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Review

Liquid phase methods for design and engineering of two-dimensional nanocrystals

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ABSTRACT

Recently, a great need for high-quality two-dimensional nanocrystals appeared. Because of their extraordinary physical and chemical properties, these nanomaterials find various applications in nanotechnology and are of great interest for engineering of advanced materials, particularly heterostructures with the unique properties that cannot be found in natural materials. In response to this demand, different methods for obtaining two-dimensional nanocrystals are developed and chemical synthetic methods are the most universal among them. They provide freedom, variability and functionality to engineering of 2D nanocrystals. The complex formation is known to provide solubility of components of the reaction system and stability of colloidal solutions. Within this context, the present review aims to consider and emphasize the crucial role of complex formation in the synthesis of 2D nanocrystals using soft templates based on amines and carboxylic acids. The methods of synthesis of 2D nanocrystals in the double electrical layer and templated by the perfluorophenyl ligands are summarized and emphasized. Finally, it is shown that the side reactions can significantly change composition of the reaction mixture, but 2D nanocrystals are nonetheless obtained, so the reaction medium is changeable within a wide range.

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1. Introduction

The regular shift in the light absorption spectrum of CuCl semiconductor nanocrystals smaller than 31 nm with change of their size was experimentally detected in the early 1980s [1]. This fact meant that the electronic structure of solid-state microcrystals was size-dependent. Soon this phenomenon was theoretically substantiated [2] by quantization of the conduction band of a semiconductor due to size confinement of electrons in a crystal. Thus, a tempting possibility of controlling electronic structures of semiconductor and metal microcrystals, including the band gap width, magnetic properties and even the type of conductivity via regulation of the crystal size was theoretically and experimentally justified. Since then an active study of the nanosized materials and directed construction of nanoparticles and nanomaterials with the especially useful physical and chemical properties radically different from those of the same substances in bulk state began. The main consideration was that engineers could control these specific properties, simply changing size of nanoparticles. Because of these properties, multiple applications in various areas of science and technology were found for nanoparticles in due course [3–5]: electronics, optoelectronics, photonics and light detection [6]; chemical sensors and biosensors, catalysis [7], power engineering [8,9], medical diagnostics etc., and the number of these applications continues to grow.

Specific size and morphology govern the unique properties of nanoparticles [1,2,7–12]. Small size of nanoparticles comparable with interatomic distances and the de Broglie wavelength for electron creates spatial confinement for electrons therein, leading to the conduction band quantization [2]. Spatial confinement radically changes the electronic structure and properties of a crystal and consequently, its electron-optical [12,13] and magnetic characteristics [14], electroconductivity type [15] and heat conductivity of material [11,16–18]. However, small size of nanoparticles results in the extremely high (for solids) surface/volume ratios defining their chemical activity characteristics, which are essentially different from those of the bulk materials [7].

According to the size dependence of the properties, nanoparticles can be divided into three simple groups, and all other nanomaterials can be considered as heterostructures composed of nanoparticles belonging to these groups. The first group is 0D particles, or quantum dots [12,17]. Clusters and nanocrystals with dimensions restricting electron movement in all directions and comparable with the de Broglie wavelength for electron inside this particle belong to this group. It should be noted that the zero dimensionality in these cases means only the quantum dimensional constrain for electron [2], but not the zero size of a nanoparticle in a physical sense. Structures restricted in two dimensions in such a way and having one free dimension are designated as 1D nanoparticles; nanofibers or nanorods belong to the second group. Nanoparticles with thickness restricted in the same way and having two free lateral dimensions are designated as 2D nanocrystals, or nanosheets. 3D nanostructures are also considered, but they are usually a combination of 1D and 2D structures, i.e. they are composite materials.

In addition to the above given definition, considering 2D crystals, one should keep in mind that only monolayer sheets, one-atom thick for monoelemental materials [10,16] or one-molecule thick for chemical compounds, may be regarded as true 2D crystals. The thicker crystal structures consisting of two and more identical layers (including a layer with the thickness of one unit cell of bulk crystal) are considered as *quasi-two-dimensional* crystals until their thickness does not exceed the de Broglie wavelength. As evidenced by the experimental data, the true 2D crystals significantly differ from quasi-2D crystals in electron-optical properties, and this difference becomes noticeable already in a bilayer structure [11]. The functionalities of 0D, 1D and 2D nanoparticles of the same substance are also different [3], first, due to different degree of size confinement for electrons, second, due to different accessibility of the surface and inner atoms for the external chemical interactions. It should be stressed that the term "*quasi-two-dimensional* crystals" is not used in papers cited below, so we follow the originals in our review.

One specific feature of the monolayer 2D nanocrystals compared with the other simple classes of nanoparticles should be noted. 0D and 1D nanoparticles can be easily obtained from 2D crystals by the *top-down* nanotechnology approach [19–23], whereas 3D multilayer nanostructures can be obtained from 2D sheets by the *bottom-up* assembly [24–26]. The reverse procedure, that is obtaining of the monolayer 2D crystal from 0D and 1D particles, appears to be much more complicated and often impossible at all without complete destruction of the initial material. So, the monolayer 2D crystals can be considered as the universal raw material for production of other nanoparticles and nanostructures.

The idea of artificial assembly of the layer heterostructures by stacking of various monolayer 2D crystals is not only widely discussed for a long time [24,25,27] but is already implemented [26,28–33], giving not only experimental van der Waals structures but also operating electronic devices based on these heterostructures, for example, light emitting diodes [26]. Moreover, in March 2016 the research group headed by Prof. K. Novoselov from Manchester University was granted by EPSRC (Engineering and Physical Sciences Research Council) with the fund more than 4 million GBP for the research and development project "Engineering van der Waals heterostructures: from atomic level layer-by-layer assembly to printable innovative devices" in order to develop technologies of industrial printing of various heterostructures using the ink containing monolayer 2D nanosheets [34]. However, this approach to production of electronic devices requires raw materials of high quality, namely the high-quality 2D crystals. In relation to this topic and especially after thorough studies of the most famous 2D material, graphene [11], multiple studies aimed on development of the efficient technologies of production of 2D nanomaterials were performed. These studies were analyzed in a number of informative reviews, e.g. [35–41] considering various aspects of the nature, properties, production and applications of 2D nanoparticles.

Engineering of 2D nanocrystals is performed by various methods, each of them having its merits and demerits. For example, molecular epitaxy on substrates or exfoliation of crystals is highly technological and cheap, but molecular epitaxy is preferable if a certain structural similarity of 2D nanocrystal and substrate is available, and exfoliation is limited by the naturally predetermined layer structure of a crystal. Chemical synthetic methods – their principles and results we shall consider and summarize in this review – provide more freedom, variability and functionality to engineering of 2D nanocrystals. We shall review the synthetic processes in an accord with their chemical nature and also consider