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Sonochemical syntheses of a nanoparticles cadmium(II) supramolecule as a precursor for the synthesis of cadmium(II) oxide nanoparticles

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ABSTRACT

Nanoparticles of a three-dimensional supramolecular Cd(II) compound, $[Cd(L)_2(H_2O)_2]$ (**1**), (L^- = 1H-1,2,4-triazole-3-carboxylate), have been synthesized by a sonochemical process and characterized by scanning electron microscopy, X-ray powder diffraction, IR spectroscopy and elemental analyses. The thermal stability of compound **1** in both its bulk and nano-size has been studied by thermal gravimetric (TG) and differential thermal analyses (DTA) and compared with each other. Concentration of initial reagents effects on size and morphology of nano-structured compound **1**, have been studied. Calcination of the single crystals and nano-sized compound **1** at 650 °C under air atmosphere yields CdO nanoparticles.

1. Introduction

Chemical and physical properties of solid materials strongly depend on both the size and the shape of the microscopic particles they are made up from. This is especially true for materials with morphological features smaller than a micron in at least one dimension, which are commonly called nano-scale materials, or simply nano-materials. In these materials the ratio of surface area to volume is vastly increased when compared to compounds with larger grain sizes and quantum mechanical effects such as the "quantum size effect" begin to play a significant role. These effects only play a minor role when going from macro to micro dimensions, but become increasingly important when reaching the nanometer size range [1–5]. Supramolecular architectures, on the other hand, exhibit potential applications as molecular wires [6], electrical conductors [7], molecular magnets [8], in host–guest chemistry [9] and in catalysis [10]. In contrast to inorganic materials, the specific syntheses of nano-structured supramolecular compounds seem to be surprisingly sparse. Equally, the use of organometallic supramolecular compounds as precursors for the preparation of inorganic nanomaterials has not yet been investigated thoroughly. Cd^{2+}, as a d^{10} metal ion, is particularly suited for the construction of supramolecular compounds and networks. The spherical d^{10} configuration is associated with a flexible coordination environment, so that geometries of these complexes can vary from tetrahedral (CN = 4) to dodecahedral (CN = 8) and severe distortions in the ideal polyhedron easily occur. Furthermore, due to the general lability of Cd(II) complexes, the formation of coordination bonds is reversible, which enables metal ions and ligands to rearrange during the process of polymerization to give highly ordered network structures. Consequently, Cd can readily accommodate all kind of architectures and a selection of topological types of 1D, 2D and 3D polymers is given [11–16]. Thus, their preparation is challenging owing to their ability to tailor their physical and chemical properties [17]. On the other hand, cadmium oxide ($E_g \sim 2.3$ eV) is an n-type degenerate semiconductor with high electrical conductivity. Due to its large linear refractive index ($n_0 = 2.49$), it is a promising candidate for optoelectronic applications and other applications including solar cells, photo transistors, photodiodes, transparent electrodes and gas sensors [18,19]. Because of these interesting applications, efforts to prepare nanoparticles of CdO using a variety of methods have been reported in the literature. Among others, solvothermal synthesis [20] and a microemulsion method [21] have been reported for preparing CdO nanoparticles [22–26]. 1H-1,2,4-triazole-3-carboxylic acid (HL) contains 1,2,4-triazole and one carboxylic acid functional group and to date some interesting supramolecular compounds with the ligand have been reported [27–31]. In this paper we describe a simple synthetic sonochemical preparation of nano-structures of a cadmium(II) supramolecular with ligand 1H-1,2,4-triazole-3-carboxylate. Sonochemistry is the research area in which molecules undergo a reaction due to the application of powerful ultrasound radiation (20 kHz–10 MHz) [32]. Ultrasound induces chemical or physical changes during cavitation, a phenomenon involving the formation, growth, and instantaneously implosive collapse of bubbles in a liquid, which can generate local hot spots having temperatures of roughly 5000 °C, pressures of about 500 atm,

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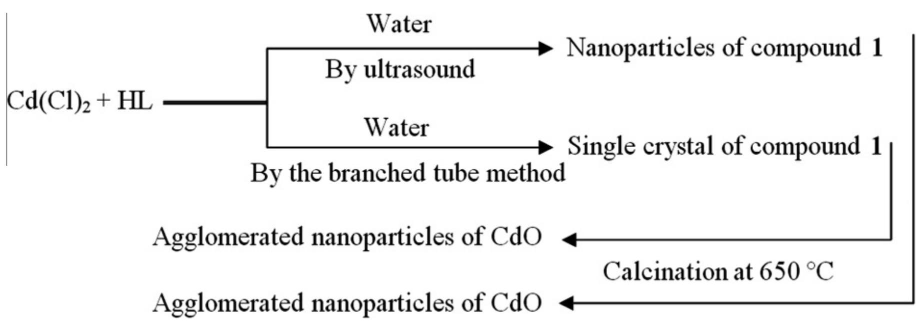
and a lifetime of a few microseconds [33]. These extreme conditions can drive chemical reactions, but they can also promote the formation of nano-sized structures, mostly by the instantaneous formation of a plethora of crystallization nuclei [34]. This has been widely used to fabricate nano-sized structures of a variety of compounds [35], and in recent years many kinds of nano-sized materials have been prepared by this method [36–42]. So far little attention has been given on synthesis of nano-sized supramolecular compounds.

2. Experimental

2.1. Materials and physical techniques

All reagents for the synthesis and analysis were commercially available from Merck Company and used as received. Doubly-distilled water was used to prepare aqueous solutions. Ultrasonic generators were carried out on a SONICA-2200 EP, input: 50–60 Hz/305 W. Melting points were measured on an Electrothermal 9100



Scheme 1. Materials produced and synthetic methods.

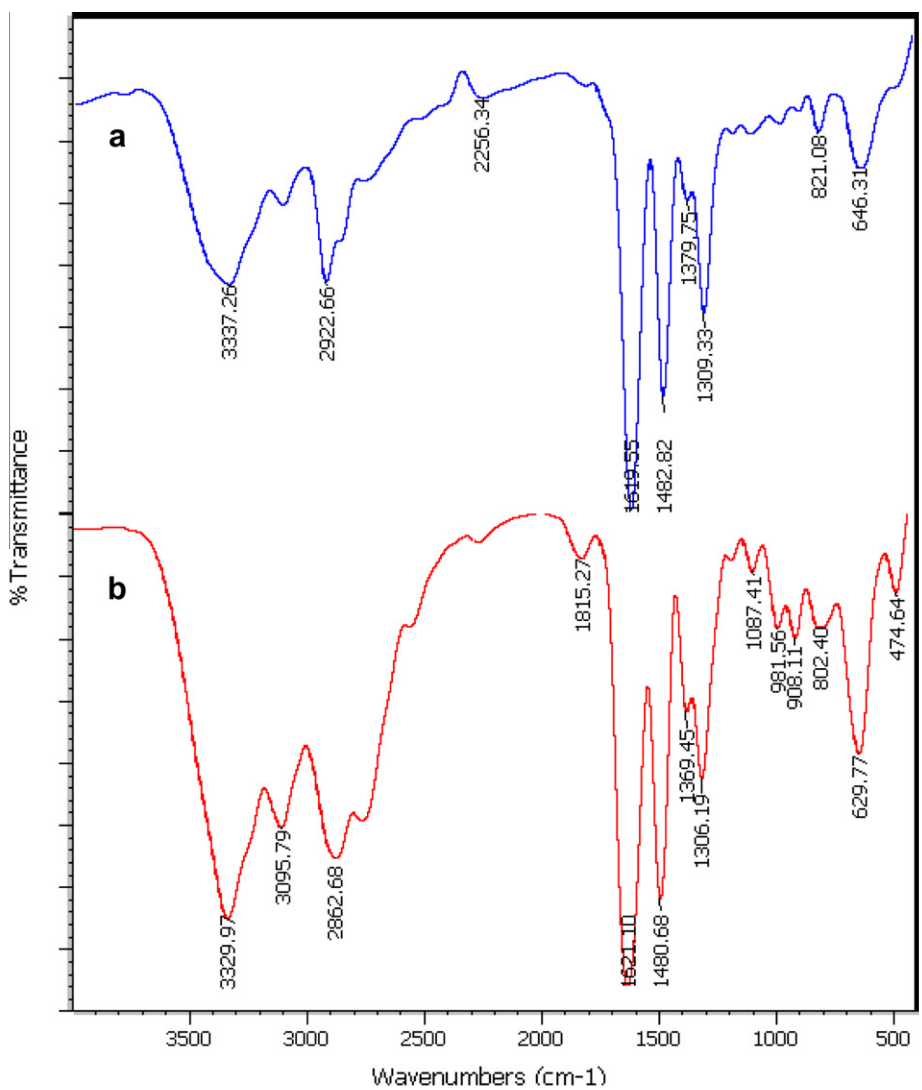


Fig. 1. IR spectra of (a) nano-particles of compound **1** produced by sonochemical method and (b) bulk materials as synthesized of **1**.