Edited by C. N. R. Rao,
A. Müller, A. K. Cheetham

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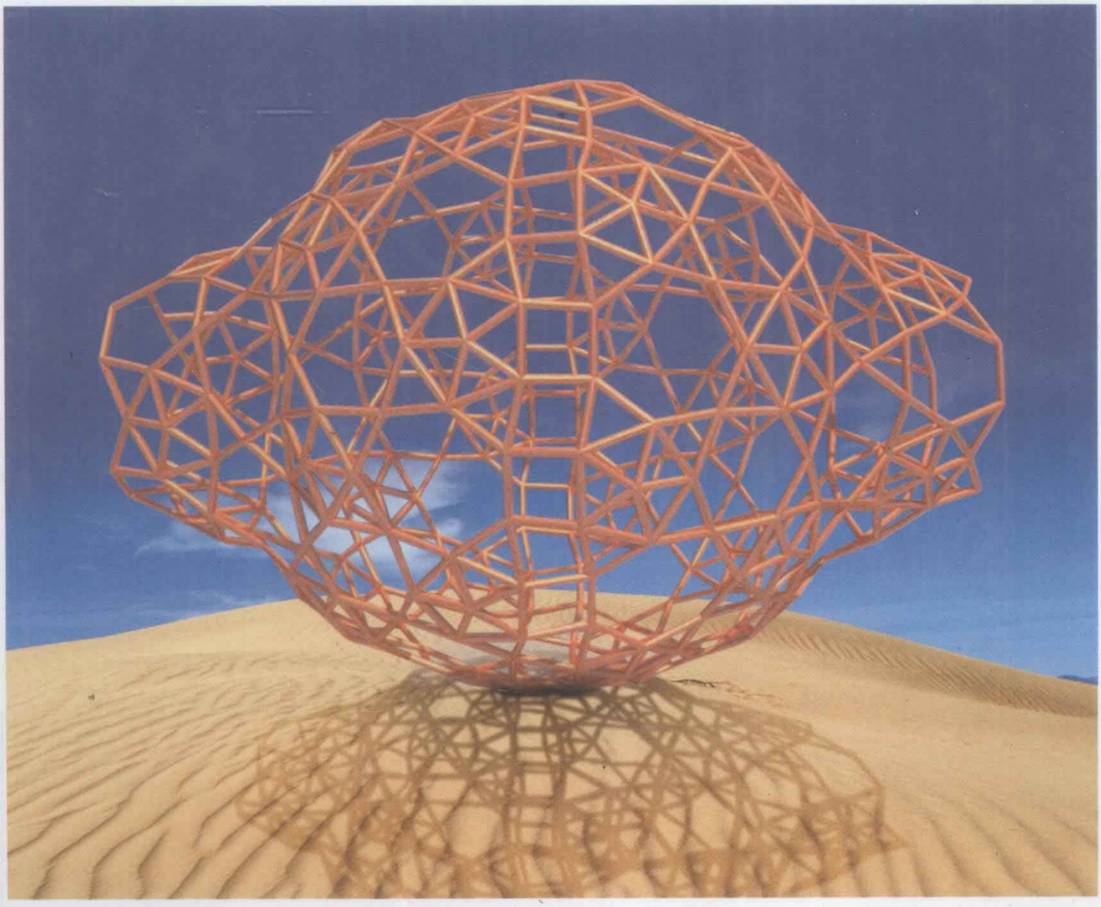
Nanomaterials Chemistry

Recent Developments and New Directions



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Preface

The subject of nanoscience and technology has had an extraordinary season of development and excitement in the last few years. Chemistry constitutes a major part of nanoscience research and without employing chemical techniques it is difficult, nay impossible, to synthesize or assemble most of the nanomaterials. Furthermore, many of the properties and phenomena associated with nanomaterials require chemical understanding, just as many of the applications of nanomaterials relate to chemistry. Because of the wide interest in the subject, we edited a book entitled Chemistry of Nanomaterials, which was published by Wiley-VCH in the year 2004. This book was extremely well received. In view of the increasing interest evinced all over the world in the chemistry of nanomaterials, we considered it appropriate to edit a book covering research on nanomaterials published in the last 2 to 3 years. This book is the result of such an effort. The book covers recent developments in nanocrystals, nanotubes and nanowires. The first two chapters dealing with nanocrystals, nanotubes and nanowires broadly cover all aspects of these three classes of nanomaterials. There are also chapters devoted to topics such as peptide nanomaterials, dendrimers, molecular electronics, molecular motors and supercapacitors. We believe that this book not only gives a status report of the subject, but also indicates future directions. The book should be a useful guide and reference work to all those involved in teaching and research in this area.

C. N. R. Rao
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Contents

Nanomaterials Chemistry. Edited by C.N.R. Rao, A. Müller, and A.K. Cheetham

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1
Recent Developments in the Synthesis, Properties and Assemblies of Nanocrystals

P.J. Thomas and P. O'Brien

1.1
Introduction

Nanocrystals of metals, oxides and semiconductors have been studied intensely in the last several years by different chemical and physical methods. In the past decade the realization that the electronic, optical, magnetic and chemical properties of nanocrystals depend on their size has motivated intense research in this area. This interest has resulted in better understanding of the phenomena of quantum confinement, mature synthetic schemes and fabrication of exploratory nanoelectronic devices. The past couple of years has seen heightened activity in this area, driven by advances such as the ability to synthesize nanocrystals of different shapes. In this chapter, we review the progress in the area in the above period with emphasis on growth of semiconductor nanocrystals. Illustrative examples of the advances are provided. Several reviews have appeared in this period, seeking to summarize past as well as current work [1–4].

1.2
Spherical Nanocrystals

1.2.1
Semiconductor Nanocrystals

There have been several successful schemes for the synthesis of monodisperse semiconductor nanocrystals, especially the sufides and selenides of cadmium. However, there is still plenty of interest in exploring new synthetic routes. Nanocrystals of lead, manganese, cadmium and zinc sulfides have been obtained by thermolysis of the corresponding metal-oleylamine complex in the presence of S dissolved in oleylamine. The metal oleylamine complexes were prepared by reacting the corresponding chlorides with oleylamine. Nanocrystals with elongated shapes such as bullets and hexagons were produced by varying the stoichiometry

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and concentration of the precursors [5]. Manganese sulfide nanocrystals in the form of spheres and other shapes such as wires and cubes have been obtained by thermolysis of the diethyldithiocarbamate in hexadecylamine [6]. Nanocrystals of cadmium, manganese, lead, copper and zinc sulphides have been obtained by thermal decomposition of hexadecylxanthates in hexadecylamine and other solvents. A highlight of this report is the use of relatively low temperatures (50–150 °C) and ambient conditions for synthesis of the nanocrystals [7]. Fluorescent CdSe nanocrystals have been prepared using the air stable single source precursor cadmium imino-bis(diisopropylphosphine selenide) [8]. Cadmium selenide nanocrystals have been prepared in an organic medium prepared without the use of phosphines or phosphine oxides using CdO in oleic acid and Se in octadecene [9]. Water soluble luminescent CdS nanocrystals have been prepared by refluxing a single source precursor $[(2,2'\text{-bipyridine})Cd(SCOPh)_2]$ in aqueous solution [10]. Nanocrystals of EuS exhibiting quantum confinement were synthesized for the very first time by irradiating a solution of the dithiocarbamate $Na[Eu(S_2CNEt_2)_4]3.5H_2O$ in acetonitrile [11]. Following this initial report, a number of single source precursors have been used to synthesize EuS nanocrystals [12].

Peng and coworkers have followed the nucleation and growth of CdSe nanocrystals in real time by monitoring absorption spectra with millisecond resolution [13]. Extremely small CdSe nanocrystals with dimensions of about 1.5 nm, with magic nuclearity have been reproducibly synthesized starting with CdO [14]. Intense emission, due to defects, spread across the visible spectrum has been observed from these nanocrystals (see Fig. 1.1). These nanocrystals can therefore be used to obtain white emission. The nanocrystals are presumed to have the structure of highly stable CdSe clusters observed in mass spectrometric studies [15].

Chalcogenide semiconductor nanocrystals have been synthesized in microfabricated flow reactors [16, 17]. The reactors employ either a continuous stream of

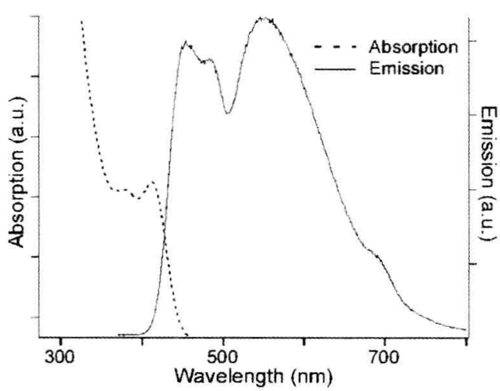

Fig. 1.1 Absorption and emission spectra of magic-sized CdSe nanocrystals (reproduced with permission from Ref. [14]).