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Ultrasound-induced 3D nano-lattice leads to 3D array of mechanonochemically induced reaction nucleation centers.

The overall possibilities of creation of 3D structured material on nano level may be unified into 2 major groups: either an attempt to arrange already synthesized nanoparticles in 3D lattice or organize the chemical synthesis in such a way so that the final structure would be 3D nano-structured.

The first approach may be summarized by the successful attempts to create the 2D structures using Langmuir-Blodgett method [1] (what may be generalized onto 3D structuring using layer by layer assembly), by using the idea of self-assembly of nanoparticles with the help of surface grafted molecular and macromolecular gradients [2] and other methods.

The inherent problem with this approach is that the nanoparticles can not be made of exactly the same dimensions. This will prevent the forming of long-range order in the macroscopic assembly of nanoparticles. Indeed, the molecular crystals are forming the long-range order [3] due to the fact that all the molecules are exactly the same, thus the separations between them are exactly the same, thus the ideal long-range order is formed (when the amount of defects is too large, the ability of other molecules to hold such an ideal lattice is lost and the amorphous solid is formed). In the case of assembly of non-identical particles the true long-range order is impossible, and instead the short-range order will be present (with correlation length, however, that may be very large, on the order of $d/\delta d$, where d is dimension of the nanoparticle, δd is the average imperfections in theirs dimensions). If the deviation of nanoparticle to nanoparticle is 1%, the correlation length of 100 is expected, what is much larger compare to liquids, but still not enough for real long-range order.

The second approach is to start the chemical synthesis of nanoparticles in such a way, that the nanoparticles synthesized would be arranged in 3D lattice with long-range order from the very beginning. Because the medium for the synthesis of the nanoparticles is assumed to be slurry [4], created sometimes by addition of the surfactants, it is possible to apply ultrasound to the system under investigation. As it was shown in [5], when the three-dimensional irradiation of solvent by ultrasound takes place, due to interference the three dimensional array of minima and maxima of ultrasound wave intensities is formed (similar to optical lattice [6]). In [5] this lattice was used to create the three dimensional array of microparticles – the approach to metamaterials – with wavelength of 200 µm. In that case the frequency of ultrasound was 9.5 MHz. However, according to [7], there is no problem to generate ultrasound of frequency of 300 GHz, what is necessary to generate the lattice with necessary 5 nm period (assuming the speed of sound in water 1500 m/s, for 5 nm wavelength the frequency is $s/\lambda=1500/5*10^{-9}=300$ GHz). According to [7], the problem with such high frequency of ultrasound is not the generation, it is the detection of such high frequency. For mechanochemical application the detection (image restoration) of ultrasound is not necessary, simple heating of the medium may be used to see the effect. In the simplest approach, the ultrasound rupture the chemical bonds of $Co(CO)_3(NO)$ particles (sonication induced chemical synthesis of nanoparticles is described in [8]), or ultrasound assisted decomposition of iron pentacarbonyl [9] thus generating the mechanochemically (sonochemically) produced nanoparticles in exactly the predetermined lattice maxima – the long-range order is generated due to the long-range order of interference pattern.

Another possibility of such an approach would be to generate the heat zones in the ready-made material, again, in perfect 3D nanoscale order. This may work for ceramic magnetics – once the region of the magnet is heated to the temperature, exceeding the critical temperature of magnetic (Curie temperature for ferromagnets, Neel temperature for antiferromagnetic or ferrimagnetic materials). If the sample is heated to almost the critical temperature of magnetic material, the application of powerful pulse of ultrasound (in order to prevent non-uniform heating due to limited thermal conductivity) will generate the 3D interference pattern with necessary period, in maxima of interference pattern the heating is obviously larger, so the temperature may exceed the critical temperature, thus forming the ordered lattice of non-magnetic regions. Or the procedure may be done in strong external magnetic field, thus the nano-periodic lattice of direction changed magnetization may be created.

Even without mechanochemical reaction induced by ultrasound, the same idea of ordered heating zones inside the precursor for material synthesis will generate the acceleration of chemical reaction in such places. Once accelerated, those chemical reactions will continue to be ahead of reaction in neighboring places, thus creating the desired 3D lattice even after the pulse is over. The problem expected is the heating, generated by such a ultrasound inside the material (due to finite thermal conductivity inside the solids the temperature inside will be larger compare to boundaries). Because the speed of sound strongly depends upon the conditions of propagation, it means that the whole pattern will be quickly smashed – even the slightest change in temperature will lead to shift of interference pattern and thus the whole lattice disappear.

The temperature dependence of sound speed in water is described by the equation [10]:

$$s=1448.96+4.591*T$$

Thus to have the correlation length of 1000 (the interference pattern will be shifted one wavelength for 1000 periods) the deviation of the macroscopic temperature inside the material should be less than 0.3 K. From equation for thermal conductivity, assuming the thermal conductivity of water 0.6 W/(mK), for the cube of 1 cm side the estimation of the power possible for the continuous sonication will give:

$$J=æ*S*\Delta T/l$$

Where J is the power, æ is the coefficient of thermal conductivity, S is the surface for heat transfer (1 cm^2), ΔT is temperature gradient over the length l (assuming stationary case). For 1 cm^3 the power would be 0.0018 Watt – too small for real mechanochemistry. So the only possible regime would be pulse regime, when the pulses are strong enough to create the feasible temperature increase in predetermined 3D lattice.

In [7] for the generation of ultrasound at frequencies larger than 100 GHz the molecular gas lasers are proposed. In the case of pulse regime that may be the best approach.

In general sense this approach is material-agnostic. However, for materials with initial porosity it will definitely not work. Also despite the long-range order will be present in any case, the possibility of

reflected waves from macroscopic defects like twin boundaries may generate locally present disorder near the defect.

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