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SOLID STATE PHYSICS

SYNTHESIS OF GRAPHENIC CARBON MATERIALS ON NICKEL PARTICLES WITH CONTROLLED QUANTITY OF CARBON

V. Grehov^{1*}, J. Kalnacs^{1**}, A. Mishnev², K. Kundzins³ ¹Institute of Physical Energetics, 21 Aizkraukles Str., Riga, LV-1006, LATVIA ²Latvian Institute of Organic Synthesis, 21 Aizkraukles Str., Riga, LV-1006, LATVIA ³Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga, LV-1063, LATVIA

A cheap, comparatively simple and effective method is proposed for the large quantity production of the sheets of graphenic carbon materials (GCM) by annealing the mixture of nickel powder with a suitable carbon amount at the temperatures close to 1000 °C. The number of graphene layers in the sheets of GCM may be varied by altering the amount of carbon in the mixture and parameters of annealing and drying of the obtained products. Samples of GCM were prepared in the form of heat-dried GCM paper and in the form of graphene sponge with freeze-drying. The appearance of GCM on the surface of Ni particles was identified using a scanning electron microscope (SEM) at a low accelerating voltage of 5 kV. The thickness and properties of the layers were investigated by electron microscopy and X-ray diffraction. The fabrication processes were carried out at the concentrations of added carbon from 0 to 1 at%. The results obtained are fully consistent with the well-known solid phase reactions of carbon dissolution in Ni at 1000 °C and graphene or graphite precipitation on the surface with cooling down to the room temperatures.

Keywords: graphene structures, few layers graphene sheets, carbon

1. INTRODUCTION

Graphene, a 2D carbon allotrope, has drawn significant interest among scientists due to a number of intriguing properties [1]–[4].

The methods for graphene production, excluding mechanical exfoliation [1], can be divided into two groups: chemical cleavage, including the step of graphite oxidation [5], [6]; and the methods for dosed position of carbon atoms on the substrate where under certain conditions graphene is formed [7]–[11].

The chemical cleavage methods provide graphene in considerable quantities; however, the quality of such graphene is rather poor, since it usually contains

^{*} Corresponding author. Tel: 0037128253782. E-mail: v.v.grehov@gmail.com (V.Grehov)

^{**} Corresponding author. Tel: 0037126321168. E-mail: jkalnacs@edi.lv (J. Kalnacs)

oxygen-containing groups [5], [6]. High-quality graphene with a large area can be prepared on substrates of a catalytic transition metal – such as Ni or Cu – by thermal chemical vapour deposition (CVD) [7], [8]. Good quality graphene and direct control of the number of layers are achieved using the methods of the dosed deposition of amorphous carbon under the layer of Ni catalyst on Si/SiO₂ substrate [9], ion implantation of carbon clusters in the Ni catalyst layer [10], and pulsed laser carbon deposition [11]. Graphene can also be obtained using Ni powder as a catalyst in the thermal decomposition of SiC powder [12] and by pyrolysis of poly(methyl methacrylate) on particles of Ni powder [13].

The aim of the present research has been to create a simple and available method for production under the laboratory conditions of graphenic carbon materials (GCM) which consist of sheets (flakes, plates) with a predefined number of graphene layers.

GCM particles may be as 2D graphene materials (graphene, multilayer graphene (MLG) with the number of layers <10) and 2D graphite materials (graphite nanoplates or sheets with the thickness of <100 nm), as well as bulk graphite.

2. EXPERIMENTAL SECTION

Our method for producing GCM is based on the well-known solid phase reaction of carbon dissolution in nickel at high temperatures and graphene precipitation on the surface of nickel with cooling to the room temperature (RT) [14]. For GCM production a special nickel-carbon powder mixture was heated in inert atmosphere to a temperature of 900–1000 °C and cooled to RT. The carbon material was extracted from the mixture and studied using scanning (SEM) and X-ray diffraction (XRD). As a result, a significant portion of the carbon material was transformed into GCM.

For dissolution of carbon and precipitation of GCM, as the catalyst the commercial Ni powder (purity 99.8 %, the main grain size $\sim 10 \ \mu\text{m}$) was chosen. On this catalyst, GCM was successfully obtained from methane by chemical vapour deposition (CVD) method [15]. As the source of carbon, Carbopack X powder (Sigma-Aldrich) was taken. The choice of initial materials in form of powders gave us the possibility to vary composition of mix and, as initially was supposed, the GCM sheet thickness. During the research, it was found that Ni raw powder contained carbon as an impurity. The carbon concentration of the starting powder was determined by dissolving Ni powder and carbon residue weighed after filtering the solution. The obtained values were 0.043 wt% or 0.21 at%.

Mixing of Ni powder with appropriate amount of carbon was carried out by ball milling for 30–35 min at the mix and ball weight ratio 1:4.

The first series of experiments was done manually [16]. The annealing of the quartz cuvette with 40 g of mix Ni-C was carried out in a horizontal movable quartz pipe of tubular furnace. The cuvette was loaded in the working zone of furnace and the pipe was pumped out to $5 \cdot 10^{-3}$ bars; then Ar and H₂ flows (400 ml/min and 50 ml/min, respectively) were let in, and after furnace heating up to 400–600 °C the cuvette was kept for 30 min. Further, heating up to 900–1000 °C and 12–80 min annealing proceeded in the flowing atmosphere of Ar (400 ml/min). Cooling down to RT took

place in the Ar atmosphere – either fast (~ 200° /min, outside the furnace) or slowly (~ $1-5^{\circ}$ /min inside the furnace).

The second series of experiments carried out on the thermogravimeter SET-SYS-1750 (Setaram, France) allowed us to automatically carry out processes with programmed sequences of gas flows and furnace temperatures. The 3 g of Ni-C mix in the alumina crucible (1300 mkl) was placed in a vertical furnace of SET-SYS-1750. After air evacuation from the furnace, the flow of Ar and H₂ of 200 and 10 ml/min, respectively, through the furnace was started. The furnace temperature was raised to 200–450 °C at a rate of 8–20 °C/min, and aged for 0.5–1 h.



Fig. 1. SEM image of the initial Ni powder particles (a) and after annealing with the added carbon (b). GCM sheets are seen on the particle surface as dark covering on light particles. GCM sheets after removal of Ni and freeze-drying (c) (1049 mix070) the GCM sponge or after thermo-drying (d) (1053 mix070) the GCM paper.

Then, the flow of H_2 was reduced to 2ml / min; the furnace temperature was raised to 950–1000°C at a speed of 7–20 °C / min and maintained for 0.5–1 hour. Fast cooling of the sample took place in the furnace, while the heater was off and the coolant was circulated. In the beginning, the cooling rate reached 65 °C per minute. Time for cooling to 500 °C was less than 9.5min. Slow cooling rate was 2 °C / min.

Mode programmable experiment (400/1000) means temperature of the first heating in the presence of hydrogen and the second heating in a stream of argon. The heating rate was 20 °C per minute. Warm-up time at the elevated temperature was 1 hour in both cases.

At high temperatures, the sintering of the individual particles of Ni powder by evaporation of Ni atoms from the tips of convex sites and deposition of Ni atoms into the concave sections (in places of contact) particles take place. All particles become connected, and the powder sinters forming an ingot. The initial Ni powder and Ni powder with added carbon after heat treatment are shown in Fig. 1 (a), (b). On the surface of Ni sheets, GCM are seen as dark strips and rings. The contrast between these surfaces with and without GCM can be observed at a low SEM acceleration voltage (5 kV) [17], [18].

Freestanding GCM sheets were obtained after dissolution of the Ni ingot in diluted to 7 wt% nitric acid, with stirring and heating up to 70 °C. In the course of Ni ingot dissolution, the GCM covering seen in Fig. 1(b) could disintegrate into separated GCM sheets, or linkages between the GCM sheets which emerged at their formation could remain. In the first case, GCM samples were obtained by vacuum filtration of the etchant containing GCM through a nitrocellulose membrane filter with a pore size of 1.2 µm. After such filtration, GCM samples were washed with distilled (DI) water and dried at 100 °C; then GCM was separated from the membrane in the form of a *GCM paper* (Fig. 1(d)). Some samples were so thin that could not be removed from the filter; they were investigated as a *layer of GCM on the filter*. In the second case, a carbon body remained in etchant in the form of the original ingot and then it was boiled in DI water (three times) and dried or by heating between two membranes under small load or this wet carbon body was frozen and dried by vacuum sublimation of water at the temperatures from -10 °C to -3 °C. After thermal drying, carbon body samples were looking like the GCM paper samples. After freeze-drying carbon body samples had the form of GCM sponge [19] (Fig. 1(c) and Fig. 2 (c, d)).

Appropriate GCM samples were analysed by means of SEM (Hitachi TM3000), high resolution SEM LYRA3 XMU (Tescan, Czech Republic) and XRD (Japan Rigaku ULTIMA IV, Cu–Ka radiation $\lambda = 0.154184$ nm).

The thickness of these sheets was estimated by Scherrer's equation [20] from the XRD (002) peak broadening (Fig. 3). All calculations were done with Scherrer's scale factor 0.9.

From Fig. 1(c) it is seen that the GCM sponge consists of randomly placed freestanding GCM sheets. Individual GCM sheets have a bend and shape similar to the dark covering on the particles of Ni powder after annealing (Fig. 1 (b)).

Samples in the form of GCM paper consist of randomly aggregated crumpled sheets closely linked to each other. In Fig. 1 (d), the single graphene sheets are distinguished and under them the alternation of light and dark areas can be seen. They are the separate sheets of graphene which are corrugated in lumps. Bright areas are less conductive; they probably have some excess charge.

Observations of the structure for thermally dried GCM samples by high resolution transmission electron microscope (HRTEM) [21] confirmed that our samples contained MLG sheets. Our thermally dried GCM samples by SEM with high resolution [21], as well as samples with freeze-drying are shown in Fig. 2. The graphene sheets crumpled in lumps are shown with arrows. We believe that all the pieces of light material in Fig. 1 (d) and Fig. 2 (a) are graphene sheets crumpled in clumps like those shown by arrows in Fig. 2. Clumping of graphene sheets begins in the step of etching nickel from the disintegration of the carbon coating onto individual sheets and flakes in suspension in acid solution or in water. While maintaining the carbon body in ingot form this does not happen.

The density of GCM sponges determined from the ratio of the weight in a dry state with respect to the wet weight (after boiling in water) gives the values of 10-14 mg / cm³.

3. RESULTS AND DISCUSSION

To perform some preliminary estimates on how much carbon was required in the mix, we proceeded with simple geometrical considerations in particular, the Ni powder was considered as a sum of identical spherical particles with size of 10 μ m in diameter. This size was chosen based on SEM observations. Assuming that all carbon dissolves in the volume of Ni particles at heating and precipitates on their surfaces when cooling, it was easy to calculate the carbon concentration required for obtaining a definite number of graphene layers on these surfaces. The maximum carbon concentration is estimated by its solubility at different heating temperatures. At heating up to 1000 °C this concentration is up to 1.2 at% according to the temperature dependence of carbon solubility in Ni [14]. For such concentration of carbon in the initial mix, in an ideal case it is possible to form a GCM with 50 layers on all surfaces of Ni particles with diameter of 10 μ m.

In practice [14], [18], [22], [23], [24], the GCM structures which are grown on polycrystalline Ni surface are not uniform in thickness. The non-uniformity of thickness occurs due to the presence of two different ways of graphene growth on the Ni surface. Monolayer or bilayer graphene on the polycrystalline Ni usually grows on the surface of large Ni grains with (111) or (011) orientation [18] and the absence of grain boundaries (i). In this case, carbon precipitates to the surface by diffusion of Ni directly through bulk Ni.

In contrast, graphene formed near the grain boundaries for the most part is multilayer graphene, and grain boundaries serve as nucleation sites for multilayer graphene growth (ii). Escape of carbon atoms on the surface occurs through the favourable domain boundaries, which in the places of entrance to the surface form the nucleation sites for multilayer graphene growth along the Ni surface [25]. It should be noted that some grain boundaries act as a fast diffusion path or enhanced local carbon sources in comparison with diffusion through the bulk Ni.

For limiting the heterogeneity of graphene coating by CVD, several steps were taken to improve the structure of the deposited polycrystalline nickel substrate – for the approximation to the Ni single crystal structure [25]. The resulting coating was epitaxially grown graphene with areas up to 1 mm. It was topped with the individual multilayer sheets arranged turbostratically relative to epitaxial graphene. Locations of sheets were above the twin boundaries in the nickel substrate.

Another approach for limiting the heterogeneity of graphene in the CVD method is based on suppression of carbon diffusion through the grain boundaries. For this purpose, after carburizing Ni with CH_4 the substrate temperature rises under H₂ to a segregation temperature (onto 50 C° above) [26]. This results in dissolution

and removal of disordered graphene layers on the Ni surface.

In the present research, we assumed that in the case of annealing powder mixtures with various dose of carbon a regime might be found when the average value of thickness of GCM layers would depend on the amount of carbon in the initial Ni-C mix. It should be noted that the average value of thickness corresponds to real thickness, if the main growth of GCM layers occurs fiberwise on domains (111) during the diffusion directly through bulk Ni [24], [26].

In Fig. 4, the XRD curves for GCM samples are given. It is known that the width of diffraction (002) maximum for graphite is determined by the crystallite size in the direction of C axis [20], which in the case of GCM layers is its thickness and defines the number of graphene layers in it.

For thickness determination by Scherrer's equation, the diffraction peak (002) was approximated by the Voigt or Gauss profile using standard software (X'Pert HighScore or Origin 8.6). The obtained diffraction peaks were asymmetric, which was seen as an increase in the peak width at lower angles. A similar asymmetry in the case of carbon nanostructures is associated with heterogeneity of the studied substance, e.g., when there is partial oxidation [27], disordered graphite planes and/ or amorphous sites [28]. Approximation of such peaks by a symmetrical profile can give some effective GCM sheet thickness (Fig. 4 (a)). In some cases, distortions of the diffraction peak clearly indicate the presence of sample material in two components: the less ordered, thin (<1nm) layer, giving a broad peak (10–15°) and thick (about 10 nm) layer GCM giving a narrow peak (\sim 1°) (Fig. 4(b)).



Fig. 2. High-resolution SEM images of (a) – GCM thermo dried sample (#31) in form of graphene paper with some particles on the surface (indicated with arrow); (b) – freely suspended GCM sheets with some particles on the surface (indicated with arrow), (c, d) – GCM samples (1037) and (1052) in form of GCM sponges.



Fig. 3. XRD patterns of the GCM samples after Ni dissolution, (a) – for manual experiments in tubular furnace (GCM paper), and (b) – for programmed experiments (400/1000) in the Setaram furnace (GCM layers on the filter).



Fig. 4. XRD patterns of the GCM samples, (a) – GCM paper (#40_2), (b) – (GCM paper #53_2), (c) – GCM sponge (1037), (d) – GCM sponge (1052F-1).



Fig. 5. Thickness of GCM layers vs. concentration of the added carbon for different annealing regimes. Orange colour: slow-cooling samples. The point corresponding to the zero carbon concentration is obtained without carbon addition. Magenta colour: fast-cooling samples made in furnace in different manual regimes. Green colour: samples made in Setaram TG furnace in (400/1000) regime with fast-cooling. Lines: a linear fit of the data. All samples were thermo-dried after water rinse and investigated in the form of GCM paper.



Fig. 6. Green squares – thickness of GCM layers vs. concentration of the added carbon for samples made in Setaram TG furnace in the program regime (400/1000) with fast-cooling and thermo drying after water rinse; blue circles – fraction of output carbon weight to the initial carbon weight before annealing. Samples are investigated in the form of GCM paper.

Fig. 7. Green squares – thickness of GCM layers vs. concentration of the added carbon for samples made in Setaram TG furnace in the program regime (400/1000) with fast-cooling and freeze-drying after water rinse; blue circles – fraction of output carbon weight to the initial carbon weight before annealing. Samples are investigated in the form of GCM sponge.



In Fig. 5, the thickness of GCM sheets is shown depending on the concentration of the added carbon in the processes which after water rinse were thermo-dried. The large deviation of GCM sheet thickness from the common trend line (Fig. 5, magenta circle) is connected with variation in time and temperature in the first annealing in the H2 flow and final annealing in Ar in manual processes.

In Fig. 6, data points of GCM sheet thickness for programmed experiments (green squares) are shown, with data points for carbon weight output fraction to the initial carbon weight, for which the last operation was thermo- drying (blue circuits). GCM sheet samples with thermo-drying have the tendency of thickness growth with increasing concentration of added carbon. This trend is not stored for samples in the form of a GCM sponge which can be obtained in the same programme regime, only drying from water takes place by freezing and sublimation (Fig. 7 – green squares). The thickness of these samples changed slightly between 8 and 11 nm, with a change in the dosage of added carbon from 0.25 to 0.7 at%. In the both cases, the weight fraction of obtained GCM was growing identically from 10 % to 70 % by increasing added carbon concentration from 0 to 0.8 at% (Figs. 6, 7 -blue circles). The sample of these GCM sponges is shown in Fig. 1 (c) and Fig. 2 (c). This result casts doubt on the determination of the thickness of GCM layers formed on the surface of nickel powder by measuring the width of the peak (002) on the X-ray diffraction patterns for the samples have passed the stage of thermal drying. Evaporation of water from the liquid phase during heat drying causes contraction inside pairs of individual sheets due to surface tension of water and further gluing them by the van der Waals forces. This causes an increase in thickness of the individual sheets or in some areas of the sheets. The degree of restacking of sheets with nearly equal thicknesses is proportional to their number or common square or output carbon weight, that grows along with the concentration of carbon in the initial mix. That is the reason of thickness dependence of GCM sheets vs. initial concentration of carbon. In contrast to thermal drying, freeze-drying does not lead to such a drastical change in the morphology of the GCM samples.

The thickness values derived from the X-ray spectra are the actual thickness of the GCM layers formed on the surface of the nickel powder (Fig. 7 – green squares). Please note that a slight change in the morphology may occur during freeze-drying, and especially for the thinnest layers of GCM. From the above, it can be assumed that in this (400/1000) regime of annealing the thickness of the layers obtained at different quantity of carbon in the initial mix may be connected with the growth of layers on the grain boundaries as nucleation sites which form a step with height of 8–10 nm. It is the reason why the thickness of layers is almost the same and only the area or weight of the sheets grows (Fig. 7). Roughness of this size is typical of polycrystalline layers of nickel [24]. This result indicated that graphene growth on the surface of Ni powder particles was determined by the roughness of its surface.

To limit roughness, the heating rate [24] was reduced to 8 °C/ min, the temperature of preheating in H₂ was increased to 470 °C [29], and the temperature of the annealing was reduced to 930 °C. For this mode of annealing with last operation of freeze-drying GCM sponges were obtained with a small number of layers (See Fig. 2 (d), and Fig. 4 (d)). The number of layers was estimated as 3 by comparing with Fig. 5 from [30].

For Fig. 5(a) it should be noted that the thickness of GCM sheets obtained in slow-cooling processes is always greater than that of GCM sheets obtained in fast cooling at the same concentration of the added carbon (Fig. 5(a), orange points). The reason may be related to a limited rate of diffusion of carbon in nickel, which does not allow precipitating all of the carbon to the surface of nickel particles from

particle volume in case of fast (non-equilibrium) cooling. It can be understood as follows: At high temperatures, the diffusion length of carbon in nickel is large, but the solubility of carbon in nickel is high and there is no excess concentration for separation on the surface. When cooling down to the temperature at which the concentration of dissolved carbon exceeds its solubility, the carbon starts precipitating on the nickel surface. Excessive concentration occurs at a lower temperature but the length of the diffusion of carbon reduces. It can be shown that at a fast cooling rate a considerable part of carbon would not escape from the bulk of Ni due to restriction of near-surface area by decreased diffusion length and reduced time for this process. All the arguments mentioned above can be attributed to the growth of GCM layers in the both variants (i, ii). The obtained data allow suggesting that at a high cooling rate area of nickel particles, while at a slow cooling rate – from the entire bulk of Ni particles.

The relationship between the thickness of GCM sheets and the cooling rate becomes more complicated due to the recrystallisation of the surface of Ni particles in the cooling stage towards the orientation (111) and decrease in the number of nucleation sites of multilayer graphene on the film [29].

The presence of the (100) and (101) peaks in Fig. 8 is indicative of crystalline regions with "AB" structure in the sample [31]. The width of peak (100) in Fig. 8 (c) gives an estimate of the longitudinal crystallite size La \sim 1-1.2 nm in GCM sheets of sample.

The spectra shown in Fig. 8 were obtained on samples with approximately the same manufacturing conditions. The main difference was in the method of drying after washing with water: thermal drying (a), (b) and freeze-drying (c). Figure 8 (a, b) in the diffraction peak (004) for thermally dried samples dominates over the peaks (100) and (101). This suggests that in these samples the (ab) plane with respect to the specimen (plate) has the preferred direction. The sample with randomly spaced individual sheets of GCM (volumetric the spongy body Fig. 1 (c) and Fig. 2 (c, d)) has a predominance of diffraction peaks (100) and (101) corresponding longitudinally along the plane of the graphene sheets. The preferred direction for the samples in the thermal drying under a light load may be related to the bonding of adjacent GCM sheets. The thickness of the layers will be increased (Fig. 6) and on the diffraction peak (004) shoulder (004*) appears (see Fig. 8 (a)) associated with an increase in the interplane distances in the field of accidental connection of separate GCM sheets.

Presence of this shoulder means that the GCM samples contain regions of turbostratic-like structure in which the individual sheets are rotated relative to the adjacent graphene sheets at an arbitrary angle. The analysis of data in Fig. 8 (a), (b) shows that the centre of peak 004 corresponds to d 004 = 1.68 Å, i.e. to graphite, while for the centre of additional peaks (004*) the distance d 004* = 1.70–1.72 Å is equal to the interplanar d_{004} distance of turbostratic graphite [32]. Note that the centre of peak (004) for graphene sponge with randomly spaced individual sheets corresponds to 1.68 Å of interplanar spacing and absent additional peak (Fig. 8 (c)). It should be noted that turbostratic packaging of graphene layers in the MLG grown on polycrystalline nickel is often shown by electron diffraction [25].

4. CONCLUSIONS

The approach to synthesis of GCM sheets on nickel particles by mix of Ni powder with carbon powder proposed in the present research has been tested. In the experiments, GCM were obtained in the form of graphene sponge and/or paper. It has been shown that thermal drying of GCM samples after water rinse leads to significant changes in the morphology of the GCM samples. The bonding of GCM individual sheets occurs. The thickness of the sheets increases and peak (002) width decreases in the X-ray spectra. The additional peak (004*) appears near the peak (004), which corresponds to an arbitrary (rotated) position of glued GCM sheets and an increased interplanar distance.

Structurally, our GCM consist of nanocrystalline sheets with a size of crystallites about of 10 nanometres (Fig. 8 (c)), at the external sizes up to $1-10 \mu m$ (Fig. 1 (c) and Fig. 2 (b), (c), (d)).

For the mode of annealing (400/1000) for Ni-C mixture, it has been shown that the mechanism of growth is associated with the grain boundaries of crystallites having a step about 8-11 nm. The GCM sponges with sheets of this thickness were obtained.

For special mode of annealing, the GCM sponges with a small number of layers (~ 3) were obtained (Fig. 2 (d)).

Controlling the surface roughness by annealing regime change and variation, the amount of added carbon can further lead to GCM sponge with a predetermined number of layers.

In compliance with the method presented, GCM sponges with a different number of layers can be prepared and used as sensors, contacts for supercapacitors, adsorbents, thermal conductors that can give a lot of perspective applications.

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GRAFĒNA STRUKTŪRU IZVEIDE UZ NIKEĻA GRAUDIEM AR KONTROLĒJAMU OGLEKĻA SATURU

V.Grehovs, J. Kalnačs, A. Mišņevs, K. Kundziņš

Kopsavilkums

Grafēna oglekļa struktūras sintezētas uz niķeļa pulvera ar graudu lielumu ap 10 mikronu. Atkarībā no gatavo struktūru žāvēšanas veida iegūtas divas formas – brīvi izvietots multislāņu grafēna "papīrs", vai grafēna sūkļveida struktūras ar dažu grafēna kārtiņu biezumu. Iegūtās struktūras pētītas ar rastra elektronu mikroskopu, augstas izšķirtspējas caurstarojošo elektronu mikroskopu un rentgenstaru difrakciju.

Iegūtie grafēna slāņi ir nanokristāliski ar graudu lielumu 1 - 10 nanometri. Sūkļveida struktūras ir ļoti perspektīvas kā absorbenti, tās tiek pielietotas superkondensatoros, sensoros u.c.

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