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Design of 2D-nanocrystals in water: preparation, structure and functionalization

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Abstract: A new method for synthesis of 2D nanocrystals in water was proposed. The use of perfluorothiophenolate ions as surfactant allowed us to produce 2D single-crystal nanosheets of CaS at pH = 9 and flat nanocrystals of PbS at pH = 9 at room temperature. Mesocrystalline nanobelts of CdS and mesocrystals of PbS were obtained at pH = 3–5 and pH = 10–12, respectively. Morphology, structure and chemical composition of nanoparticles were characterized by high-resolution transmission electron microscopy, electron diffraction and energy dispersive X-ray spectroscopy. A mechanism of nanoparticles formation was discussed.

Keywords: CaS; CdS; 2D nanocrystals; MAM-17; nanosheets; PbS; sodium perfluorothiophenolate surfactant; soft templates.

Introduction

Unique properties of nanoparticles attract great attention of researchers. Nanoparticles can be used as a base material for production of various devices such as light sources (lasers and light-emitting diodes), photovoltaic cells, memory devices and luminescent probes for biological imaging [1]. Nanoparticles are applied in cancer therapy, in production of nanomedicines and also in targeted or novel drug delivery systems [2]. There are a large number of physical, chemical, biological, and hybrid methods available for various types of nanoparticle synthesis [3–6], physical and chemical methods being more promising for this [7]. At the recent time investigations of so called 2D nanocrystals have a great importance. First of all, let us consider some terms, which are used below.

Definition of 2D nanocrystal

Generally speaking, the preferable name of the 2D nanocrystal is now a nanosheet, because it is impossible to introduce the only name which covers all diversity of plane nanocrystals.

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Various definitions of 2D nanocrystals can be met in literature. As stated by some authors, 2D nanocrystals are objects possessing monoatomic thickness [8, 9]. Such a definition is often applied to substances whose bulk crystals have a layer structure, e.g. graphene obtained from graphite, transition metal chalcogenides (MoS₂, WS₂, WTe₂) [10, 11], hexagonal boron nitrides h-BN [12]. The corresponding 2D nanocrystals are monoatomic nanosheets without the broken bonds on the facets. If saturation of the valence of atoms composing these nanosheets is required, this is attained due to addition of ligands, as for example, in 2D nanosilicon [13, 14]. Nanocrystals corresponding to this definition can be conductors as well as semiconductors and insulators.

Another viewpoint is that multilayer platelets can be also considered as 2D nanocrystals, if they have thickness of several nanometers (nanometer scale). This definition is usually applied to substances which do not form layer crystals. It is usually supposed that for semiconductors, the thickness of such platelets should not exceed the Bohr diameter of exciton, and this value strongly depends on the nature of substance. For example, it is 3.6, 42.8 and 92 nm for ZnO, PbS and PbSe, respectively, [15–17]. Sometimes the thicker objects are also called nanocrystals: for example, ZnO platelets 100 nm thick and with lateral dimensions 6000 nm [18] have been thus characterized. However, in this case a term ‘2D nanocrystal’ does not seem justified, because the quantum confinement effect cannot manifest itself at the thickness significantly exceeding the Bohr diameter of exciton.

For metals [19–22], there is no criterion for definition. So, 2D nanocrystals of metals are called intuitively, subjectively taking into account their shape.

The number of reviews and feature articles on 2D nanocrystals grows rapidly since the moment of the very first publication by Novoselov and Geim in 2004 about graphene [23], because graphene possesses unique physical properties. The area of the possible application of nanosheets ranges from electronics and optoelectronics, where silicon is traditionally used [24], and now MoS₂ appears to be a very promising material [25] to medical practice where hydrosols containing 2D nanocrystals of magnesium hydrophosphate can be used for healing of broken bones due to the unique thixotropic properties of these nanocrystals [26].

One more reason for strict attention to 2D nanocrystals is that they are widely used in engineering of hybrid nanomaterials. The number of publications on this topic is growing rapidly: a search with the keyword “nanosheets” in the Web of Science gives 2864 results for 2013 year, 5830 for 2015 and 8744 results for 2017 year.

“Top-down” methods for obtaining 2D nanocrystals

2D nanocrystals can be obtained by destruction of bulk solids. For instance, graphene was prepared by mechanical exfoliation using adhesive Scotch tape [23]. This method is very simple and efficient. However, it is not productive and it does not yield the uniform samples, giving a lot of flakes with the different number of layers [27].

Liquid exfoliation is a very important and widely used method [28–30]. There are many techniques for liquid exfoliation. This method usually includes a stage of intercalation of a layer crystal and a stage of its delamination for separate monolayers under mechanical or (and) chemical action [27].

Exfoliation of layer crystals takes place in one step in supercritical carbon dioxide [31, 32]. When the pressure is released, carbon dioxide (penetrated into interlayer gaps) turns into gas and breaks layer crystals into the separate nanosheets.

Osmotic swelling [33, 34] of layer crystals is one of the most effective methods for exfoliation. Osmotic power appears due to the difference in ion concentrations inside interlayer gaps and surrounding solution and pushes water in the interlayer gaps of a crystal. Interlayer distances in final crystals increase by two orders of magnitude in comparison with those in bulk structure. The destroyed crystal decomposes into the separate 2D nanocrystals.

Electrochemical methods are very effective for intercalation of layer crystals with anions [35], for example sulfate ions, which turn into a mixture of gases – oxygen and sulfur dioxide – as a result of electrochemical
reduction of sulfate ions. These gases delaminate crystal, producing dispersion of 2D nanocrystals in water. One can intercalate the layer crystals with lithium atoms using butyl lithium [36, 37], but electrochemical intercalation of layer crystals with metallic lithium [38] provides a reliable control of intercalation process. The intercalated crystal is treated with water and hydrogen thus produced breaks the crystal into layers that is, 2D nanocrystals.

Exfoliation of a crystal with the layer structure can occur also as a result of chemical action. For example, treatment of CaSi$_2$ with acid gives monoatomic silicon layers: the broken silicon valences are saturated by hydrogen atoms [13] or hydroxyl, alkoxyl and alkyl substituents [14].

Another example – carbides, e.g. Ti$_3$AlC$_2$: in its crystal structure, layers of titanium carbide alternate with aluminum layers [39, 40]. Ti$_3$AlC$_2$ is treated with HF, aluminum dissolves in HF and titanium carbide surface becomes to be covered with the hydroxyl groups. The subsequent ultrasonic treatment yields dispersion of single-crystal titanium carbide nanosheets in water (evidenced by diffraction pattern).

All the methods based on exfoliation have the same limitation: they can be applied only to substances forming the layer crystals. Moreover, the structure of layers of the initial crystal completely predetermines the structure of the resulting 2D nanoparticles, and this is sometimes disadvantageous from the viewpoint of their properties, since activities of various crystal facets are unequal, for example, in catalysis.

“Bottom-up” methods for obtaining 2D nanocrystals [41]

Chemical vapor deposition (CVD) is a well-known example of this approach. CVD is very promising for applications in electronics, optoelectronics, spintronics. For instance, MoS$_2$ nanosheets were obtained by this method [42, 43]. However, application of CVD is limited: either the deposited substance or its precursor should possess volatility.

The methods based on “wet synthesis” of nanocrystals from the corresponding precursors are free of the abovementioned limitations. Such methods are widely used for preparation of 0D nanocrystals – quantum dots, but under the certain conditions they can yield the extended 2D formations. There are a lot of examples of application of wet synthesis in literature, and various authors consider different key origins for formation of 2D crystalline nanosheets [41].

There is a widespread opinion that 2D nanocrystals can grow on soft templates [44]. The double layers consisting of diphilic molecules in organic liquids can play a role of such templates. For example, to obtain CdSe nanosheets, cadmium chloride, selenium and oleylamine were used [44]. Diphilic molecules of oleylamine formed the double layers with the amino groups on the surface, which formed complexes with metal ions located between the double layers. The disproportionation reaction of selenium with water yielded hydrogen selenide which reacted with the coordinated metal ions, thus producing CdSe nanosheets. The fruitful growth of 2D nanocrystals on soft templates is possible only if metal ions composing 2D nanocrystals and template molecules can form complexes [41].

Double layers and monolayers able to act as soft templates also can be formed in aqueous solutions of surfactants both in volume and on the surface of water [45]. If there is an excess of surfactant in aqueous system, it is inside dispersion in the form of double layers. Micelles with nanocrystals in the nucleus and stabilized with the double electrical layer coagulate in the vicinity of the surfactant layers due to high ionic strength of solution [41]. For example, CdTe 2D nanocrystals were obtained in this way in the presence of 2-(dimethylamino)ethanethiol in a weak acidic medium (pH = 5.5–6) [46].

It is supposed that the growth of certain crystal facets may be hindered (growth anisotropy) and this is a key origin of formation of 2D nanocrystals [47]. In the case of 2D nanocrystals of metals, growth anisotropy arises from formation of crystal defects and twinning [21, 22].

Several authors [48, 49] are inclined to rationalize the growth specificity of 2D nanocrystals of cadmium chalcogenides not only by the template effect, but also by hindering of growth of certain facets of crystalline seeds due to their shielding by ligands: anions of fatty acids and so on. Hindering of growth of (001) facets of the nonstoichiometric SnO$_2$-δ 2D nanocrystals in a strongly basic medium can be rationalized in analogous
way [50]. It is likely that binding of hydroxide anions to these facets results in their enhanced thermodynamical stability, that is why their growth stops.

Growth of the definite facets can be also hindered if nanocrystals are formed as a result of chemical reaction on the interface, each of the reagents being in its phase. Flat ZnO crystals were obtained in this way [18].

Under certain conditions, synthesis of 2D nanocrystals proceeds in two stages by self-assembly: at first, small objects are formed, then they combine with each other into nanosheets. This was observed in synthesis of lead chalcogenides [51–53].

In some cases, any specific conditions are not required for formation of 2D nanocrystals, if the resulting substance by itself is inclined to formation of the layer structures. For example, interaction of molybdenic and tungstenic acids with selenium and sodium borohydride yielded MoSe₂ and WSe₂ nanosheets with 75% yield [54]. Their lateral dimensions varied from 300 nm to several microns and their thickness was 1.7 and 1.3 nm for MoS₂ and WS₂, respectively.

We have developed an original method of 2D nanocrystals synthesis using surfactants whose molecules contain the perfluoroaryl groups. We prepared silicon 2D nanocrystals covered by the perfluorophenyl ligands in organic media [55]. The high-resolution electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) data indicated that the single-crystal 2D silicon nanoparticles were flat and rather thin (3.3 nm, and that the Si-C bonds and fluorine atoms were present on their surface).

Specific interactions arise between the fluoroaryl fragments due to the specific distribution of electron density in them. Density Functional Theory (DFT) calculation demonstrates that electron density of the perfluorophenyl groups is concentrated on fluorine atoms, whereas there is deficiency of electron density on carbon atoms [56]. As a result, Coulomb attraction appears between the adjacent perfluorophenyl groups: the positively charged carbon atoms of one ring interact with the negatively charged fluorine atoms of another ring [57, 58]. Due to C₆F₅···C₆F₅ interactions, the perfluorophenyl groups form specific patterns, which can promote self-assembly of 0D nanoparticles into the extended structures.

The method of perfluorophenyl-assisted self-assembly can be applied to other chemical systems. Sulfides were chosen as substances for growth of nanocrystals, with the perfluorothiophenolate ions as surfactants. Water is the most profitable and environment-friendly reaction medium, that is why we have studied aqueous systems in which 2D nanocrystals of metal sulfides can be possibly obtained.

**Experimental**

**Materials**

In the present study, we used the following reagents: CdCl₂·2.5H₂O (79.5–81% purity) from Sigma-Aldrich (USA); pentafluorothiophenol (99% purity) from PIM Invest (Russia); all other reagents: Na₂S·9H₂O, Na₂H₂EDTA, NaHCO₃, Ca(NO₃)₂, HNO₃, KOH – were of pure or analytically pure grade and produced in Russia. In order to prepare acetate buffer, concentrated acetic acid was diluted to 1 M, and the subsequent amount of sodium acetate was taken (both pure reagents were of Russian production). Distilled water was used for preparation of all solutions.

**CaS** nanocrystals were obtained by addition of 10 mL of 0.1 M Ca(NO₃)₂ to the same volume of 1 M Na₂S solution pre-mixed with 0.25 mL of perfluorothiophenol and stirred up to finishing of hydrogen sulfide evolution.

**PbS** synthesis: in a typical synthetic procedure, 20 mL of 2·10⁻³ M Pb(NO₃)₂ solution was added dropwise to the same volume of 5.6·10⁻² M Na₂S solution pre-mixed with 0.25 mL of perfluorothiophenol and stirred up to finishing of hydrogen sulfide evolution. The color of the reaction mixture changed from light brown to black, then black precipitate was formed and the supernatant became transparent. When more basic pH = 10–12 was
required, several drops of 2 M Na₂S solution was added to the portion of Na₂S stock solution under pH control. Analogously when more acidic pH = 5 was required, one drop of concentrated HNO₃ was added to the portion of Na₂S stock solution. After 1.5 h mixing was stopped and the final mixture was left for 2–6 days. The black precipitate was isolated by centrifugation, washed with distilled water and again centrifuged at 2000 rpm.

In the experiments with acetate buffer, the stock solutions of 2 M Pb(NO₃)₂ or 1 M CdCl₂ were prepared by dissolution of crystalline salts in 1 M acetate buffer. Na₂S solutions were equimolar to Pb(NO₃)₂ and CdCl₂ solutions.

**CdS** preparation: in the “basic” version of synthesis, 10 mL of 1 M CdCl₂ was added dropwise to the same volume of 1 M Na₂S solution pre-mixed with 0.25 mL of perfluorothiophenol and ~1.5 mL of 2 M KOH and stirred up to finishing of hydrogen sulfide evolution. Light orange precipitate was formed immediately. After 1.5 h mixing was stopped. The orange precipitate was isolated by centrifugation, washed with distilled water and again centrifuged at 2000 rpm.

**TEM images** were obtained using a JEOL JEM 2100F/Cs electron microscope (JEOL Co. Ltd) equipped with a field emission electron gun (FEG), a spherical aberration image-corrector (CEOS GmbH, Germany), a Tridiem energy filter and an electron energy loss spectroscopy detector (Gatan Inc., USA). TEM data were obtained at 200 kV accelerating voltage. The data were processed and interpreted using Digital Micrograph (Gatan), TIA (FEI) and JEMS (Switzerland) packages.

**Results and discussion**

**Calcium sulfide**

Crystal growth of metal sulfides in water mainly depends on their solubility product, that is why for our studies we have chosen sulfides with the different solubilities. Of the selected substances, calcium sulfide possesses the best solubility: in luminophore production, it is used as a matrix doped by rare-earth metals. The large CaS nanosheets with up to several microns in the lateral sizes were synthesized (Fig. 1a). The EDX data confirmed CaS chemical composition with a trace amount of cadmium (Fig. 1c). Electron diffraction
pattern obtained from the selected area (white circle on Fig. 1a) showed that nanosheets have a single-crystal structure (Fig. 1b). Unusual distribution of diffraction spots intensity can be due to cadmium. It looks like that Cd as a dopant somehow influences the structure of CaS nanosheets.

**Lead sulfide**

Usually PbS 2D nanocrystals were synthesized in organic media [54, 59, 60], but as described in [61], synthesis of these nanocrystals is also possible in basic medium in water. Perfluorothiophenol is a medium-strong acid in water (pKa = 2.68 [62]), that is why sodium perfluorothiophenolate solution has pH > 7 due to partial hydrolysis. Due to specific distribution of electron density via the fluorine and carbon atoms, the perfluorothiophenyl ligands are subjected to nucleophilic attacks of hydroxide anions and water molecules on carbon atoms. As a result, perfluorothiophenol is decomposed at temperature ~100 °C. We have studied conditions for preparation of PbS nanocrystals at various pH values at room temperature, taking into account the fact that the nucleophilic attack of water molecule on perfluorothiophenol is less active in acidic medium.

The well-shaped PbS mesocrystals consisting of numerous self-assembled PbS nanocrystals were obtained at pH = 10–12 (Fig. 2a). The longest edge of PbS nanocrystals attained 40 nm. Diffraction pattern corresponds to the polycrystalline structure of PbS (Fig. 2b). Chemical composition corresponds to PbS (Fig. 2c). The absence of a fluorine peak in the EDX spectra indicates that the perfluorothiophenyl ligands do not compose the surface layer of PbS mesocrystals which were synthesized in the basic medium.

At pH = 9 of the reaction medium, mesocrystals are shapeless and consist of the flattened nanocrystals. Contrast of HRTEM image indicates that thickness of nanocrystals is less than their lateral dimensions (Fig. 3a). According to HRTEM image simulation data, the crystals thickness is estimated as 7–10 nm (Fig. 3b inset). Nanoparticles have a single-crystal structure. The EDX data show PbS chemical composition and do not reveal the presence of fluorine in these crystals. It means that surfactant is not included into the surfaces of PbS nanocrystals.

![Fig. 2:](image)

(a) TEM image: PbS mesocrystal obtained at pH = 9 is alongated hexagone covering all picture; TEM image and (b) polycrystalline ED of PbS mesocrystal. (c) EDX spectrum corresponds to PbS chemical composition.
The most acidic medium we used in this series of experiments had pH = 5–6, Pb(NO₃)₂ concentration being 2⋅10⁻³ M. In this sample there were large areas (Fig. 4a, one of these areas has number 1) which have PbS composition with a great amount of fluorine (Fig. 4e). Area 2 (Fig. 4a) consisting of thick PbS crystals contains little amount of fluorine or no fluorine at all. Both areas 1 and 2 correspond to polycrystalline sheets what follows from electron diffraction patterns (Fig. 4c and d) or HRTEM image of a mesocrystal (area 1 Fig. 4b): diameter of PbS quantum dots is less than 5 nm and there is no preferable orientation of the quantum dot fringes.

The increased Pb(NO₃)₂ concentration (2 M) in acetate buffer (pH = 5) results in formation of mesocrystalline objects like tubes and rods (Fig. 5a). They have polycrystalline structure and do not contain fluorine (Fig. 5b,c). So, in acidic medium the morphology of PbS mesocrystals differs from morphology of PbS mesocrystals obtained in basic medium (Fig. 2).

Cadmium sulfide

Quite similarly, the 2D nanomesocrystals of CdS at pH = 3–5 were obtained. They had a shape of nanoribbons (Fig. 6). The length of nanoribbons reached several microns and width about 50 nm. Electron diffraction revealed mesocrystallinity of nanoribbons and the sphalerite structure type of nanocrystals (Fig. 6a and b, respectively). The EDX data evidenced the chemical composition CdS (Fig. 6c). Area for analysis and diffraction is marked with a circle with number 2 inside in Fig. 6a. The EDX spectrum indicated quite a large number of the fluorinated ligands in nanoribbons.

To clarify the role of perfluorophenyl groups in formation of CdS nanocrystals and mesocrystals in the presence of perfluorothiophenol, we determined the crystal structure of poly(µ-pentafluorobenzenethiolato)
Fig. 4: (a) TEM and (b) HRTEM image (area 1 on Fig. 4a) of a PbS nanocrystals formed in acidic medium. (c, d) Diffraction patterns from selected areas 1 and 2 at Fig. 4a, respectively. (e) EDX spectrum from area 1.

Fig. 5: (a) TEM image of PbS nanotubes obtained at pH = 5–6, (b) ED from selected area and (c) EDX spectrum of PbS mesocrystals.
cadmium DMF solvate] obtained in acetone/N,N-DMF system by the opposite diffusion of solvents. In this structure, cadmium atoms are connected via $\mu_2$-S bridges into ribbons, so each cadmium atom is bound to four sulfur atoms, as presented in Fig. 7. The perfluorophenyl groups form two “wings” at both sides of cadmium sulfide ribbon. Cadmium atom is coordinated by seven atoms: four sulfur atoms, oxygen atom of DMF solvate molecule and two fluorine atoms (F2 and F12) of two perfluorophenyl groups. Dihedral angle subtended by the planes of perfluorophenyl groups is 1.8(5)$^\circ$, the shortest contacts (C⋅⋅⋅F) between them

Fig. 6: (a) TEM image of CdS nanoribbons (circle designates the place of SAED and EDX analysis), (b) ED pattern and (c) EDX spectrum of CdS nanoribbons.

Fig. 7: A view of the structure of poly[(μ-pentafluorobenzenethiolato)cadmium DMF solvate].
(vertical red lines) 3.28(2) Å demonstrate specific interactions of the perfluorophenyl rings. Complete results of structure determination of \([\text{Cd(SC}_6\text{F}_5)_2 \cdot \text{DMF}]_n\) were deposited with CCDC, deposition number 1582707.

The polymeric structure analogous to that of poly[(μ-pentafluorobenzenethiolato)cadmium DMF solvate] can be located on the surface of CdS nanocrystals (solubility of CdS is around \(3 \cdot 10^{-2}\) according to our estimation), so the morphology of CdS mesocrystals obtained at \(\text{pH}=3–5\) is formed due to interactions of perfluorophenyl rings of the adjacent CdS nanocrystals.

However, synthesis at \(\text{pH}=11\) yielded CdS mesocrystals in the form of plates not ribbons and without fluorine (Fig. 8). It is possible that in basic medium the hydroxide ions on the surface of CdS mesocrystals hinder the self-assembly of quantum dots into a crystal. Complexation of perfluorothiophenolate ligands by cadmium cations hampers recrystallization of a mesocrystal into single crystal in acidic medium.

**Conclusion**

The perfluorothiophenolate ions in water at room temperature promote the self-assembly of nanoparticles into large 2D nanocrystals of CaS and mesocrystals of CdS and PbS. In order to obtain the large 2D nanocrystals in water at room temperature, the individual approach to the choice of conditions for each of the substances is required.

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**References**

