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ABSTRACT

The extended project dealt with the characterization of magnetic nano-colloids prepared by wet chemical process using FTIR absorption spectroscopy. FTIR indicated that the nano-particles were more likely made of Fe_3O_4 . New method and apparatus was developed for laser spark milling of magnetic micro-powders into nano-powders. Two compounds were tested: $\text{Fe}_2\text{O}_3\text{:TiO}_2\text{:MgO}$ water and MnAs in water/alcohol. In both cases nano-colloids were made out of micro-powder suspensions. Provisional patent application has been submitted to USPTO for the method and apparatus.

1. INTRODUCTION

During the initial period of performance of the subcontract (starting from October 1, 2005) it was found that the extension of this effort beyond March 31, 2006 is needed in order to study newly developed, more efficient nano-colloids (based on iron and manganese oxides, iron nitrates, manganese arsenide, and others) and the techniques of making nano-powders replacing chemical wet process and ball milling.

The scope of the extension of this sub-contractual work was to characterize the properties of magnetic nano-colloids made of compounds of iron and manganese through optical studies and also to investigate a laser assisted milling techniques to convert micro-powder of the compounds into nano-powder.

The goal was to establish the relationship between optical properties of the magnetic nano-particles and their characteristics, such as average size, dispersion of size, dielectric permittivity and magnetic permeability in different ambient media, solid and liquid and also to investigate feasibility of laser assisted milling of dry powders consisting of micro-particles (particularly, manganese arsenide) into nano-powders.

The objectives were the following:

1. To conduct additional literature search
2. To design and built experimental setup for laser-assisted milling and investigate the feasibility
3. To conduct optical characterization of newly developed nano-colloids using single-photon absorption spectroscopy, single- and two-photon laser spectroscopy of absorption and fluorescence, infra-red absorption spectroscopy, and atomic force microscopy.
4. Based on the experimental data, to make conclusions on the characteristics of the nano-particles and the feasibility of the laser-assisted milling.
5. Reporting on the extended effort

In the course of the research the customer suggested to put more emphasis on the IR spectroscopy of the samples produced and on the development of the potentially patentable laser milling method. The initially planned objective of multi-photon spectroscopy of the nano-powders was replaced by more rigorous development of the laser spark milling approach.

2. LITERATURE REVIEW

Additional literature search was conducted with the focus on the optical properties of magnetic nano-colloids. In Ref. 1, review of the processing routes of magnetic nano-colloids for biomedical applications, the IR absorption spectra are presented for (γ -Fe₂O₃) nano-particles of different sizes prepared by different methods in comparison with magnetite (Fe₃O₄) nano-colloid. The samples prepared by solution techniques (co-precipitation), the one with the largest particle size (14 nm) shows the infrared features of γ -Fe₂O₃ crystallites, which are at least partially ordered, as evidenced by multiple lattice absorption bands between 800 and 200 cm⁻¹. Meanwhile, in the sample with the lowest particle size (5 nm) a significant reduction in the number of lattice absorption bands associated with increasing disorder is detected. The IR spectrum of the 5-nm sample prepared by pyrolysis only displays two broad maxima at around 600 and 450 cm⁻¹

indicating random distribution of vacancies and therefore is expected to behave differently in the presence of applied magnetic field. On the other side, magnetite has two strong peaks at 570 and 360 cm^{-1} . IR spectroscopy thus makes possible to differentiate easily between maghemite and magnetite.

3. IR ABSORPTION SPECTROSCOPY OF NANO-COLLOIDS

FTIR spectroscopy of the Fe-nano-powder produced by thermal decomposition of iron pentacarbonyl $\text{Fe}(\text{CO})_5$ in ether bubbled with 5%-ammonia/nitrogen gas mixture was conducted. The obtained nano-particles of approximately 25 nm were extracted from ether showed stability in air, water, and alcohol. They were placed between two PTFE IR cards and dried for several days in baking oven at 80°C. The obtained specimen was studied with FTIR absorption spectrometer with a blank PTFE card as a reference. The IR absorption spectrum (Fig. 1) was taken between 400 and 4000 cm^{-1} . A series of weak and shallow absorption peaks were observed between 400 and 1000 cm^{-1} : 420.19, 442.68, 456.92, 638.51, 667.74, 775.43, and 994.00 cm^{-1} . None of them matched the peaks of magnetite Fe_3O_4 [1]. According to Ref. 1, the peaks could be more likely attributed to the crystalline phase of $\gamma\text{-Fe}_2\text{O}_3$ with highly ordered lattice.

4. LASER SPARK MILLING MICRO-POWDER INTO NANO-POWDER

Several processes have been devised for fabricating nano-powder materials. They generally fall into one of three categories, namely, chemical processing, physical processing, or mechanical processing.

With chemical processes, nano-materials are created from a chemical or electrochemical reaction that precipitates particles of varying sizes and shapes. The approach sometimes involves a high cost of raw materials and capital equipment limiting its commercial acceptance. In some cases the chemical synthesis is also associated with the use or release of environment hazardous byproducts.

Physical, usually thermal, processing, involves the formation and collection of nano-particles through rapid cooling of a supersaturated vapor (gas phase condensation). Thermal processes create the supersaturated vapor in a variety of ways, including laser ablation, plasma torch synthesis, combustion flame, exploding wires, spark erosion, electron beam evaporation, sputtering (ion collision). It is possible to produce a variety of nano-powders on laboratory scale. However, poor control of many parameters, their strong dependence on the nature of a particular nano-material, cost of the equipment, and low output often make the approach unsuitable for industrial scale production of nano-powders.

In mechanical processes, nano-powders are commonly made from large particles, usually micro-powders, using crushing techniques such as high-speed ball milling. The mechanism of the process is basically crushing micro-particles by the rolling balls. The micro-particles can be mixed with a liquid in the process. The process is simple and inexpensive. However, there are several disadvantages with this approach. The process is slow: it might take several weeks to obtain a minute amount of nano-powder. This is

mostly due to low energy involved in mechanical crushing. The nano-powder can be contaminated with the residues of the material of the ball milling apparatus. The milling balls and the chamber of the milling apparatus must be made of a material with hardness greater than that of the micro-particles.

Recently, a new method and apparatus for crushing large particles into smaller size powders have been proposed (Ref. 2), which uses electrically induced spark in a slurry made of particles mixed with a liquid. The detailed explanation of the crushing effect does not exist, but it is more likely due to a high-energy shock wave generated by the spark and transmitted through the liquid to the particles. The process is somehow a hybrid of physical and mechanical processes. It proved to be cost efficient and capable of yielding a commercially sizable amount of the nano-powder material. However, the approach is restricted to the non-conductive particles.

The disadvantages of the prior art are: (1) the initial powder material and the liquid must be non-conductive in order to achieve the maximum effect; (2) the equipment for generating a high-energy electric spark can be costly, it requires high voltage to be generated and consequently severe precautions against high-voltage shock hazard to an operator; (3) the energy of the electric spark still remains low, it is hard to expect efficient crushing of particulate matter into homogeneous nanopowder; (4) electrodes used to generate spark rapidly erode, contaminate powder being crushed, and require frequent replacement.

The purpose of the proposed method and apparatus is to crush micropowder material into nanopowder by means of a spark without the limitations of the prior art. The spark is induced by a pulsed laser beam. The beam is sent vertically downwards and tightly focused by a focusing lens in the suspension of the micro-powder in a liquid below its surface. The peak intensity of the beam in the focus is of the order of 10 GW/cm² or higher. The spark crushes micro-particles into nano-particles. Additionally, the shock wave produced by the spark in the liquid assists in circulation of the suspension and delivery of the micro-particles to the location of the spark for crushing. The shock wave also generates a splash of suspension droplets streaming upward and being crushed on-flight by secondary sparks generated by the beam when it meets the droplets on its way downwards. The latter effect increases the speed of the process.

A method for crushing micro-powder material into nano-powder includes:

- (1) Preparation of the suspension of said micro-powder in liquid;
- (2) Pouring the suspension in a container open from the top;
- (3) Directing the beam from a pulsed laser source vertically downwards (along gravitational field) through the opening of the container in the suspension;
- (4) Focusing the beam with a focusing lens in order to generate a spark; the intensity of the beam in the focus must be 10 GW/cm² or higher;
- (5) Positioning the container with respect to the beam in such a way that the spark is generated by the focused beam below the surface of the suspension;
- (6) Exposing the suspension to the sparks periodically generated by the laser for the period of time sufficient to turn the required amount of the micro-powder into nano-powder;
- (7) Separating nano-powder in the form of nano-colloid from the suspension; the nano-colloid can be subsequently dried to generate the nano-powder in a dry form.

An apparatus for crushing micro-powder material into nano-powder (Fig. 2) includes the suspension of micro-powder in a liquid 1, container 2, table 3, laser source 4, light beam 5, focusing lens 6, mirror 7, and splash reflector 8.

Suspension of micropowder 1 is prepared by adding the micropowder in a liquid. Said suspension is poured in open container 2. The container is mounted on table 3. Pulsed laser 4 produces horizontal beam 5. Said beam passes lens 6 and gets reflected downwards by mirror 7. Said lens focuses the beam below the surface of said suspension.

The radius w_0 of said beam in its waist is given by equation (Ref. 3)

$$w_0 = (2\lambda/\pi)(f/D), \quad (1)$$

where λ is the wavelength of the laser radiation; f is the focal distance of the lens; and D is the diameter of the beam before entering the lens. The beam from the laser before entering said lens is assumed to have low divergence. The focused beam preserves its small size within the Rayleigh range z_R near the focus given by equation

$$z_R = \pi w_0^2 / \lambda. \quad (2)$$

Said focused beam attracts the particles to its center by a gradient force (Ref. 4) that is described by equation

$$F = 2\pi\alpha |\text{grad } I| / (cn_m^2), \quad (3)$$

where

$$\alpha = n_m^2 a^3 [(m^2 - 1)/(m^2 + 2)], \quad (4)$$

n_m is the refractive index of the liquid; a is the diameter of the particles; $m = n_p/n_m$ is the ratio between the refractive indices of the particles and the liquid respectively; c is the speed of light in vacuum; $|\text{grad } I|$ is the absolute value of the average gradient of the intensity of the laser beam, which can be approximately estimated as

$$|\text{grad } I| \approx 4P/\pi w_0^3, \quad (5)$$

where P is the power of the laser beam.

Said focused beam generates a spark 9 in suspension 1. Said spark crushes the micron-size particles attracted and trapped in the center of the beam into nanoparticles. It also produces splashes 10, which fly upwards and meet incoming beam 5. Said beam produces secondary sparks 11 in the splashing droplets 10 thus crushing microparticles on-flight. Splash reflector 8 is used to return splashed liquid back in container 2 and also to protect lens 6 and mirror 7 from contamination. Spark 9 in suspension 1 generates a shock wave that forces said suspension to circulate as outlined by flow lines 12 and to deliver more uncrushed microparticles to the location of said spark. Table 3 can be moved in vertical and horizontal directions 13 in order to optimize the depth of the spark in the suspension.

Alternate embodiment can have additional splash reflector 14 (Fig. 2) made of transparent material that blocks completely occasional splashes 10 moving toward the

surfaces of lens 6 and mirror 7. Said splashes are removed automatically from reflector 14 by laser beam 5 due to the process of heating and vaporization.

Yet another alternate embodiment of the apparatus has beam 5 sent at an angle with respect to the vertical direction in order to have the most of the splashing droplets 10 missing the opening of reflector 8 but yet interacting with said beam. This provides additional avoidance of the surface of mirror 7 by said splashing droplets.

Novel features of the proposed method and apparatus: A) method: (1) sparks 9 in the crushing process are generated by focused pulsed laser beam 5; (2) additional sparks 11 crush the splashing suspension 10 on its way up against laser beam propagating downwards; (3) position of container 2 is precisely changed in horizontal and vertical directions in order to optimize the depth of spark 9 in suspension 1 and achieve the best crushing effect; (4) the power of the spark is controlled by adjusting the power of the laser and the degree of focusing of beam 5 by choosing lens 6 of different focal distance; (4) occasional droplets of suspension 1 on splash reflector 14 are automatically evaporated from said reflector by heating laser beam 5; B) apparatus: (1) splash reflector 8 attached to container 2; (2) additional splash reflector 14; (3) beam 5 propagates downwards through the opening of container 2; (4) beam 5 meets on its way splashing droplets 10 of suspension 1 and crushes them with additional sparks; (5) beam 5 is inclined with the respect to the vertical direction thus reducing the probability of splashing droplets 10 to come out through the opening and contaminate optical components; (6) container sits on the table with precise vertical and horizontal motion;

Advantages of the innovation are: (1) there is no conductivity limitation: initial micropowder and liquid can be conductive as well as nonconductive; (2) the equipment is simple (based on a standard pulsed laser), no danger of electric shock hazard to an operator; (3) the energy of the spark can be very high, and it can crush particulate matter into homogeneous nanopowder; (4) crushing process is stable, no degradation due to erosion of electrodes.

The following test data was obtained:

Example1: Micron-size powder of ferrite compound Fe_2O_3 (ferric oxide): TiO_2 : MgO was suspended in water at a proportion 50 mg solids per 100 mL liquids. The container was a 10-cm-tall glass cylinder with a diameter of 2.54 cm (1 inch). The height of the liquid level was 14 mm from the bottom of the container. The suspension appeared light brown and extremely opaque. All the solids precipitated on the bottom of the container in less than 10 min. The laser source was Q-switched Nd:YAG pulsed infrared laser DCR-2A from Quanta Ray. The wavelength of the laser radiation was 1.064 μm , the pulse duration was 9 ns, the energy of the pulse was 0.36 J, the beam diameter was approximately 10 mm. The power of the laser beam was approximately 4.0×10^7 W. The focusing lens was made of glass BK7 and had focal distance 0.2 m. The container was covered with a cone-shape splash reflector made of nylon with a central opening for the laser beam. The photograph of the experimental setup is presented in Fig. 3. The beam radius in its waist calculated from Eq. (1) was 12.7 μm . The intensity of the laser beam in the focus was 7.9 TW/ cm^2 . The gradient force of attraction was calculated using Eq. (3) for the following parameters: $n_m = 1.33$ (water), $m = 1.5$; $a = 0.1 \mu\text{m}$. The force was estimated as $F = 1.54 \times 10^{-7}$ N, which is 5×10^9 times greater than the weight of the particles. The laser beam generated a stable major spark few millimeters below the surface of the liquid and multiple secondary sparks in the column of the liquid splashed

up. The crushing process was kept running for 1 h 25 min. During the process some droplets of the suspension were deposited on the mirror (dielectric mirror optimized for maximum reflectance at 45° at 1.064- μm wavelength). The self-cleaning effect took place: the laser beam heated and evaporated the droplets thus cleaning the mirror without any damage to it. The suspension after laser crushing was let to precipitate for two weeks. Some portion of it precipitated. However, the remaining liquid was clear but colored in light brown. This was the evidence of the presence of nanocolloid, which was not there before laser crushing. Fig. 4 shows the photograph of the resulting nanocolloid (on the right) compared to the suspension, that was not crushed (on the left). Two liquids have different appearance. The liquid after laser crushing is clear but colored. Then the colloid obtained after laser spark crushing was processed in a centrifuge Galaxy 16D (fixed angle rotor) from VWR at a speed of 14000 rpm (relative centrifugal force $\approx 16000 \times g$) for 20 min in order to separate nanocolloid from bigger-size particles. This resulted in a clear colored (light brown) liquid.

Example 2: The suspension of the powder of magnetic material MnAs from Electronic Space Product International (Stock No. K3222p) in ethyl alcohol was ball milled for two weeks. This resulted in a black color suspension. It precipitated in less than twenty minutes making liquid clear without color. Water was added to the suspension. It was poured in the glass container as described in Example 1. All the processing conditions were the same as in Example 1. The only difference was that the splash reflector was mounted off the center and the laser beam was sent at a small angle to the vertical direction. This was done to eliminate the droplets of the liquid coming on the surface of the mirror. In this case the process of self-cleaning did not work well and the mirror appeared to be damaged after few minutes of operation. The total time of laser spark crushing was 45 min. The result was a light brown hazy liquid. It was left for one week to precipitate. The photograph of the liquid taken for comparison together with the initial suspension (Fig. 5) clearly shows the change produced by laser spark process. The liquid is clear and light brown versus initially black suspension that quickly precipitates. The liquid after laser spark crushing is more likely a nanocolloid.

5. CONCLUSIONS

Instead of initially planned multi-photon spectroscopy of magnetic nano-colloids, additional FTIR spectroscopy of the Fe-nano-powder produced by thermal decomposition of iron pentacarbonyl $\text{Fe}(\text{CO})_5$ in ether bubbled with 5%-ammonia/nitrogen gas mixture was conducted. Then it was found that the proposed method of laser spark milling of magnetic micro-powders into nano-powders was patentable. More rigorous study of the method and the apparatus was performed. The provisional patent application was submitted to USPTO. The obtained results are summarized below.

1. FTIR spectroscopy identified the obtained Fe-based nano-powders as magnetite Fe_2O_3 .
2. Laser spark milling process of the suspension of micro-powder of compound Fe_2O_3 (ferric oxide): TiO_2 : MgO in water, which rapidly precipitated, resulted in a clear colored nano-colloid after 1 h 15 min of milling.

3. Laser spark milling process of the rapidly precipitating suspension of micro-powder of compound MnAs in water/alcohol being previously ball milled for two weeks resulted in a clear colored nano-colloid after 45 min of laser milling.
4. Laser spark milling turned to be highly efficient method of milling (crushing) of micro-powders due to high energy concentrated in the laser spark and due to effect of attraction of micro-particles to the focused laser beam because by the gradient forces.

6. REFERENCES

1. P.Tartaj, M. del Puerto Morales, S. Veintemillas-Verdaguer, T. Gonzalez-Carreno, and C.J. Serna, The preparation of magnetic nanoparticles for applications in biomedicine, *J. Phys. D: Appl. Phys.* 36 (2003) R182–R197.
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APPENDIX

A1. STATEMENT OF WORK (for the extended effort)

Scope

During the initial period of performance of the subcontract (starting from October 1, 2005) it was found that the extension of this effort beyond March 31, 2006 is needed in order to study newly developed, more efficient nano-colloids (based on iron and manganese oxides, iron nitrates, manganese arsenide, and others) and the techniques of making nano-powders replacing chemical wet process and ball milling.

The scope of the extension of this sub-contractual work is to characterize the properties of magnetic nano-colloids made of compounds of iron and manganese through optical studies and also to investigate a laser assisted milling techniques to convert micro-powder of the compounds into nano-powder.

Goal

The goal is to establish the relationship between optical properties of the magnetic nano-particles and their characteristics, such as average size, dispersion of size, dielectric permittivity and magnetic permeability in different ambient media, solid and liquid and also to investigate feasibility of laser assisted milling of dry powders consisting of micro-particles (particularly, manganese arsenide) into nano-powders.

Objectives

1. To conduct additional literature search
2. To design and built experimental setup for laser-assisted milling and investigate the feasibility
3. To conduct optical characterization newly developed nano-colloids using single-photon absorption spectroscopy, single- and two-photon laser spectroscopy of absorption and fluorescence, infra-red absorption spectroscopy, and atomic force microscopy.
4. Based on the experimental data, to make conclusions on the characteristics of the nano-particles and the feasibility of the laser-assisted milling.
5. Reporting on the extended effort

Schedule of tasks

TASK1: Additional literature search (Month 1, first half)

TASK 2: Design and construction of the experimental setup for laser-assisted milling and investigation of the feasibility (Months 1, second half, Month 2, first half)

TASK 3: Optical characterization of single-photon and two-photon absorption and fluorescence (Month 2, second half)

TASK 4: Infrared absorption spectroscopy and atomic force microscopy (Month 3, first half)

TASK 5: Final reporting on the extended effort (Month 3, second half)

Milestones

1. Additional literature search finished (report delivered by the end of Month 1)
2. Experimental setup built (end of Months 1)
3. Feasibility of laser-assisted milling investigated (end of Month 2)

4. Optical characterization of single-photon and two-photon processes finished (experimental data presented by the end of Month 2)
5. Infrared spectroscopic and atomic force characterization finished (experimental data presented by the end of Month 3)
6. Final report on the extended effort submitted (end of Month 3)

A2. MONTH 7 TECHNICAL REPORT

Period of Performance: 4/1/2006 – 4/30/2006

Accomplishments

1. In accordance with SOW for the extended period of performance, additional literature search was conducted with the focus on the optical properties of magnetic nano-colloids. In Ref. 1, review of the processing routes of magnetic nano-colloids for biomedical applications, the IR absorption spectra are presented for maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nano-particles of different sizes prepared by different methods in comparison with magnetite (Fe_3O_4) nano-colloid. The samples prepared by solution techniques (co-precipitation), the one with the largest particle size (14 nm) shows the infrared features of $\gamma\text{-Fe}_2\text{O}_3$ crystallites, which are at least partially ordered, as evidenced by multiple lattice absorption bands between 800 and 200 cm^{-1} . Meanwhile, in the sample with the lowest particle size (5 nm) a significant reduction in the number of lattice absorption bands associated with increasing disorder is detected. The IR spectrum of the 5-nm sample prepared by pyrolysis only displays two broad maxima at around 600 and 450 cm^{-1} indicating random distribution of vacancies and therefore is expected to behave differently in the presence of applied magnetic field. On the other side, magnetite has two strong peaks at 570 and 360 cm^{-1} . IR spectroscopy thus makes possible to differentiate easily between maghemite and magnetite.
2. The experimental setup was designed and built for laser-assisted milling of magnetic micro-powders into nano-powders. The setup consists of an Nd:YAG Q-switched, pulsed laser (1.064- μm wavelength, 10-Hz pulse repetition rate, 1-J energy per pulse) and focusing optics to excite a spark in a liquid suspension of micro-particles and decompose the particles by the induced shock wave.
3. Additionally, FTIR spectroscopy of the Fe-nano-powder produced by thermal decomposition of iron pentacarbonyl $\text{Fe}(\text{CO})_5$ in ether bubbled with 5%-ammonia/nitrogen gas mixture. The obtained nano-particles of approximately 25 nm were extracted from ether showed stability in air, water, and alcohol. They were placed between two PTFE IR cards and dried for several days in baking oven at 80 $^\circ\text{C}$. The obtained specimen was studied with FTIR absorption spectrometer with a blank PTFE card as a reference. The IR absorption spectrum was taken between 400 and 4000 cm^{-1} . A series of weak and shallow absorption peaks were observed between 400 and 1000 cm^{-1} : 420.19, 442.68, 456.92, 638.51, 667.74, 775.43, and 994.00 cm^{-1} . None of them matches the peaks of magnetite Fe_3O_4 [1]. According to Ref. 1, the peaks can be more likely attributed to the crystalline phase of maghemite $\gamma\text{-Fe}_2\text{O}_3$ with highly ordered lattice.

Difficulties and back-up strategies

1. The IR absorption peaks of the Fe specimen were weak and shallow. In order to enhance the peaks, it would be desirable to use KBr IR card as a holder of the nano-powder. Another option could be to prepare a pellet by pressing together the powder of crashed KBr crystal and the Fe nano-powder in a pellet.
2. Is expected that by the time of the beginning of the experimental study of laser-assisted milling the customer will obtain the optical dynamic scatterometer for the evaluation of the size of the nano-powders produced by milling of micro-powders.

Plans for the next month

1. To conduct testing of the laser-assisted milling setup.
2. To conduct single- and two-photon absorption and fluorescence spectroscopy of the obtained nano-powders alone and in the mixtures with organic fluorescence compounds.

References

1. P.Tartaj, M. del Puerto Morales, S. Veintemillas-Verdaguer, T. Gonzalez-Carreno, and C.J. Serna, The preparation of magnetic nanoparticles for applications in biomedicine, J. Phys. D: Appl. Phys. 36 (2003) R182–R197.

A3. MONTH 8 TECHNICAL REPORT

Period of Performance: 5/1/2006 – 5/31/2006

Accomplishments

1. In accordance with SOW for the extended period of performance, the experiment on laser-assisted milling of magnetic micro-powder into nano-powder was conducted using the experimental set-up built during April 2006. The maximum energy of 9-ns pulses from a Q-switched Nd: YAG laser (1064-nm wavelength) was 0.36 J/pulse. The pulse repetition rate was 10 pulses per second. A micro-powder of compound FeO:MgO:TiO was mixed with distilled water at a proportion 50 mg solid per 105 mL liquid. This resulted in a light brown clay-like opaque suspension. Several configurations of the experiment were tried as described below.
2. The first configuration used a focusing lens (100-mm focal distance) right after the laser. The plastic container with flat vertical walls (spectroscopic cell) was horizontally lined up with the lens with the lens focus in the middle of the cell. The suspension of the micro-powder was poured in the cell. The spark produced by the focused laser beam even at a mid-power destroyed the cell by making hall in its wall from the side of coming laser beam. The experiment was a failure. The suggestion was made that relatively long focal distance of the chosen lens caused an increase of the region where the beam stayed tightly focused (Rayleigh region). As a result, the wall of the cell got burned.
3. The second configuration was similar to the 1-st configuration, but used the spectroscopic cell made of glass and a lens with 50-mm focal distance. The wall was

not destroyed. However, the scattering of the beam that entered the cell from the side wall was so great in the suspension that the beam did not focus in the middle of the cell producing no spark. There was always a danger of destroying the wall by the focused beam, anyway. The suggestion was made to change the configuration from horizontal to vertical where the focused laser beam enters the suspension right from the top through air.

4. The third configuration used a dichroic mirror with optimized reflectance at 1064 nm and 45°-angle. The mirror reflected the laser beam propagating horizontally to vertical direction. A 50-mm focusing lens was placed after the mirror. Below the lens was a glass bottle with the suspension. The top of the bottle was covered by an anti-splash funnel-shaped cover with the hole in the middle to let the laser beam in. The focused laser beam produced a spark right under the surface of the suspension. But the splashes coming vertically on the lens (despite the anti-splash cover) created droplets of water suspension on the bottom surface of the lens thus disrupting the process of laser-assisted milling. The suggestion was made to return back to a lens with longer focal distance and to place it before the mirror.
5. The forth configuration used a 250-mm focusing lens placed right after the laser and before the 45°-mirror. The experiment was conducted at full laser power. The spark in the liquid created a vertical column of the droplets splashed out almost vertically to the mirror. This effect turned out to be favorable for the laser-assisted milling because the laser beam generated a vertical column of sparks along the column of the droplets thus breaking micro-particles in the droplets on their way up. At the same time, the beam automatically cleaned the mirror from the splashes by evaporating the droplets of the suspension coming to the surface of the mirror. The process became self-sustaining. The first laser-assisted milling was carried out for 25 min. Three days later the resulting suspension was compared against the suspension without milling. The milled suspension did not precipitate completely showing light-brownish color of the top water. The top water of the precipitated suspension without milling was clear with no color. The colored water on the top of the milled suspension was the evidence of the presence of the nano-particles that did not precipitate. The nano-particles were produced from the micro-particles by the laser-assisted milling. This was the evidence of the success of the experiment.
6. The experiment was conducted again for one hour and resulted in even more prominent colored water on the top of the precipitate: more nano-colloid was generated that time.

Difficulties and back-up strategies

1. It was expected that by the time for the laser-assisted milling to produce some nano-colloids the customer would obtain the optical dynamic scatterometer for the evaluation of the size of the nano-particles. It turned out that the equipment was not coming. The only methods remained available were visual estimation of the nano-colloid by the rate of precipitation and also by separating nano-colloid from micro-suspension in a centrifuge.

Plans for the next month

1. To conduct laser-assisted milling with several other magnetic micro-powders provided by the customer.
2. To conduct evaluation of the produced nano-colloids based on the precipitation rate and separation in a centrifuge.
3. To conduct single- and two-photon absorption and fluorescence spectroscopy of the obtained nano-powders alone and in the mixtures with organic fluorescence compounds.

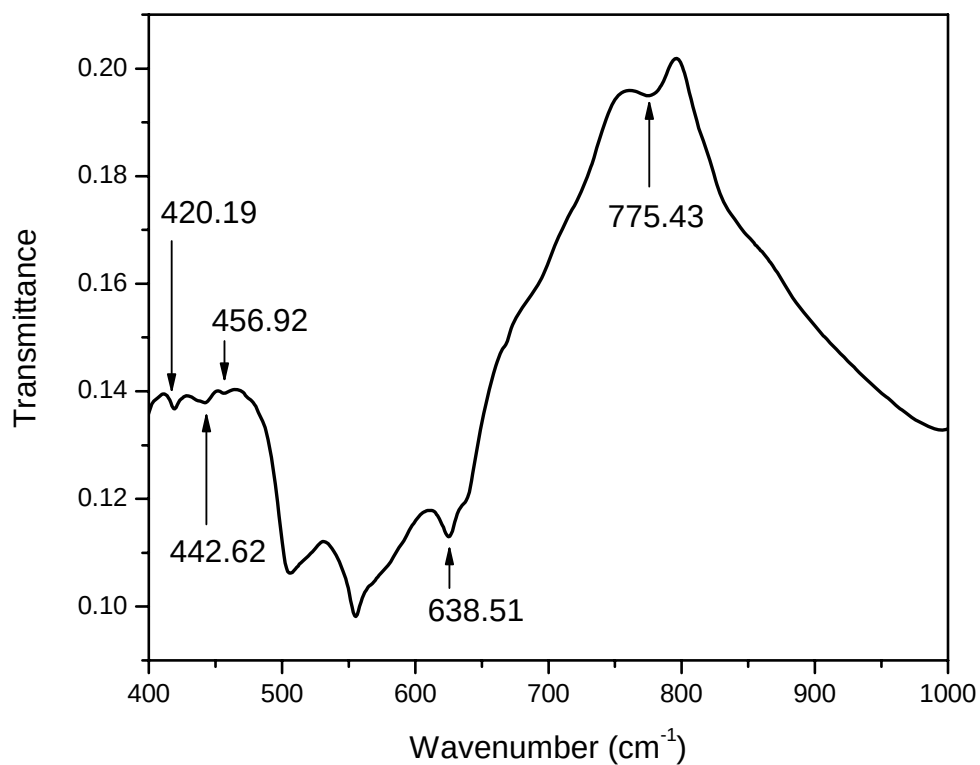


Fig. 1. FTIR transmission spectrum of the iron nano-colloid sample prepared by thermal decomposition of iron pentacarbonyl $\text{Fe}(\text{CO})_5$ in ether bubbled with 5%-ammonia/nitrogen gas mixture was conducted.

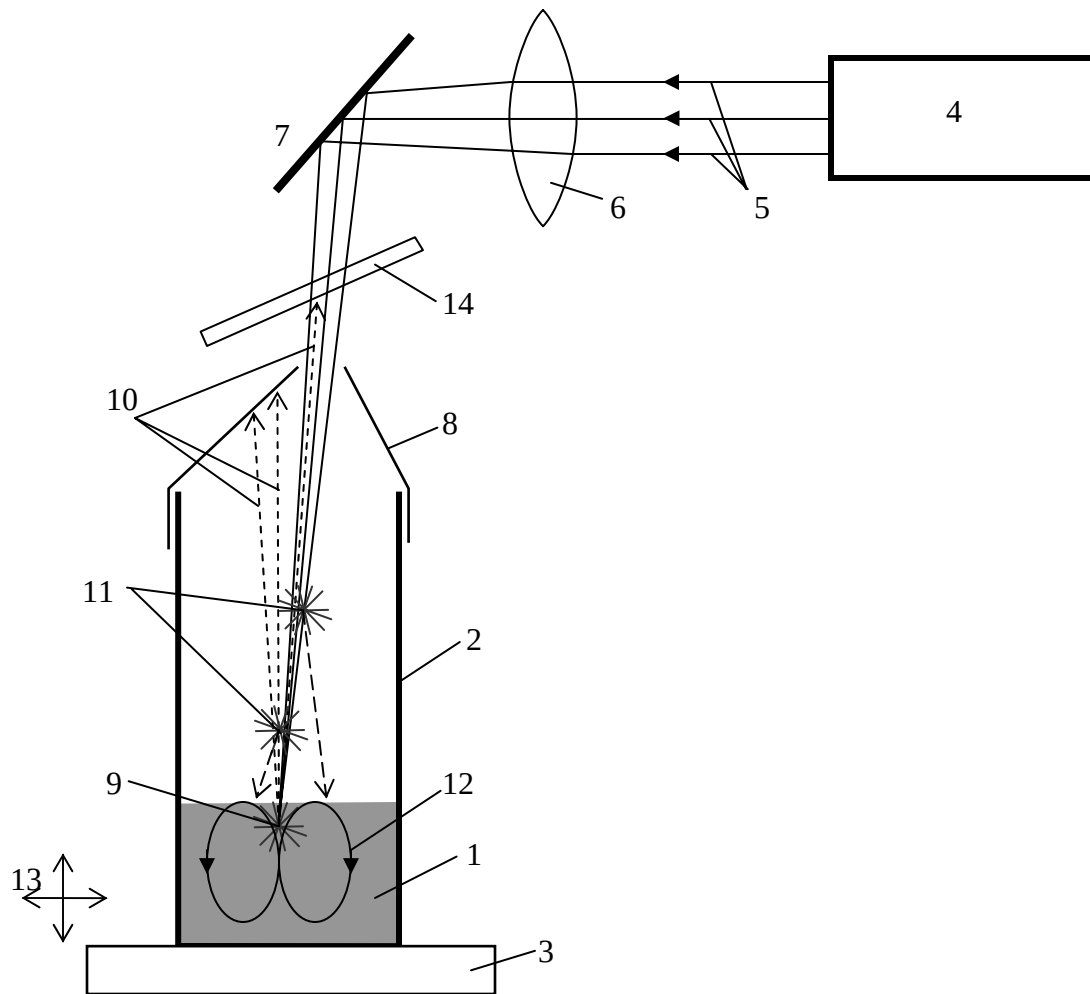


Fig. 2. Schematic of the proposed apparatus for laser spark crushing of micropowder into nanopowder



Fig. 3. Photograph of the conceptual prototype of the laser spark crushing apparatus

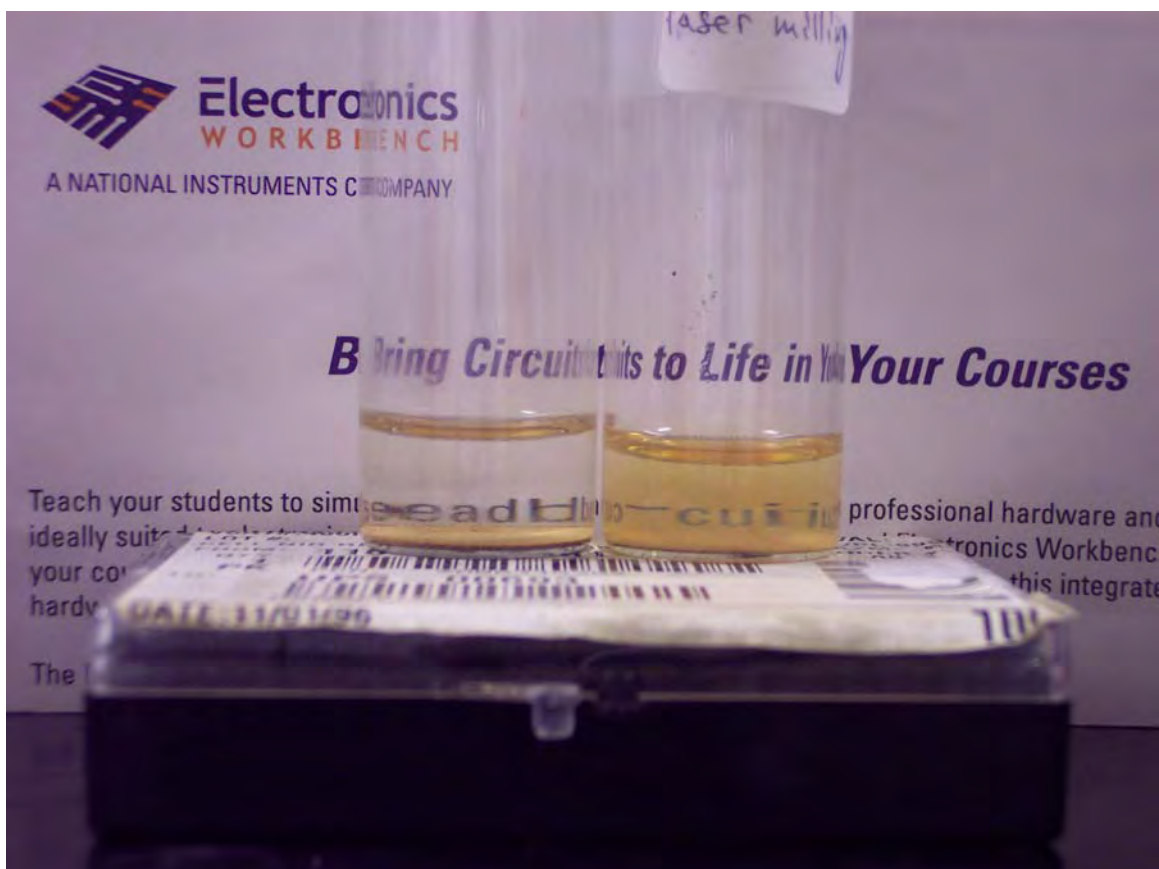


Fig. 4. Photograph of the precipitated suspension of $\text{Fe}_2\text{O}_3:\text{TiO}_2:\text{MgO}$ ferrite compound described in Example 1 without laser spark crushing (left) and processed with laser spark (right)

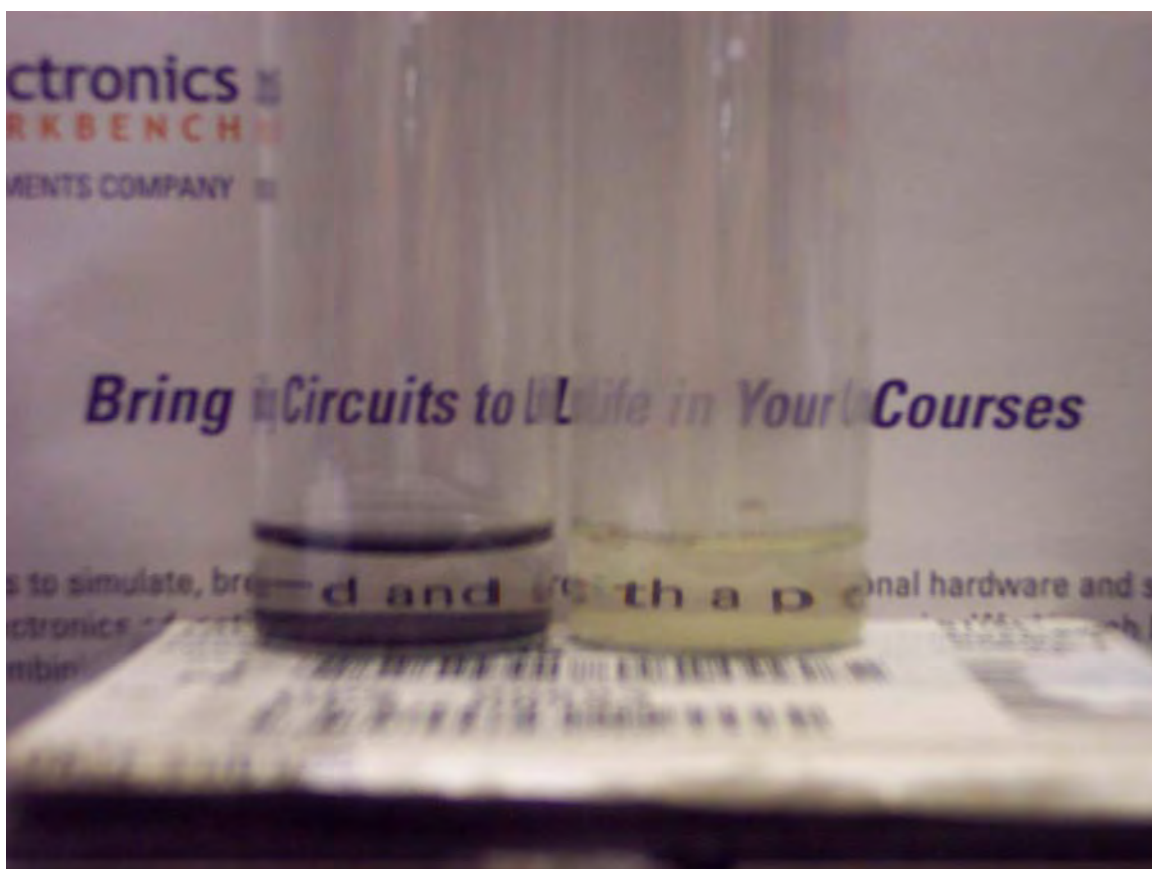


Fig. 5. Photograph of the precipitated suspension of MnAs magnetic compound described in Example 2 without laser spark crushing (left) and processed with laser spark (right)