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VERSITA

Liquid exfoliation – new low-temperature method of nanotechnology

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Two-dimensional nano-crystals, nanosheets, are a new special type of nanomaterials recently discovered. They have attracted interest due to their unique potential applications especially in electronics. In this mini review, we present the current status of liquid exfoliation of layered crystals – an original new method of production of nanosheets. This "top down" synthesis is a low-temperature physico-chemical process already used to graphene production.

Keywords: *nano-sheets; graphene; liquid-adhesion; milling; sonication*

1. Introduction

Two-dimensional (2D) nanoparticles in the form of very thin sheets with a nanometric thickness have been known since 1962 [1], and in 2004 [2] their abilities and significance were appreciated. They constitute a new original material differing specifically from bulk solid bodies as well as from spherical nanoparticles.

The electronic properties of nanosheets (transport of electrons, phonons, etc.) are, owing to their relatively large surface area, similar to those of solids, but greatly enhanced, and even altered, because of the lack of inter-layer interactions which take place in bulk crystals. This is why they have become a new promising materials with exceptional electric and thermal conductivity, exceptional elasticity and transparency. Fig. 1 shows a graphene nanosheet with a surface area of $\sim$400 μm^2 and the thickness < 100 nm.

Nano-materials can be produced using either "bottom-up" or "top-down" technique [3]. The known "bottom-up" methods of nanosheets fabrication consist in depositing a thin coating on a substrate, using thermo-chemical, CVD [4–8] or PVD [9–12] methods. In all these processes, the priority efforts are made in avoiding the formation

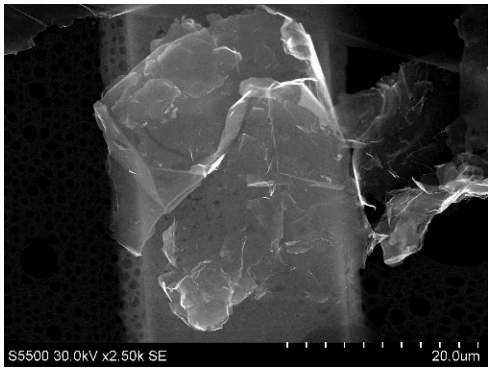

Figure 1. Graphene nanosheet (SEM image HITACHI S5500 SEM/STEM).

of strong chemical bonds between the coating and the substrate, promoting the formation of an interface, and preventing the coating from amorphization and nano-crystallization. Therefore, the basic factors important during the crystallization process are the nucleation on the substrate, small density of the critical nuclei, and coalescence of large islands. The "top-down" technique, on the other hand, uses subtle thinning of the coatings and exfoliation of layered crystals.

2. Physicochemical basis of the exfoliation of layered crystals

Layered crystals are exceptionally anisotropic solids built of layers with strong covalence or

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covalence-ionic bonds, kept together by van der Waals forces, whose energy is hundred-times smaller. As a result, the properties of the layered crystals can be drastically different, depending on the type of bonds engaged in a given action. The best example is graphite, which has the same compressive strength as diamond (in graphene layers, σsp2 bonds are responsible for the compressive strength) whereas its tensile strength is lower by two orders of magnitude because the interlayer van der Waals forces are responsible for the tensile strength.

This specific anisotropy of layered crystals is the basic factor to facilitate their exfoliation into flake-shaped nanoparticles. The known exfoliation methods utilize the co-action of two different, relatively weak fields, without the participation of heat. It is an original synergic low-temperature process.

The exfoliation of a layered crystal was first used for producing graphite nanosheets, i.e. graphene. In these experiments the mechanical work done in pressing a self-sticking (scotch) tape on the graphite crystal was utilized to peel off a "flake" from the crystal surface, which, thanks to the energy of adhesion of graphene to the tape, exceeded the van der Waals forces, active in graphite [2]. This was the earliest synthesis of graphene, which was then often used in laboratories. Obviously, this simple method is not suitable for mass production of nanosheets.

Exfoliation tests showed that the basic process of a new low-temperature method to produce nanosheets could utilize the impact of the adhesion of a liquid. Further experiments with the exfoliation of layered crystals went in two directions. Some experiments consisted in using the mechanical work done during milling a crystal and the work done by the adhesion forces of a liquid. Other experiments utilized the mechanical work done by ultrasonic vibrations excited in a liquid, and the adhesion forces of this liquid.

2.1. Adhesion of liquids

Numerous mechanisms of adhesion have been proposed to explain the adhesion phenomenon. In solids-exfoliation it is the mechanism of chemical interaction between the surface atoms, which has been found to be fundamental. These interactions can be described as the difference in surface energies of two phases (ΔE) or as the surface tension between these two phases (γ_{ij}).

$$\Delta E = E_i - E_j \tag{1}$$

$$\gamma_{ij} = \sigma_i - \sigma_j \tag{2}$$

where i, j denote the individual phases, and $\sigma = E/l$ is the surface tension.

The interactions between different phases depend on the type of the chemical bonds, which may have the dipole-dipole character when they are covalent-ionic, or the dispersive character in the case of covalent bonds.

$$\sigma = \sigma_D + \sigma_P \tag{3}$$

where D is the dispersive interaction, and P is the polar interaction.

Fowkes [13] assumed that the interactions are only possible if the bonds are of the same type. For example, a liquid with non-polar bonds will only interact with the non-polar fragment of the solid body. This assumption has been confirmed experimentally.

Taking into account the geometry of the interatomic interactions, the inter-phase surface tension is given by Eq. 4.

$$\gamma_{ij} = \sigma_i + \sigma_j - 2\left(\sqrt{\sigma_{iD} \cdot \sigma_{jD}} + \sqrt{\sigma_{iP} \cdot \sigma_{jP}}\right) \tag{4}$$

The possibility of utilizing the strong adhesion of a liquid to the surface of a given solid in order to achieve its exfoliation is determined by the condition that the cohesion work W_k of the crystal is equal, or smaller than the adhesion work of the liquid W_a. In the case of a layered crystal, this condition is given by the equations 5 and 6.

$$W_k = 2\sigma_s - \gamma_{s(1-2)} \tag{5}$$

$$W_a = \sigma_c + \sigma_s - \gamma_{c-s} \tag{6}$$

where: s denotes the solid, c denotes the liquid, $\gamma_{s(1-2)}$ is the interlayer surface tension in the solid, and γ_{c-s} is the solid-liquid surface tension.

Taking $W_a = W_k$ we obtain the condition for σ_c:

$$\sigma_c = \sigma_s - \gamma_{s(1-2)} + \gamma_{c-s} \tag{7}$$

In selecting an appropriate liquid to adhere to a solid, the criteria are that the surface tension of the liquid and the type of its chemical bonds should be matched with the chemical structure of the solid. In accord with the above rule, the exfoliation of graphite requires a liquid with a prevalence of σ_D, whereas with h-BN the liquid should have a prevalence of σ_P.

A solid-liquid system can also be described in terms of the thermodynamics of the mixing process. Hernandez et al. [14] proposed that the basic condition of exfoliation should be the minimum mixing enthalpy ΔH.

$$\frac{\Delta H}{V} = \frac{2}{d}(\delta_G - \delta_L)^2 \phi \tag{8}$$

where: V is the volume, d is the nano-sheet thickness, ϕ is the volume of the exfoliation product and δ is square root of the surface energy of graphene (G), and liquid (L).

According to this concept, the condition of successful exfoliation is the similarity (equality) of the surface energies of the liquid and the solid. The authors did not attach any importance to the type of the chemical bonds in the two bodies.

The experiments performed so far showed that the adhesion forces of the liquid alone are not sufficient to provide effective exfoliation of a solid so as to obtain nanosheets. The participation of an additional exfoliating agent appears to be unavoidable.

2.2. Mechanical work of collisions

The known methods of the exfoliation of layered crystals utilize the mechanical work done in non-elastic collisions between the crystal and another body, such as the balls in a milling process. The collisions that take place during this process are characterized by a wide spectrum of contact angles and energies, so that macroscopically the process has no preferred direction and can be considered to be isotropic.

In the disintegration of the material being milled, the crucial role is played by non-elastic collisions during which the energy of the impact is chiefly consumed for the changes of the crystal structure (besides the thermal and thermo-chemical effects). Depending on the energy absorbed in the formation of defects in the crystal subjected to milling, its structure may be amorphisized, which is a reaction controlled by diffusion, or it may be refined in a reaction controlled by cracking.

In solid bodies which withstand a great concentration of defects, if the stress level exceeds the critical value, the dislocations begin to form intergranular low-angle boundaries. The sub-grains thus formed are free of stresses and the entire energy of collision is consumed for the formation of their boundaries [15]. The crystal disintegrates through the mechanism of brittle fractures, forming nanoparticles with atomically pure surfaces [16]. The minimum grain size obtained by milling depends on the balance between the structural effects of the plastic deformation and its temperature-evoked recovery [17].

In the case of layered crystals, the milling process has a specific character determined by their strong anisotropy, which is primarily reflected in their dislocation structure. The dislocations occurring in graphite are mainly of the screw-type, parallel to the c-axis, with a relatively large Burgers' vector (45 nm) [18]. We can therefore expect that the "sub-grains" will have the form of plates composed of a few graphene sheets. The authors of [19] examined the stacking disordering induced in h-BN by shear that occurred in the milling process. They found that high-energy defect structures had appeared in the grains, such as e.g. shearing of the lattice planes, stacking-disordering with basal planes, basal plane twinning and the like. It should however be noted that these authors considered the anisotropic aspect of the milling process.

2.3. Effect of mechanical energy with ultrasonic frequency

Ultrasounds with low frequencies (ranging from 20 kHz to 100 kHz), are used when high energy supply and low wave attenuation are required [20]. The most typical application of "power ultrasounds" is the assistance in mechanical treat-

ments, such as drilling, cutting, and grinding. These ultrasounds are also invaluable in the processes that involve particle dispersion, in surface cleaning, and in biology where they are used for rupturing cell walls.

The application of ultrasounds for the exfoliation of layered crystals seems to be a simple analogy to the homogenization of suspensions. The principal factor which alters the dispersion of suspended solid or liquid particles is the mechanical energy of the acoustic wave, defined by the parameters of the acoustic field. Estimation based on the Eq. 9

$$I = \frac{P_A^2}{2\rho c} \tag{9}$$

where: P_A is the maximum pressure amplitude, ρ is liquid density and c is sound wave velocity, describing the intensity – "*I*" of the sound wave, leads to the conclusion that particles suspended in water are subjected to forced vibration and suffer twenty thousand times per second acceleration in a row $1.45 \cdot 10^4$ m/s^2, which is 1600 times larger than the gravitational forces [20]. For the calculation, frequency of 20 kHz and intensity of 1 W/cm^2 were taken.

However, especially for low-frequency waves, we can expect additionally very significant results, with a completely different character. The complex physicochemical reactions which occur in colloids during sonication are due to the energy delivered when the bubbles and voids present in the liquid collapse. This effect is known as cavitation. The bubbles and voids are forming when the liquid is rarefied under the action of the ultrasonic vibrations, and then they cave, which is accompanied by the local increase of pressure to hundreds of atmospheres and the rise of the temperature to several thousand Kelvin degrees [21, 22].

It is considered that cavitation is an important disintegrating factor. Its mechanism involves the cavitation-induced erosion which occurs when the bubbles at the liquid/suspended solids interfaces undergo cavitation [23].

There are also other phenomena which may affect the process, such as friction at the liquid/solid interfaces, elastic and non-elastic collisions between the particles, and absorption of the ultrasonic energy. All these processes are accompanied by the dissipation of heat whose amount can be measured and used for calculating the effective acoustic energy delivered to the sonicated liquid. This energy can be calculated from the formula 10.

$$P = \frac{dT}{dt} M C_p \tag{10}$$

where: P is the delivered acoustic power, dT/dt is the variation of the temperature versus time, M is the mass of the liquid, and C_p is the specific heat of the liquid.

It should be noted that cavitation occurs when the intensity of the sound wave exceeds a certain value, called cavitation threshold. The cavitation threshold depends on the type of fluid, wave frequency and the presence of solid particles and dissolved gas which are the nuclei of cavitation bubbles [20].

Typical values of power density for the most common frequency (20 kHz) and various solvents, in which the cavitation effect occurs, are in the range of 50 – 500 W/cm^2.

2.4. Effect of electric energy

The effect of electric field on the movement of nanoparticles is well known and used for their segregation through electrophoresis [24]. The mobility of particles in a dielectric medium during electrophoresis depends on its dielectric constant, the size of the particle, and its electric potential, whereas the electric field only affects the length of the path along which the particles travel. During the electrophoresis, the electric field does not interfere in the internal structure of the particles. In dielectrophoresis, the effect of electric field is similar. Non-uniform alternating electric field is here used as the force exerted on the particles suspended in a medium (usually a liquid) [25, 26]. This method is well suitable for depositing the nanoparticles on e.g. electronic structures without interfering with the transported material.

W. Lu et al. [27] analyzed theoretically what would happen when two dielectric nanoplates would be placed in a constant electric field E.

The dipoles then induced may attract or repel each other, depending on their orientation with respect to the electric field direction. As a result, the nanoplates may aggregate or separate from one another, respectively, but the chemical reactions between the individual nanoplates should gradually force them to arrange in parallel.

In a dielectric medium (a liquid) the free energy involved in the formation of a new nanoplate depends, in addition, on the dielectric properties of the liquid. The numerical analysis performed by the authors [27] has shown that the change of the free energy due to the exfoliation in a dielectric medium is determined by the dielectric properties of the two materials, the size of the new nanoplate, the intensity of the electric field, and the mutual configuration of the nanoplates. It also follows from this analysis that it is advantageous for the exfoliation if the dielectric constant of the crystal exceeds that of the liquid.

Approximate calculations of the authors [27] indicate that, for the exfoliation to be effective, the electric field should exceed 10^6 – 10^7 V/m (which is rather a high value).

3. Production of nanosheets by the exfoliation of layered crystals.

Layered crystals are distinguished by their exceptional physical properties such as e.g. the high melting temperature, small friction coefficient, high compressive strength (graphite and h-BN), superconductivity, photo-catalytic abilities, high efficiency thermoelectric effects (transition metals chalcogenides). The band model of nanosheets of these materials differs from that for their bulk form. For example, new forbidden zones may appear with direct inter-band transitions, or the phonon transport may not encounter scattering. These new nanometric materials appear to be very promising. Liquid exfoliation assisted with a "gentle" mechanical treatment seems to be a simple, cheap, ecological and energy-saving process of producing nanosheets from layered crystals.

3.1. Ultrasonic waves-assisted liquid exfoliation

The exfoliation of graphite by sonication in liquid was for the first time realized by Y. Fernandez et al. [14]. They obtained a lyozol with a high concentration (0.01 mg/ml) of nanosheets. Their thorough studies on the exfoliation of graphite by sonication in various liquids confirmed that the matching between the surface energies of the graphite and the solvent plays a crucial role here. The highest efficiency appeared to be achieved with N-methyl-pyrolidone, and the lowest with H_2O. The result, in our opinion, confirms well the Fowkes theory. D. Nuvoli et al. [28], who used an ionic liquid, namely 1-hexyl-3-methyl-imidazolium hexafluoro-phosphate, obtained few-layer graphene sheets with excellent process efficiency. Ionic liquids provide a very high level of environmental safety.

Extensive studies on the sonication-enhanced liquid exfoliation of layered crystals of chemical compounds in the form of suspensions in various liquids were made by J.N. Coleman et al. [17]. By optimizing the selection of the liquids, they achieved the exfoliation of h-BN, MoS_2, and WS_2 into single-layer and few-layer nano-sheets.

The sonication assisted liquid exfoliation appears to be a simple, efficient, and inexpensive method of producing 2D nanomaterials. In exfoliation processes, the ultrasonic wave is generated by a probe immersed in a liquid/colloid (direct sonication), or by introducing a sample container with the suspension into a bath containing a liquid through which ultrasonic waves are propagated (indirect sonication). If higher energies are needed, it is recommended to use direct sonication, but this process has a drawback as the morphology of the particles may undergo undesired modifications. The total energy delivered during sonication depends not only on the power output of the converter but also on the sonication time. There are converters which can operate alternatively in the continuous or in the pulse mode. Such converters permit better control of the process temperature.

The typical procedures involved in the sonication assisted liquid exfoliation include:

1. a powder of the crystal to be exfoliated is suspended in an appropriate liquid (its concentration is low – e.g. 1g/l),
2. the suspension is subjected to sonication (50 – 350 W, 20 – 50 kHz) in the time ranging from few minutes to few hours,
3. the lyosol thus obtained is centrifuged for 15 – 90 min.

Increasing concentration increases the cavitation threshold. Increasing temperature increases the coagulation level.

Some investigators support the liquid exfoliation by transforming the starting material chemically. Graphite oxide easily undergoes exfoliation e.g. in water, but additional reduction processes require a solvo-thermal treatment [29]. Intercalate graphite undergoes liquid exfoliation more easily than graphite [30]. $MoSe_2$ sheets, one-molecular layer thick, were prepared by lithium intercalation through a chemical reaction and subsequent repeated washing with water [31]. Mono-layer and few-layered h-BN nanosheets were prepared by liquid exfoliation of the material complexed with the Lewis bases [32]. The surface-terminated nanoplates, thus obtained, are dispersible in various fluids.

The action of a liquid upon the crystal can result not only in physical exfoliation. The authors of [33] observed a chemical reaction (hydrolysis) which occurred during the exfoliation of h-BN in water. The N-OH, OH groups that formed during the exfoliation additionally 'cut-up' the B-N plates.

3.2. Liquid exfoliation enhanced by milling

Grinding is a relatively simple manufacturing technique because of simple tools (grinders) and the availability of grinding media with a wide range of diameters in the form of spheres produced commercially from almost any material. To ensure adequate stress allowing the separation of the planes (the most desirable is the shear stress), rotary or planetary ball mills are most often used in the exfoliation process. Low rotational speed leads to the reduction of high-energy collisions effect not only on the material being processed but also on the surfaces of the spheres used in the process. Steel balls, typically used for this purpose, is not always a good choice. We suggest that one should pay special attention to the nature of the chemical bonds of material to select appropriate grinding medium. Both the speed and time of the process, from several to tens of hours, ought to be estimated empirically. There are no calculations in the literature which would allow to determine the optimum amount of energy required to complete the exfoliation of a certain amount of layered crystals.

The typical procedures involved in the grinding assisted liquid exfoliation include:

1. a powder of the crystal to be exfoliated is suspended in an appropriate liquid (concentration depends on the method used, from low to as high as 200 g/l),
2. milling is performed at a low rotational speed of 150 – 300 rpm from several to tens of hours, at the presence of grinding media,
3. centrifugation of the suspension for 15 – 90 min.

One of the first significant works published by Janot and Guerard [34] described the process of exfoliation conducted in a planetary mill, using steel balls with the diameters of 5.10 and 20 mm. The used milling time ranged from 12 to 72 h, and speeds from 50 – 200 rpm. As a liquid, water and n-dodecane were applied. The starting material was a graphite with an average particle size of 40 μm. The grinding led to a very thin flakes of graphite with a high crystalline anisotropy, which confirmed the defoliation process. The received particles had different morphologies related to the type and amount of liquid used (1 – 50 cm^3). The thinnest and least defected particles were obtained for a n-dodecane suspension. In the case of water, the excess led to covering the flakes with iron oxide magnetic particles (contamination from the grinding media), while low water content caused agglomeration and partial amorphization of the graphite.

In other paper, Zhao et al. [35] reported a production of the suspension of multilayer graphene flakes, previously prepared by sonication of expanded graphite in several

organic solvents (ethanol, formamide, acetone, tetrahydrofuran (THF), tetramethyluren (TMU), N, N-dimethylformamide (DMF), and N-methylpyrrolidone (NMP)). The suspension with a concentration of 0.4 g/l was milled for 30 h using zirconia balls at a speed of 300 rpm. They obtained stable suspensions of graphene flakes for the three types of solvents, reaching reduction of the flakes thickness from 80 nm to 0.8 – 1.8 nm, which indicated the presence of single graphene sheets.

Lu at al. [36] made an attempt of exfoliation of approximately 1 μm thick h-BN flakes. The liquid used was benzyl benzoate, and the process was carried out with steel balls in a planetary mill at 150 rpm speed for 15 h. They used a fairly high concentration of hBN (83 g/l). The procedure led to the formation of very thin (2.3 – 3.7 nm) flakes which participation was the greater the longer was the time of centrifuging. The suspension had a trace amounts of impurities in the form of particles of iron, which was a result of iron balls friction. The h-BN flakes obtained had a slightly increased number of point defects.

Some modification of the previous techniques with the use of grinding media (balls) is the use of a mortar. Antisari et al. [37] used in their studies an agate mortar and graphite particles of the size about 200 μm. In the process, water was added at a concentration of 15 cm^3 for 3 g of graphite. The authors suggested a much milder process and the increased involvement of shear stress resulting from friction between the rotating bowl and the pestle. The average thickness of the flakes decreased to 12 nm which did not have a significant influence on the density of defects in the resulting material with respect to the powder output. The process was carried out for 60 h.

The technology of manufacturing the composites involving graphene often allows using one of the stages of the process such as mixing or grinding with simultaneous synthesis of graphene reinforcement during its preparation. One such example is the production of ceramic matrix composites Al_2O_3 proposed by Ting at al. [38]. Five percent of 325 mesh graphite was added to Al_2O_3 powder and mixed for 10 – 50 h at 250 rpm in a planetary mill. Ethanol was used as a liquid, the weight ratio of the balls to the charge was 30:1. After 30 h, the structure of the graphite powder changed the form to flakes having a minimum thickness of 3 – 4 nm (also single graphene flakes were observed), further milling only led to reduction of transverse dimensions (breaking) of the petals. According to the authors, the presence of Al_2O_3 powder grains (150 nm) had a positive effect due to absorbing the collision energy of the balls and acting as a micro-milling balls. Therefore, the exfoliation effect was significantly stronger than that of grinding the pure graphite.

4. Summary

As follows from the mini-review presented above, the exfoliation of layered crystals can be considered as a typical synergic process proceeding with the participation of various driving forces (thermodynamic stimuli), which greatly differ from one another.

One of these forces is the adhesion force, generated by the interactions between the atoms, which acts perpendicularly to the interface between the individual phases and quickly decreases with the distance from one phase to another. With the appropriately chosen liquid, the angle between the direction of the inter-phase tension and the crystal surface should be as small as possible. In our opinion, in view of the existence of the electric surface potential of the crystal and the zeta potential of the peeled-off nanosheets, in addition to the chemical interactions, we also have electrostatic effects active during the exfoliation, which should be taken into account in the analysis of the process. The electrostatic forces are also perpendicular to the surface of the solid phases and can promote exfoliation and oppose the particle aggregation or hamper the entire process. Acid-protonated graphene interlayers undergo spontaneous exfoliation in a liquid without the participation of ultrasonic vibrations but solely as a result of electrostatic repulsion [39].

Another force participating in the exfoliation is generated by the non-elastic collisions with the balls during the milling process. In view of the chaotic character of milling, we can assume that

this factor is isotropic and that the developed energy is used for the formation of defects in the crystal. However, in our opinion, through forcing the nanosheets to vibrate, the ultrasonic waves prevent their aggregation.

Nanoparticles in the form of sheets appear to be an unusual material which has already found applications in electronics and in the technology of composites.

In the fabrication of nano-electronic devices [39], such as e.g. field effect transistors (FETs), super-capacitors, photodiodes, the greatest advantage of the sonication-enhanced liquid exfoliation is that we obtain one- or few-layered nanosheets, relatively large in size, and, which is most important, free of defects. The graphene nanosheets produced by other methods, such as e.g., the chemical methods realized at high temperatures, often have carbon plane defects, which drastically degrade their electronic properties. On the other hand, the drawback inherent in the liquid exfoliation lies in the fact that the direct doping of the material is here impossible. This, however does not exclude surface termination treatment i.e. specific methods of modifying the properties of nanomaterials so as to make them also suitable for electronic applications.

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