"Nature works to maximum achievement at minimum effort. We have much to learn."
(http://www.cbid.gatech.edu/univ_labs.html)

A CASE STUDY ON NANOFIBERS

by
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INTRODUCTION/BACKGROUND

Raw materials used in Nanotechnology

Nanoparticles
Synthesis methods: One can use either a top-down (comminution and dispersion) or bottom-up (nucleation and growth) approach. The decision which to adopt depends on which can deliver the specified properties, and then on cost. Comminution and dispersion means taking bulk material and fragmenting it. Crushing and grinding have typically been treated as low-technology operations. Theoretical scientists seeking to formalize phenomenological mechanistic rules (e.g., random sequential fragmentation) have found they have had little impact on the industry! The main advantages are universality and low cost. Even soft organic matter (e.g., grass) can be ground by first freezing it in liquid nitrogen.
The main disadvantages are polydispersity of the final particles, and the introduction of many defects. Furthermore, the product may become contaminated by the material used to make the grinding machinery. The smaller the particles are, the worse the contamination is.

Nanoplates
Until now, thin coatings on a substratum have not been considered as nano-objects, but simply as thin films, because typically they have been more than 100 nm thick. Exceptions are Langmuir films, transferred to solid substrata using the Langmuir-Blodgett and Langmuir-Schaefer techniques; these films might only be a few nanometres thick. Exceptionally laterally cohesive Langmuir films can be manipulated as free-standing objects. Nevertheless, the trend is to develop thinner functional surfaces by coating or otherwise modifying bulk material, and insofar as the coating or modification is engineered with atomic precision, it belongs to nanotechnology.

Graphene-based materials

Inspired by learning about naphthalene and anthracene, countless school children have doubtless doodled endless fused polyaromatic rings. It has long been known that graphite is composed of stacks of such polyaromatic sheets, which are called graphene. Due to convincing theoretical work, it was however long believed that two-dimensional crystals cannot exist. The ostensive demonstration of their existence (graphene sheets) have, *post hoc*, led to the explanation that their stability is due to undulations of the sheet.

Graphene

The graphene lamellae stacked to make bulk graphite were from the ease of their detachment (e.g., writing with graphite on paper) known to be only weakly bound to each other. Individual sheets of graphene can actually be peeled off graphite using adhesive tape. Alternatively, a crystal of silicon carbide can be heated under vacuum to 1300 C; the silicon evaporates and the remaining carbon slowly reorganizes to form some graphene.

Carbon nanotubes

The carbon nanotube is a seamless tube made by rolling up graphene. It was long known that carbon filaments are formed by passing hydrocarbons over hot metal surfaces, especially iron and nickel. The actual nature of carbon nanotubes was however only established relatively recently. Multiwall carbon nanotubes consists of several concentric tubes of graphene nested inside each other.

The three methods for producing carbon nanotubes are the laser furnace, the carbon arc (i.e., vaporizing graphitic electrodes), and (plasma enhanced) chemical vapour deposition (Figure 1). Carbon nanotubes are often closed at one or both ends by a hemisphere of fullerene.

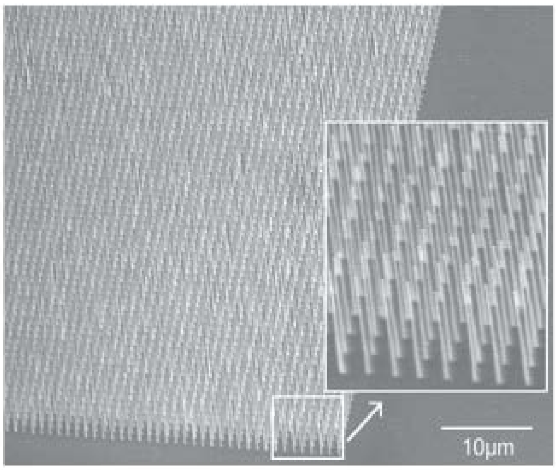


Figure 1 - A forest of carbon nanotubes produced by plasma-enhanced chemical vapour deposition

Carbon nanoparticles
Fullerenes (also known as soluble carbon or buckyballs) can be thought of as graphene curled up to form an enclosed spherical shell. They exist as C60,C70, etc. They can be made in a carbon arc, but burning a hydrocarbon feedstock with strict control of the oxygen supply is a more controllable method. The fullerenes can be separated from coproduced soot by dissolving them out.

Nanofibers
"Nanofiber" is the generic term describing nano-objects with two external dimensions in the nanoscale. A nanorod is a rigid nanofiber, a nanotube is a hollow nanofiber, and a nanowire is an electrically conducting nanofiber. Three approaches can be used to synthesize nanofibers. For some substances, under certain conditions, the natural growth habit is acicular. Therefore, the nucleation methods described in the previous section can be used to generate nuclei, followed by a growth stage to elongate them
Heterogeneous nucleation can be induced at the solid/gas interface by predepositing small catalytic clusters. Upon addition of vapour, condensation on the clusters and growth perpendicular to the solid substratum takes place. This is used as an efficient way of synthesizing carbon nanotubes. A drawback of the method is that the preparation is almost inevitably contaminated with the catalyst.
If uniform nanopores can be formed in a membrane (e.g., by laser drilling or by self-assembly) they can be used as templates for nanofiber formation. The material for the fibre should be deposited as a shell on the inner surface of the pores (if the goal is to make nanotubes), or else should completely fill the pores (for nanorods). Nanofibers, especially nanorods, formed by either of the two previous methods can also be used as templates for making nanotubes of a different material.
Nanofibers are an exciting new class of material used for several value added applications such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, and energy storage. Special properties of nanofibers make them suitable for a wide range of applications from medical to consumer products and industrial to high-tech applications for aerospace, capacitors, transistors, drug delivery systems, battery separators, energy storage, fuel cells, and information technology.
Generally, polymeric nanofibers are produced by an electrospinning process (Figure 2). Electrospinning is a process that spins fibers of diameters ranging from 10nm to several hundred nanometers. This method has been known since 1934 when the first patent on electrospinning was filed. Fiber properties depend on field uniformity, polymer viscosity, electric field strength and DCD (distance between nozzle and collector). Advancements in microscopy such as scanning electron microscopy has enabled us to better understand the structure and morphology of nanofibers. At present the production rate of this process is low and measured in grams per hour.

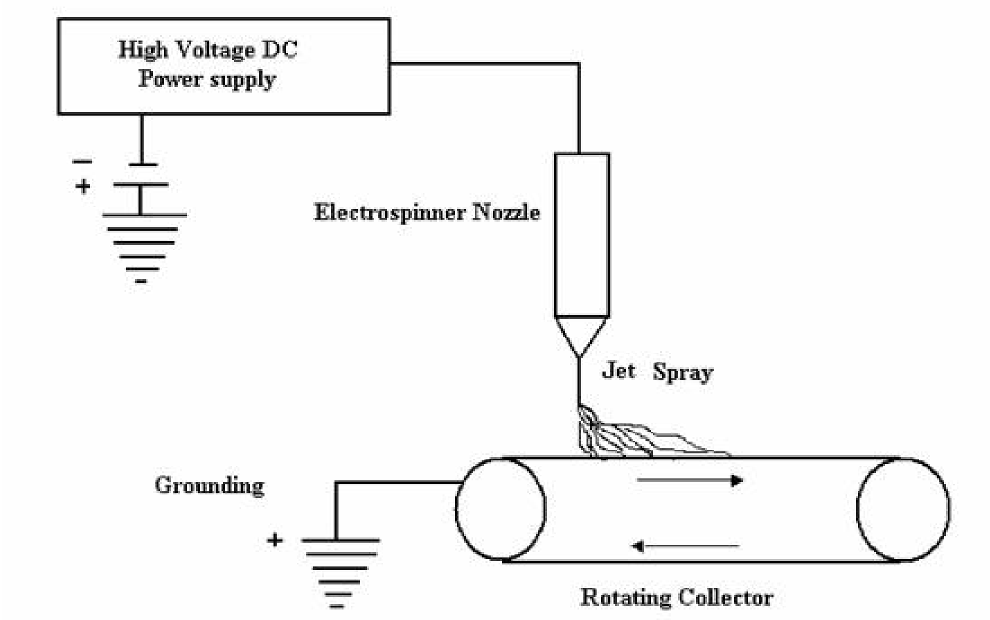


Figure 2 - Schematic representation of electrospinning process

Another technique for producing nanofibers is spinning bi-component fibers such as Islands-In-The-Sea fibers in 1-3 denier filaments with from 240 to possibly as much as 1120 filaments surrounded by dissolvable polymer. Dissolving the polymer leaves the matrix of nanofibers, which can be further separated by stretching or mechanical agitation.

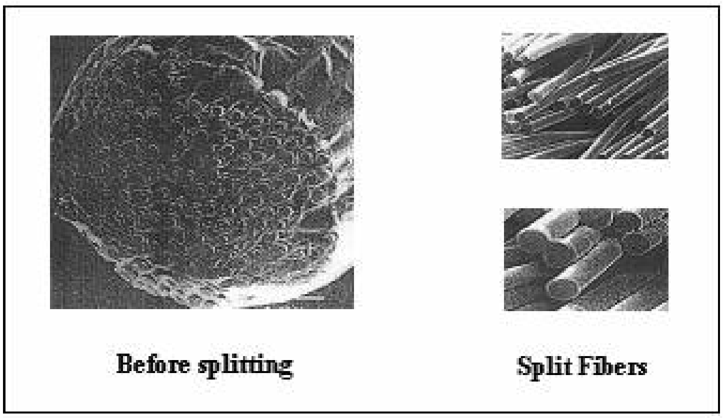


Figure 3 - Nanofibers from Bicomponent fibers

As described above, nanofibers are also manufactured by splitting of bicomponent fibers (Figure 3); most often bicomponent fibers used in this technique are islands-in-a-sea, and segmented pie structures. Bicomponent fibers are split with the help of the high forces of air or water jets.

The most often used fibers in this technique are nylon, polystyrene, polyacrylonitrile, polycarbonate, PEO, PET and water-soluble polymers. The polymer ratio is generally 80% islands and 20% sea.
The resulting nanofibers after dissolving the sea polymer component have a diameter of approximately 300 nm. Compared to electrospinning, nanofibers produced with this technique will have a very narrow diameter range but are coarser.

- ***Properties of nanofibers***

Nanofibers exhibit special properties mainly due to extremely high surface to weight ratio compared to conventional nonwovens.
Low density, large surface area to mass, high pore volume, and tight pore size make the nanofiber nonwoven appropriate for a wide range of filtration applications.
Figure 4 shows how much smaller nanofibers are compared to a human hair, which is 50-150 µm and Figure 5 shows the size of a pollen particle compared to nanofibers. The elastic modulus of polymeric nanofibers of less than 350 nm is found to be 1.0±0.2 Gpa.

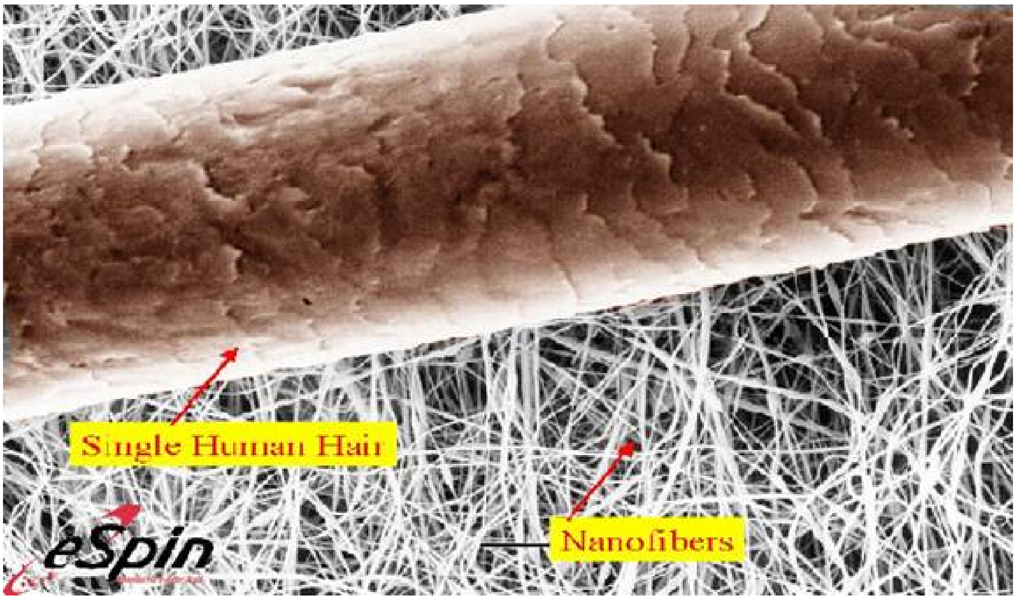


Figure 4 - Comparison between human hair and nanofiber web

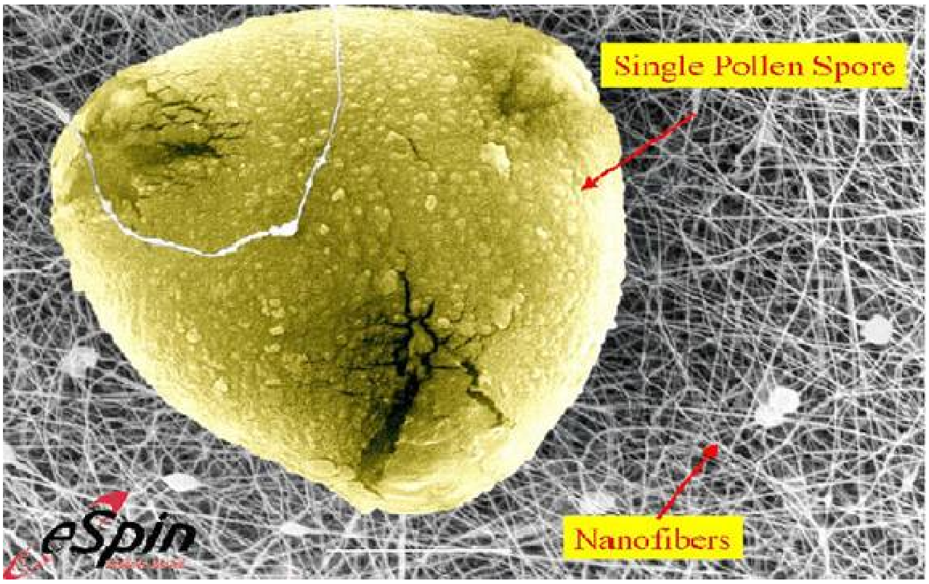


Figure 5 - Entrapped pollen spore on nanofiber web

- ***Applications of nanofibers***

Nanofibers have applications in medicine, including artificial organ components, tissue engineering, implant material, drug delivery, wound dressing, and medical textile materials. Recently, researchers have found that nanofiber meshes could be used to fight against the HIV-1 virus, and be able to be used as a contraception. In wound healing nanofibers assemble at the injury site and stay put, drawing the body's own growth factors to the injury site. Protective materials include sound absorption materials, protective clothings against chemical and biological warfare agents, and sensor applications for detecting chemical agents. Nanofibers have also been used in pigments for cosmetics. Applications in the textile industry include sport apparel, sport shoes, climbing, rainwear, outerwear garments, baby diapers. Napkins with nanofibers contain antibodies against numerous biohazards and chemicals that signal by changing color (potentially useful in identifying bacteria in kitchens).

Filtration system applications include HVAC system filters, HEPA, ULPA filters, air, oil, fuel filters for automotive, filters for beverage, pharmacy, medical applications, filter media for new air and liquid filtration applications, such as vacuum cleaners.

Energy applications include Li-ion batteries, photovoltaic cells, membrane fuel cells, and dye-sensitized solar cells. Other applications are micropower to operate personal electronic devices via piezoelectric nanofibers woven into clothing, carrier materials for various catalysts, and photocatalytic air/water purification.

Filtration

Nanofibers have significant applications in the area of filtration since their surface area is substantially greater and have smaller micropores than melt blown (MB) webs. High porous structure with high surface area makes them ideally suited for many filtration applications. Nanofibers are ideally suited for filtering submicron particles from air or water. Electrospun fibers have diameters three or more times smaller than that of MB fibers. This leads to a corresponding increase in surface area and decrease in basis weight.

Nanofibers combined with other nonwoven products have potential uses in a wide range of filtration applications such as aerosol filters, facemasks, and protective clothing. At present, military fabrics under development designed for chemical and biological protection have been enhanced by laminating a layer of nanofiber between the body side layer and the carbon fibers.

Electrospun nanofiber webs are used for very specialized filtration applications.

Medical application

Nanofibers are also used in medical applications, which include, drug and gene delivery, artificial blood vessels, artificial organs, and medical facemasks. For example, carbon fiber hollow nano tubes, smaller than blood cells, have potential to carry drugs in to blood cells (Figure 6).

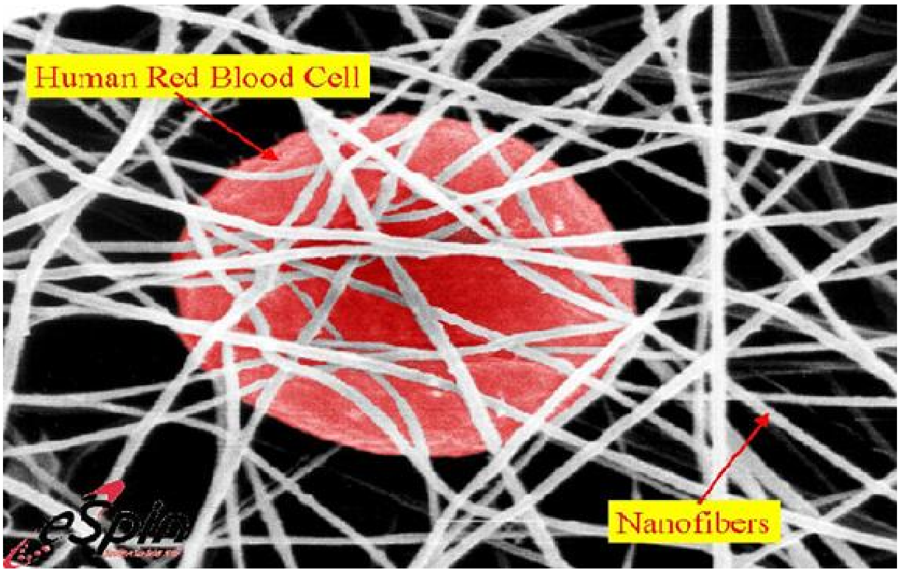


Figure 6 - Comparison of red blood cell with nanofibers web

Nanofibers and webs are capable of delivering medicines directly to internal tissues. Anti-adhesion materials made of cellulose are already available. Researchers have spun a fiber from a compound naturally present in blood. This nanofiber can be used as varieties of medical applications such as bandages or sutures that ultimately dissolve in to body. This nano fiber minimizes infection rate, blood lose and is also absorbed by the body.

To meet these varied requirements a layered composite structure is used. The bulk of the filter is generally made of one or multiple MB layers designed from coarse to fine filaments. This is then combined with a nanofiber web. The MB layer provides fluid resistance while the outer nanofiber layer improves smoothness for health, wear and comfort.

Nanofibers greatly enhance filtration efficiency (FE). Scientists studied the effectiveness of nanofibers on filter substrates for aerosol filtration. They compared filtration and filter media deformation with and without a nanofiber coating of elastic MB and found that the coating of nanofiber on the substrate substantially increases FE.

With most of the nanofiber filter media, a substrate fabric such as SB or MB fabric is used to provide mechanical strength, stabilization, pleating, while nanofiber web component is used to increase filtration performance

PURPOSE

In this activity we intend to familiarize master students / prospective teachers of science with important concepts related to nanofibers and their use in everyday life. The master students will develop an essay which must contain a virtual or real experiment that can be implemented in classroom. Having in view they are master students from Science area (Chemistry) and moreover prospective teaches, they must take care also to didactical and pedagogical aspects. Some of the selected information / examples made available to the students are presented below, most of them beeing accessible from NTSE database (Repository) under L Education (General), Technology (General), R Medicine (General) and Q Science (General) sections. Here's the proposed list:

Fiber Optics

Fiber Optics is a data-delivery system transmitting light and sound through glass fibers. In telecommunications, the fibre optic technology has replaced the copper-wire technology by delivering information 1000 times faster and 100 times farther.

The index of refraction

The index of refraction is a way of measuring the speed of light in a material. Light travels fastest in a vacuum, like in outer space. The speed of light in a vacuum is about 300,000 kilometers (186,000 miles) per second. Index of refraction is calculated by dividing the speed of light in a vacuum by the speed of light in the other medium. The refraction of a vacuum is therefore 1, by definition. The typical value for the cladding of an optical fiber is 1.52. (The index of refraction of the cladding is less than that of the core, causing rays of light leaving the core to be refracted back into the core).

The total internal reflection

The total internal reflection is a phenomenon that happens when a propagating wave strikes a medium boundary at an angle larger than a particular critical angle with respect to the normal to the surface.

Internet fibers optics

Internet fibers optics resembles the brain, because the functions depend on the ability of transmitting electrochemical signals to other cells, and responding appropriately to the signals received from other cells. Moreover, the myelin sheets covering the axons in the brain cells (neurons) resemble the claddings (Figure 7).

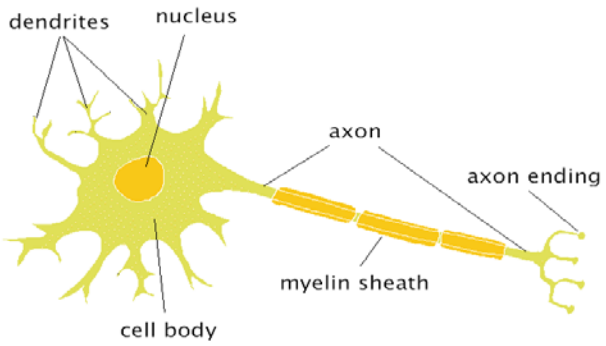


Figure 7: The brain cell (3)

The "sol-gel processing"

The term "sol-gel" refers to a process in which solid nanoparticles dissolved in a liquid (a sol), and brought back together in a controlled manner, to form a continuous three-dimensional network extending throughout the liquid (a gel). The starting materials in the preparation of "sol" are usually inorganic metal salts or metal organic compounds, like metal alkoxides.

Sol-gel is a chemical solution process used to make ceramic and glass materials in a wide variety forms of thin films, fibers, or powders. These include ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, and extremely porous aerogel materials.

In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymeration reactions to form a colloidal suspension, or a "sol". Further processing of the "sol" enables one to make ceramic materials in different forms:

- Thin films can be produced on a piece of substrate by spin-coating or dip-coating.
- Wet gels can be produced if the "sol" is cast into a mold. With further drying and heat-treatment, the gel is converted into dense ceramic or glass articles.
- Aerogel, a highly porous and extremely low density material, can be obtained if the liquid in a wet gel is removed under a supercritical condition.

- Ultra-fine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.
- Ceramic fibers can be drawn from the sol by adjusting the sol's viscosity.

An overview of the sol-gel process is presented in the Figure 8.

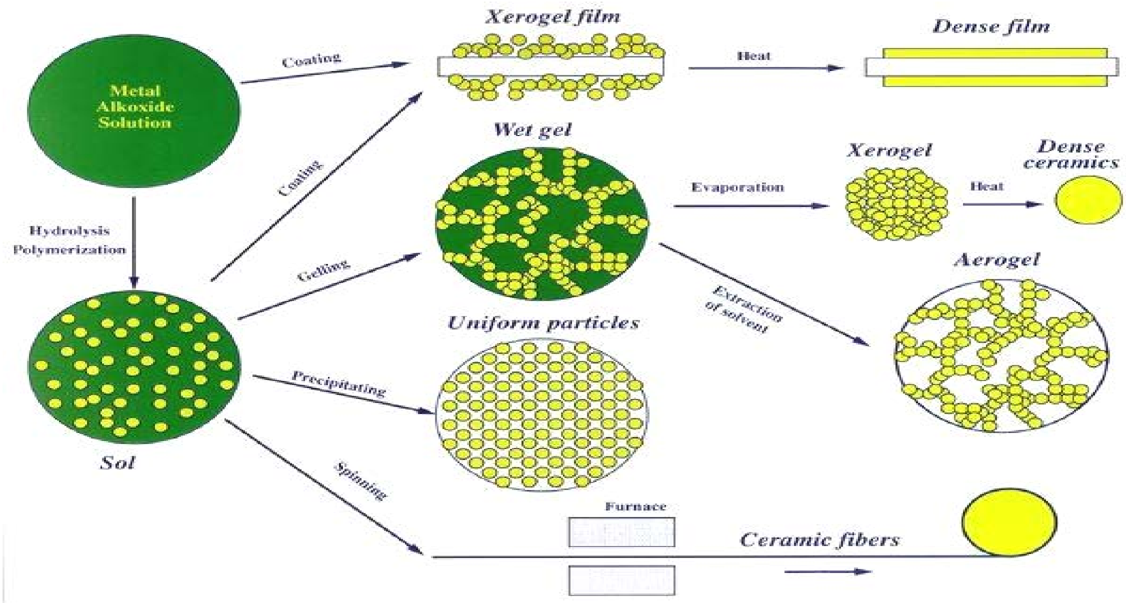


Figure 8: The sol-gel processes (6)

OBJECTIVES

In completing the activity, students develop a variety of process skills critical to their further specialization including:

- working collaboratively;
- interpreting and prioritizing data / information;
- acquiring (by students) of investigative capacities and skills;
- defending an argument;
- increasing the students' confidence and their self-esteem to be involved in the discussion of scientific issues that can be found in ordinary and specialized newspapers;
- experimenting and obtaining reliable results.

From the scientific point of view, these activities allow students to learn about the defined characteristics of:

- nanotechnologies phenomena;
- possibilities of practical application related to theoretical knowledge of nanotechnologies;
- phenomena in the field of nanotechnologies;

- physical characteristics of the phenomena in the field of nanotechnologies;
- carrying out the physical phenomena specific to nanofibers;
- application of the knowledge gained through the study of Science in related fields;
- presentation of the results of an investigative approach using specific Science terminology;
- advantages and disadvantages of nanofibers uses.

The activity designed for the *Chemistry master students (second year)*, sought to develop the knowledge, skills and attitudes of students involved, so that they can participate effectively in discussions on topical issues. At the same time, it stressed the direct exchanges of ideas and experience, laboratory work, to take a clearer picture of the investigative approach in action.

LEARNING RESULTS

When acquiring the information and after realizing the activities, students are able to:

- edit a report / essay where to submit arguments in respect of decisions taken and the related reasons;
- identify the consequences of applying nanofibers to human health, environment and society;
- retrieve specific information in the proposed websites;
- analyze selected information in relation to the proposed objectives;
- decide how to deliver structured information in terms of didactical and pedagogical issues (terms, notions, experimental stages);
- analyze the pros and cons of nanofibers;
- submit collective conclusions made in front of the colleagues, in the laboratory.

CLASSROOM MANAGEMENT & SEQUENCE OF EVENTS

At beginning of the activity starts, master students will search information related with the structure and properties of the optical fibers. Alternatively, the instructor / teacher could present them some of the basic concepts concerning “nano” term and experimental examples by using appropriated images and videos.

The students must share interesting facts and ideas found in the documented text, in order to arrive at a better understanding of the analyzed documents. It is recommended to start the documentation from the experiments proposed in the *Virtual Lab* of the *NTSE Project* (http://vlab.ntse-nanotech.eu/NanoVirtualLab/); the documentation must be made also using the *NTSE Repository* (http://ntse.ssai.valahia.ro/).

As a guideline for students this activity was divided into six “sessions” (see Table 1), some inside laboratory and some outside laboratory.

Table 1. Sequence of Events

Sequence	*Location*	*Activities*
Introduction	Outside lab	Students receive scenario / task and data and brainstorm potential main experiment to be maid. The master students research information related with the structure and properties of the optical fibers.
Session 1	Chemistry lab (50-90 min)	The teacher / instructor facilitates students discussion about nano terms and optical fibers.
Session 2	Outside lab	The students asses information and search for additional information
Session 3	Outside lab	The students outline and produce drafts of essays
Session 4	Chemistry lab (30-40 min)	The students present preliminary drafts to the teacher and verify for reagents, materials etc. in order to be available for experimental work
Session 5	Outside lab	The students revise products according to reviewers' suggestions
Session 6	Chemistry lab (90 min)	The students present products to entire group Each student reviews and evaluate one other student's designed experiment. The experiment selected (in terms of structure, didactical approach, scientific notions etc.) is made by all tstudents

RESOURCES

Procedural resources:

- methods and processes: experimenting, explanation, observation,, conversation, deliberation, discussion;
- form of organization: individual (frontal).

Material resources: video-projector, flipcharts, media texts, PCs, Internet, Colloidal Chemistry laboratory (instruments, reagents, utilities etc.)

PROCESS FINALIZATION

For finalizing the didactic process the university students from each team must express their personal opinions, answering to the following specific issues:

- Pedagogical approaches:
  - General pedagogical criteria:
    - ✓ The clarity of stated educational objectives and the expected results;
    - ✓ If the teaching materials meet the stated educational purpose;

    - The clarity of the learning objectives;
    - Tasks are clearly described;
    - If the activities are adapted to the target group.
  - Pedagogical requirements focused on teacher:
    - To set their own learning goals;
    - To search and explore information;
    - To collect and retrieve information;
    - Communicate with students;
    - To seek and receive support from experts in Nanotechnologies.
- Effectiveness of the content:
  - Information:
    - Information included are detailed and comprehensive;
    - Information included is relevant to the educational objectives set;
    - Information included are appropriate for the target group;
    - Information included helping to enrich the curriculum content;
    - Included information are related to relevant online resources;
    - Information included not contain labels or stereotypes political invoice / cultural / social / racial humiliation;
    - Information included are updated with current topics in the field of nanotechnology
    - Information sources are detailed.
  - Structure:
    - Information included are well structured and organized;
    - Included texts are well structured;
    - Labels are suitable and representative sections for the information;
    - Online resources related with information are relevant;
  - Presentation / Design:
    - Images and sounds included are properly referenced;
    - The texts are readable in terms of color, size, font type, arrangement and visual effects;
    - Graphics, images and videos included are well presented in terms of resolution, color and size;
    - Graphics, images, sound and video resources used are appropriate for the purpose;
    - Using images, videos and audio facilitates understanding;
  - Accuracy:
    - Links included in the proposed resources are appropriate and functional;
    - The language used is correct syntactically and grammatically;
    - Do you think there is a step that was omitted in the description of instructions or training materials?;

- Designed tasks:
  - ✓ The information provided was relevant and motivating for understanding topic task;
  - ✓ Do you consider appropriate / interesting the introduction of laboratory work related to nanomaterials / nanotechnologies?;
  - ✓ You find it useful to acquire additional knowledge about nanomaterials / nanotechnologies?

Important: the last part of the activity becomes very important, due to the fact that it represents a "debriefing" of everything the student has learned and lived during the whole process. The proposed questions dedicated to students substantiate in fact, the activity objectives.

ASSESSMENT SUGESTIONS

When the students make their final presentations has taken into consideration each aspect of their essay and also afterwards the laboratory work. Students receive a grade for this activity based on a combination of group score and an individual score. The individual score has been drawn from peer evaluations of the group process and evaluations of research notes collected by each student.

The evaluation of the students has to take into consideration the following items:

- ➢ understanding of the proposed / introduced concepts and terms;
- ➢ quality of retrieved information and investigation;
- ➢ clarity in the presentation of the selected information;
- ➢ active participation in various stages of the activity (power of argumentation, justification of presented opinions);
- ➢ laboratory work (abilities, skills, accuracy).

IMPACT ON STUDENTS

- ➢ using their real life perception and own life-experience as children / teenagers (especially linked to their knowledge);
- ➢ acquiring the necessary skills and capacities in their dual quality: as students and prospective teachers;
- ➢ maximizing the level of their involvement in the proposed topic;
- ➢ being eager to express their own opinions related to topic and to present their findings within the team and to the whole collective;
- ➢ being capable of gaining a deeper understanding of the current socio-scientific issues;
- ➢ better communicating with teacher and colleagues.

STUDENTS' FEEDBACK

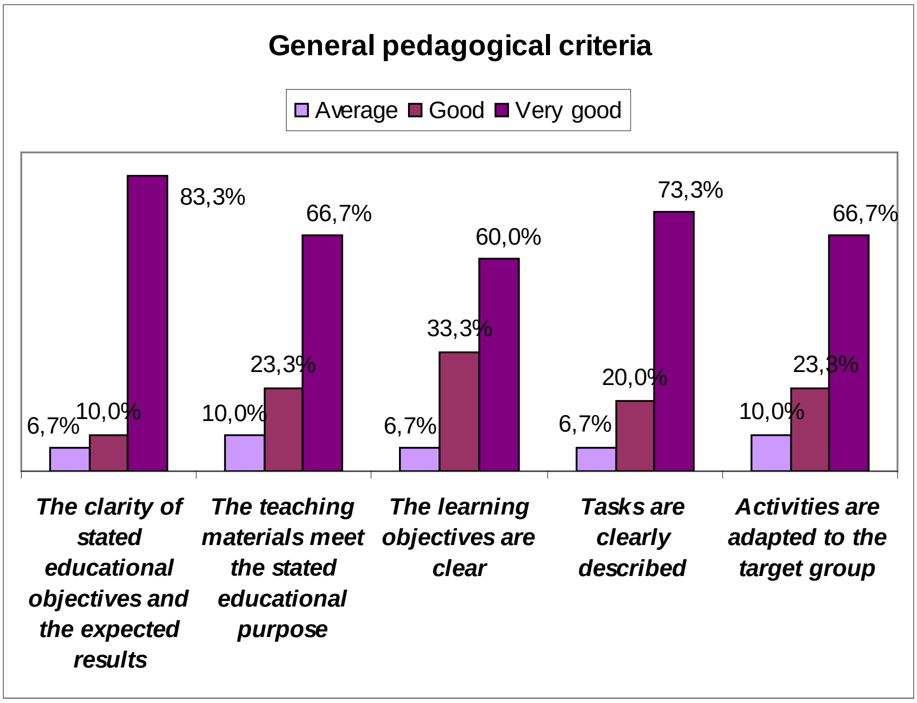
Expressed feedback:

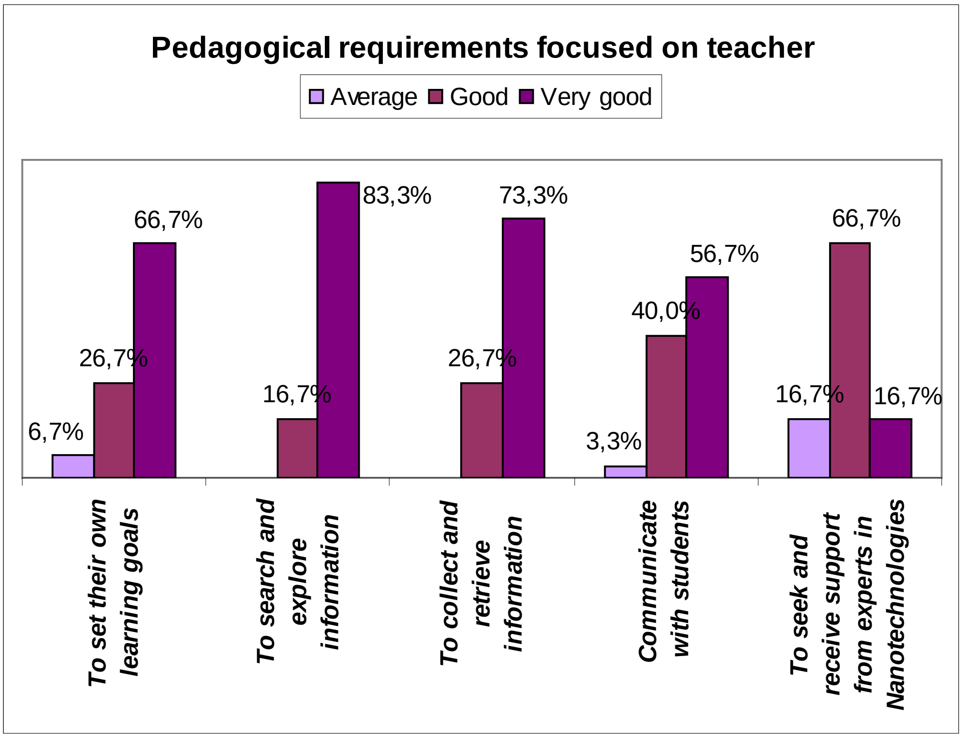
- real and actual issues have been discussed;
- opportunity to work in groups and know better the colleagues;
- possibility to express own opinion on certain issues;
- possibility to communicate without fear with the colleagues, and also with the teacher;
- proper frame to argument the own opinions, as well as listening patiently to others;
- opportunity to compile documents and find out things that otherwise are not so easy to know.

All students declared that they learn something new, interesting and actual during the activity. They were motivated and very interested to the presented / discussed subjects due to the fact that those topics aren't greatly deepened during university curricula.

Processed feedback (graphical results):

Students were invited to fill in a questionnaire, in order to design a graphical feedback after processing their answers. *"Questionnaire for master students / prospective science teachers*" aimed at assessing and collecting information and suggestions on teaching effectiveness, content and usability of educational materials dedicated to teaching / learning Nanotechnologies created in the project Nano-Tech Science Education. The main sections of the questionnaire aimed pedagogical approaches and effectiveness of the content. The results are illustrated in the following diagrams.




Pedagogical requirements focused on teacher
Average
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Very good
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To set their own learning goals
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To collect and retrieve information
Communicate with students
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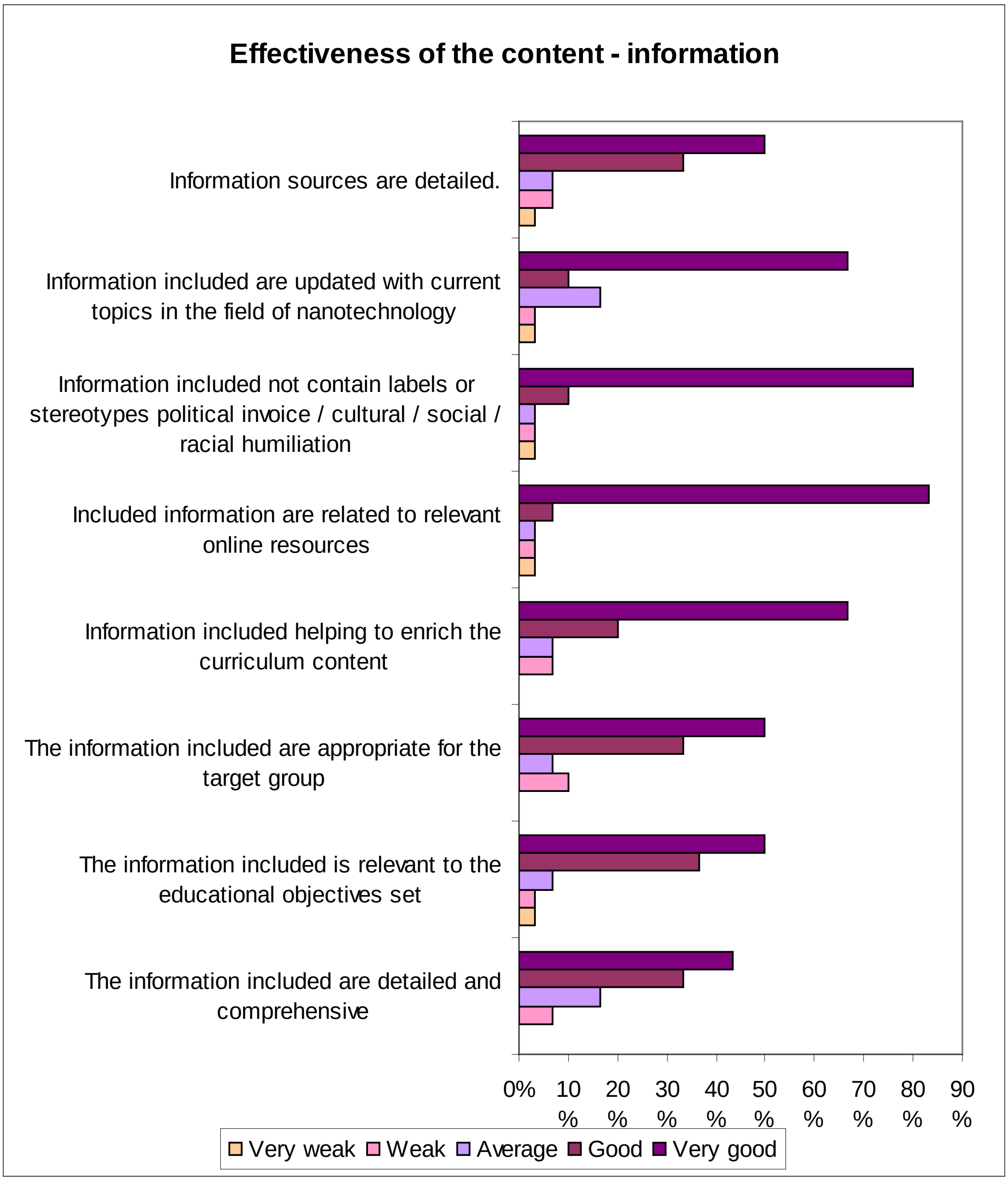
Effectiveness of the content - information
Information sources are detailed.
Information included are updated with current topics in the field of nanotechnology
Information included not contain labels or stereotypes political invoice / cultural / social / racial humiliation
Included information are related to relevant online resources
Information included helping to enrich the curriculum content
The information included are appropriate for the target group
The information included is relevant to the educational objectives set
The information included are detailed and comprehensive
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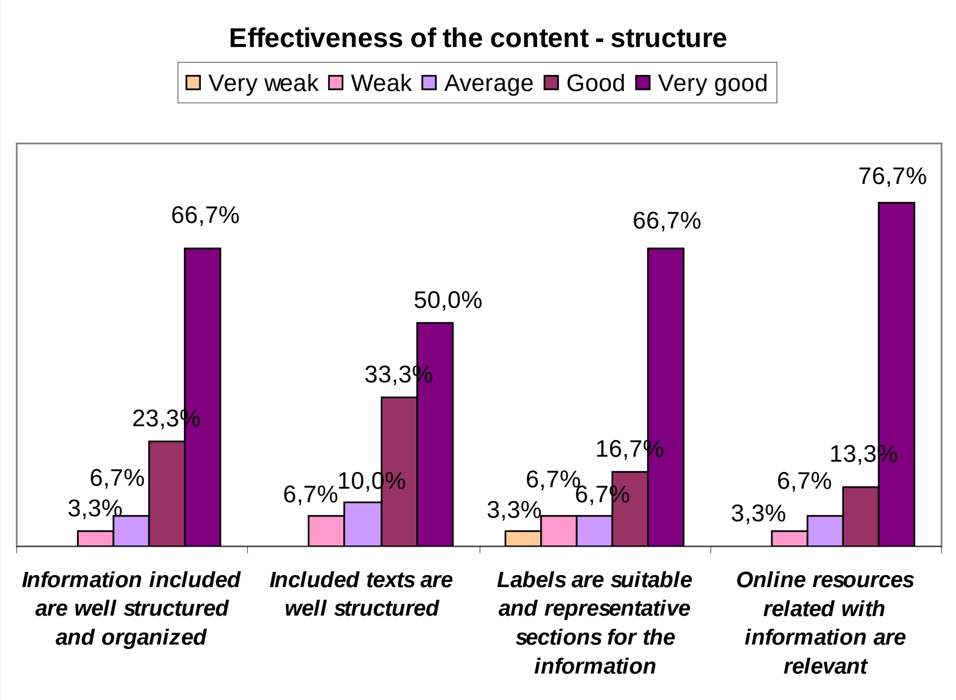
Effectiveness of the content - structure
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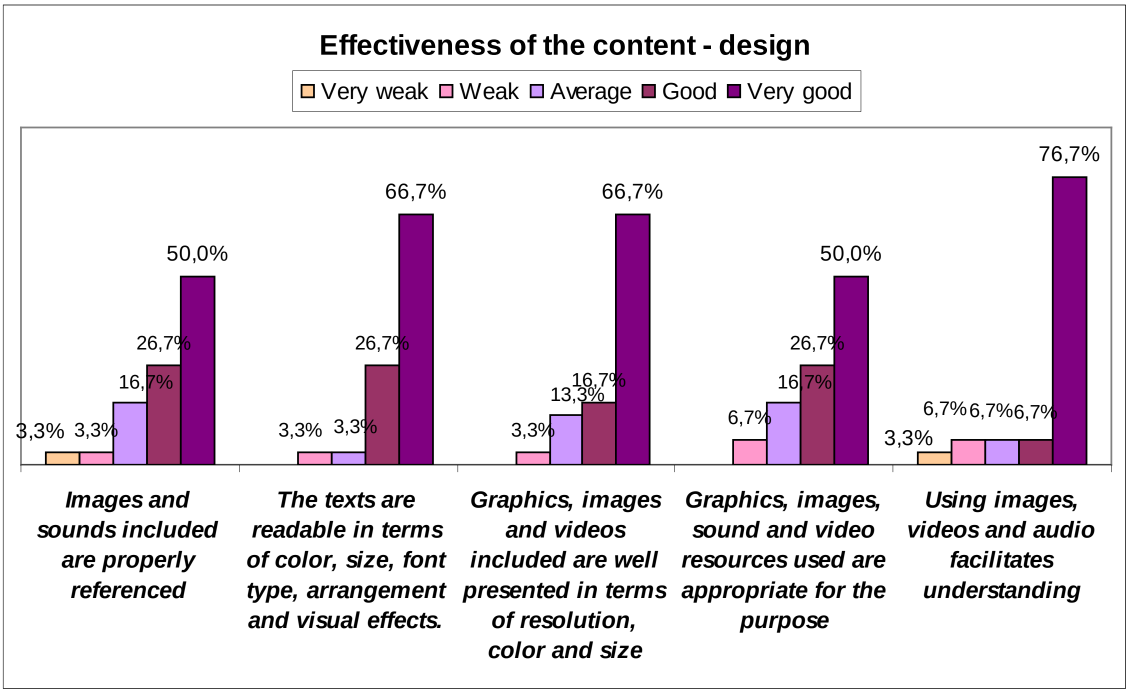
Information included are well structured and organized
Included texts are well structured
Labels are suitable and representative sections for the information
Online resources related with information are relevant


Effectiveness of the content - design
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Images and sounds included are properly referenced
The texts are readable in terms of color, size, font type, arrangement and visual effects.
Graphics, images and videos included are well presented in terms of resolution, color and size
Graphics, images, sound and video resources used are appropriate for the purpose
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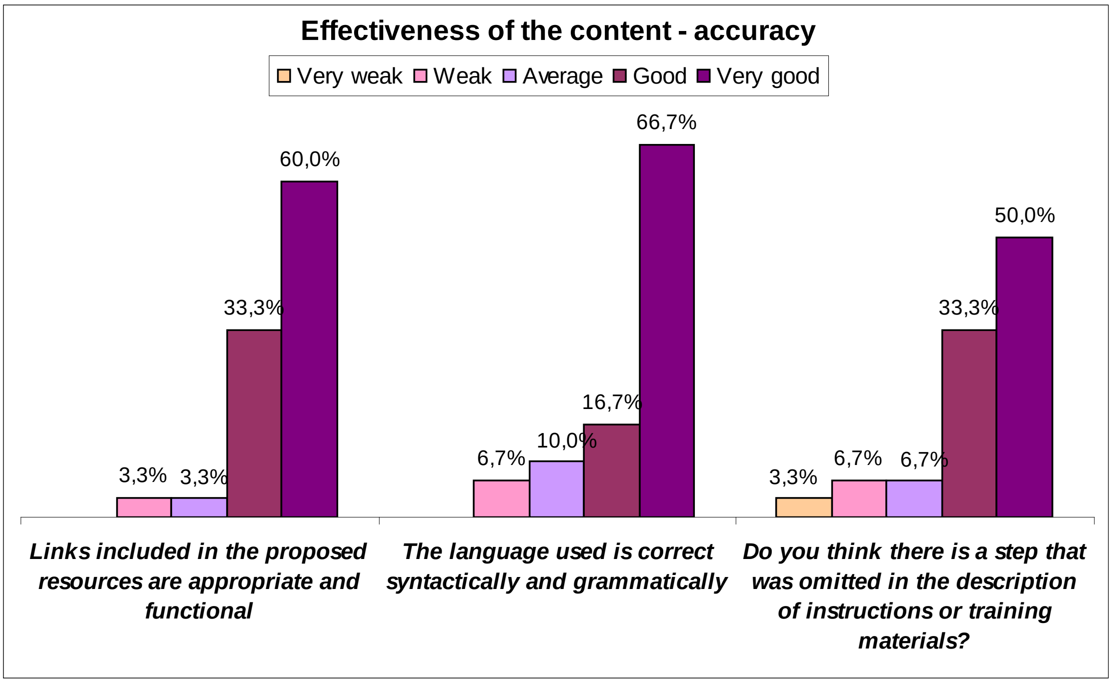
Effectiveness of the content - accuracy
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Weak
Average
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Very good
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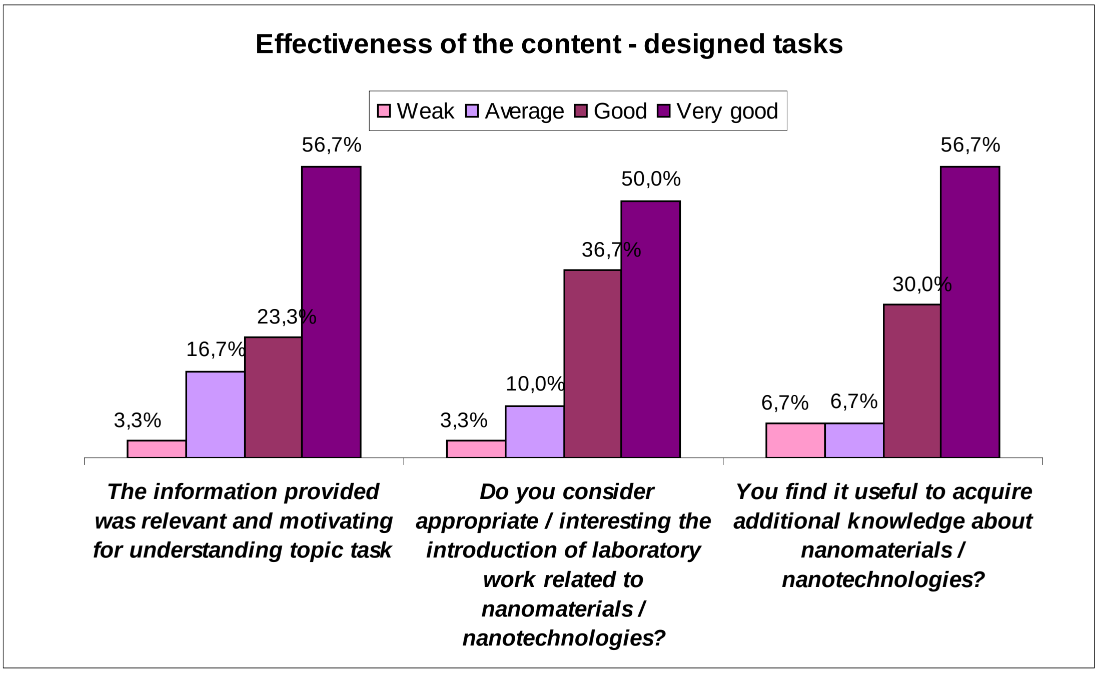
Links included in the proposed resources are appropriate and functional
The language used is correct syntactically and grammatically
Do you think there is a step that was omitted in the description of instructions or training materials?


Effectiveness of the content - designed tasks
Weak
Average
Good
Very good
3,3%
16,7%
23,3%
56,7%
3,3%
10,0%
36,7%
50,0%
6,7%
6,7%
30,0%
56,7%
The information provided was relevant and motivating for understanding topic task
Do you consider appropriate / interesting the introduction of laboratory work related to nanomaterials / nanotechnologies?
You find it useful to acquire additional knowledge about nanomaterials / nanotechnologies?

CONCLUSION

During the proposed master students' activity, they were asked to effectively participate in all the laboratory activity stages, through experimenting, discussing, direct exchanging of ideas and concluding. From the university teacher's point of view, the objectives of the laboratory activity were achieved, not just taking into account the scientific point of view related to the presence of nanotechnology in the related activities, but also from the didactical / pedagogical perspective, contributing to the formation of the students, in order to make them to discern and to take responsible decisions, as future teachers / professors / researchers.

References (web, videos, documents)

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