2 (a, b) TEM and HRTEM images of the ceria nanorods; (c, d) TEM and HRTEM images of the ceria pearl-chain-like nanostructures.

Rare earth sesquioxides (RE_2O_3) are a class of materials of great importance in catalysis and luminescence fields. Wakefield *et al.* developed a colloidal precipitation route to prepare Eu_2O_3 and $\text{Y}_2\text{O}_3:\text{Eu}$ nanoparticles [6, 7]. The luminescent properties of these materials were also examined. Oxide nanotubes of Er, Tm, Yb, Lu were synthesized by Yada *et al.* by the method of homogeneous precipitation with dodecylsulfate assemblies as templates [8]. These nanotubes can be further tailored to compose hierarchical 2D and 3D microstructures [9].

Rare earth fluorides generally exhibit good thermal stabilities and high ionic nature, and find applications primarily in solid-state lasers, lighting, and display. Pure and doped rare earth fluorides

can be readily obtained by the co-precipitation method. van Veggel *et al.* reported the preparation of $\text{LaF}_3\text{:R}^{3+}$ ($\text{R} = \text{Eu}, \text{Er}, \text{Nd}, \text{and Ho}$) nanoparticles from rare earth nitrates and NaF in ethanol/water mixed solvent. A capping ligand, namely, ammonium di-*n*-octadecyldithiophosphate, was used to prevent the particles from agglomeration, and the as-obtained nanoparticles can be easily redispersed in organic solvents [10]. Chow *et al.* also employed the co-precipitation method to prepare multicolor upconversion luminescent LaF_3 nanocrystals doped with Yb^{3+} as sensitizer ions and Er^{3+} , Ho^{3+} , Tm^{3+} as the activator ions [11]. Chen *et al.* synthesized EuF_3 nanocrystals with different morphologies, including nanoplates, nanospheres, nanobundles, nanorods, and nanowires (Fig. 1.3) [12, 13]. Many different fluoride sources (HF , NaF , KF , NH_4F , RbF , CsF , and NaBF_4) were used to precipitate the rare earth ions. Similar routes were employed by many research groups, affording different REF_3 nanoparticles with varied morphologies [14–18].

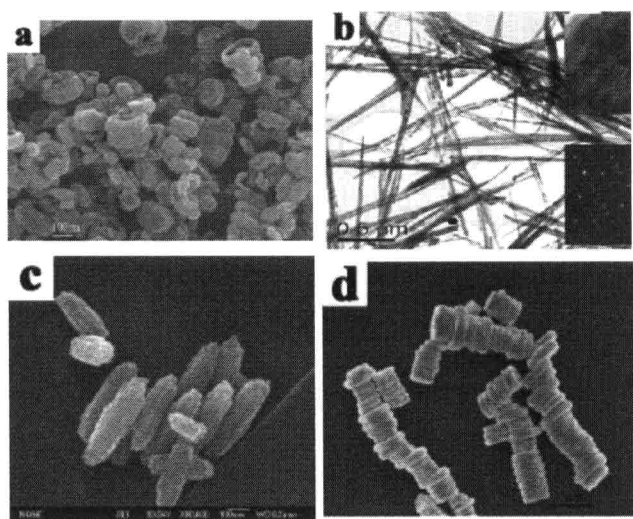


Figure 1.3 SEM images of (a) hexagonal, (b) orthorhombic EuF_3 nanocrystals, (c) EuF_3 nanospindles and (d) EuF_3 nanodisks.

In addition to fluorides, alkali-rare-earth complex fluorides (denoted as AREF_4) are also an important class of rare earth materials, which have attracted extensive attention for their applications in laser, display, and bioimaging. AREF_4 nanoparticles can be readily obtained by the co-precipitation method. Chen *et al.*

prepared hexagonal NaEuF_4 and cubic $\text{Na}_5\text{Eu}_9\text{F}_{32}$ nanocrystals by simply reacting $\text{Eu}(\text{NO}_3)_3$ and NaF in water [19]. They found that the bundle-like EuF_3 nanostructures were yielded first, which then reacted with NaF to give NaEuF_4 with one-dimensional morphology. Chen *et al.* prepared nearly monodisperse $\text{NaYF}_4\text{:Yb,Er}$ nanoparticles by co-precipitation of Y^{3+} , Yb^{3+} , Er^{3+} with NaF . EDTA was introduced as the chelating reagent, and by varying the EDTA/ RE^{3+} ratio, particle size could be effectively controlled [20]. Karbowskiak *et al.* synthesized cubic KGdF_4 and $\text{KGdF}_4\text{:Eu}^{3+}$ nanocrystals using soluble rare earth chlorides and NH_4HF_2 as starting materials based on co-precipitation process [21, 22].

Among various rare earth oxysalts, rare earth orthophosphates and orthovanadates are of particular importance. These compounds generally exhibit low water solubility, high thermal stability, and high luminescent efficiency. In particular, the vanadate matrix shows a strong charge-transfer absorption band located at 200–350 nm, which facilitates the energy migration from the host matrix to rare earth ions. This can significantly enhance the absorption and excitation efficiency of the doped luminescent rare earth ions. The above advantageous characteristics of these materials guarantee their applications as phosphors and sensors in display, lighting, and bioprobing. A typical precipitation route for rare earth phosphates and vanadates usually begins with soluble salts containing corresponding cations and anions, for example, rare earth nitrates and chlorides, and phosphate, phosphoric acid, and vanadates. The pH value of the system always plays a crucial role during the whole synthetic process, especially for vanadates because vanadium(V) exists in different forms, such as VO_4^{3-} monomers or oligomers like $\text{V}_3\text{O}_9^{3-}$ and $\text{V}_{10}\text{O}_{28}^{6-}$ anions, at varied acidities. Gao *et al.* reported pure and doped hexagonal LaPO_4 nanorods with typical dimensions of 8 nm in diameter and 80 nm in length [23]. The nanorods were prepared from NaH_2PO_4 and LaCl_3 aqueous solutions at 100°C heated by an oil bath. For heavy rare earth (Ho–Lu) and Y, the reaction temperature can be even lower. Di *et al.* synthesized $\text{YPO}_4\text{:Eu}$ nanowires at a temperature as low as 70°C [24]. Buissette *et al.* reported the colloidal synthesis of sub-10-nm $\text{LaPO}_4\text{:Ce,Tb}$ and $\text{LaPO}_4\text{:Eu}$ nanoparticles by aging a mixed solution of rare earth nitrates/chlorides and sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$, TPP) at 90°C for 3 h [25]. TPP acted as both the source of orthophosphate anions and the complexing reagent.

Huignard *et al.* exploited the room temperature co-precipitation method using $\text{Y}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$, and $\text{Na}_3\text{VO}_4/\text{NaVO}_3$ as starting materials and obtained $t\text{-YVO}_4\text{:Eu}^{3+}$ nanoparticles with sizes around 15–30 nm [26]. The as-prepared $\text{YVO}_4\text{:Eu}^{3+}$ nanoparticles could be further stabilized into a colloidal solution by introducing sodium hexametaphosphate. The Eu^{3+} quenching concentration was found to be elevated, and luminescence efficiency reduced for nanosized $\text{YVO}_4\text{:Eu}^{3+}$. This was probably due to the nonradiative de-excitation pathways resulting from the surface defects. Huignard *et al.* reported that when competitive chelating ligands like citrate anions were introduced, the growth of REVO_4 nanoparticles can be tuned in a more delicate manner, probably due to the competition between coordination and precipitation of rare earth ions [27]. Isobe *et al.* doped Bi^{3+} along with Eu^{3+} ions into the $t\text{-YVO}_4$ lattice so as to exploit the excitation energy of irradiation light 300–400 nm in wavelength [28]. The co-doped Bi^{3+} could serve as sensitizer for Eu^{3+} through the energy transfer from Bi^{3+} 6s orbital to V^{5+} 3d orbitals. Bismuth(III) citrates were used rather than nitrates for the strong hydrolysis tendency of the latter. van Veggel *et al.* prepared $t\text{-LaVO}_4$ nanoparticles with various rare earth dopants (Eu, Tm, Nd, Er, Ho, Dy, Sm, Pr) in ethanol/water media at 75°C [29]. The co-precipitation reaction was performed in the presence of surfactant $\text{NH}_4(\text{n-C}_{18}\text{H}_{37}\text{O})_2\text{PS}_2$. The dithiophosphate anion ligands were found to help to control the growth of LaVO_4 nanoparticles. As a representative, $t\text{-LaVO}_4\text{:Eu}^{3+}$ nanoparticles were obtained in irregular shapes with a size around 6–10 nm. These nanoparticles can be well dispersed in nonpolar solvents due to the hydrophobic ligands attached to the surface.

Other rare earth oxysalts can also be prepared via the co-precipitation method, for example, perovskite-structured LaAlO_3 [30], pyrochlore-structured $\text{Y}_2\text{Ti}_2\text{O}_7$, $\text{La}_2\text{Sn}_2\text{O}_7$, and $\text{La}_2\text{Zr}_2\text{O}_7$ [31, 32], monoclinic and cubic $\text{La}_2\text{Mo}_2\text{O}_9$, and $\text{La}_2\text{W}_2\text{O}_9$ [33, 34], and perovskite-structured rare earth transition metal (M) complex oxide nanoparticles (M = Mn, Fe, Co, Ni, and Cu) [35–37]. Owing to the limited pages, these works will not be discussed in details.

1.3 Sol-Gel Route

In a typical sol-gel route, precursors are mixed in solution and then hydrolyzed and polymerized to form a (meta)stable sol system, which subsequently undergoes a gelation process. The resultant gel,