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Design of a digital journal as a learning strategy for Veterinary Bacteriology

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Abstract

Nowadays, the teacher requires different strategies that allow them to take full advantage of the potential of the students in a constructive and efficient way, in order that they acquire significant learning. The use of work by projects as an educational strategy proposes to work in groups and strengthen the differences in their learning styles and skills. On the other hand, technology was used to strengthen capacities, collaboration and socialization. Therefore, the present work proposed the design and construction of a digital journal with students of the educational program of veterinarian and zootechnician, furthermore teams were integrated so that the approach of science and work by projects. The journal was covered by four sections: veterinary, cultural, sport and entertainment bacteriology. In addition, it was explained on the work by projects and the use of the Canva design platform. Finally, the students defined the name, the contents, the schemes and the images, among others. The dissemination and evaluation of the products created was carried out in the social network of Facebook in a closed group. This strategy made it possible to strengthen the teaching - learning processes, to show the active participation of learners, to increase motivation and creativity.

Learning, Projects, Journal, Technology

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1. Introduction

Education in the 21st century implies great changes in the way of teaching and instructing, teachers see the need to permanently build innovative proposals that promote learning, the desire to learn and student participation so that they feel an active part of the teaching-learning process and take your responsibility in society.

In this way, the present work proposes the construction of a digital journal in which the student will make use of elements of ICT, will strengthen the communicative and scientific activities from a cooperative and collaborative work, where each one participates actively in the realization of activities, from the study of the bacteria of veterinary interest.

In addition, it will demonstrate the learning not only of bacteriological area, but it will include sports, arts and entertainment. The construction of the proposal can be consolidated by motivating learners and guiding them in the search for information, in the use of ICT.

1.1 Justification

Academic performance is a concern inherent in teaching, so it is constantly sought to impact learning. Therefore, it is intended to investigate if the implementation of learning by projects can serve to promote the teaching - learning process, which leads to improve academic performance. This proposal aims to offer a teaching alternative that favors the meaningful learning of the students who take the subject Veterinary Bacteriology.

The present study seeks to integrate knowledge of science, culture, sports and entertainment. In addition to influencing the behavior of students, in the manifestation of affect, in their ability to critically understand the reality that surrounds them, in the development of specific skills for dialogue, self-direction, active participation, cooperation or tolerance.

1.2 Problem

The teachers of the University of Guadalajara observe a demotivation of the students for their learning. For what alternatives are sought that increase the desire to learn, the development of skills such as collaboration, project planning, communication, decision making, use of technology, among others.

The design of collaborative works encourages the active participation of students in the realization of activities. Hence, the development of a digital journal will increase their individual learning strengths, the development of collaborative activities to build knowledge and learn in a practical way the use of technology

1.3 Hypotesis

The elaboration and diffusion of a digital journal allows to raise the levels of learning and to develop the basic competences of the undergraduate students.

1.4 Objective

The objective of this research was to construct a didactic proposal for the students of the third semester of the degree in veterinary medicine, of the University of Guadalajara, for the teaching of bacteriology from a perspective of pedagogy by projects, using as a strategy the design and diffusion of a digital journal that entails an integral learning at the same time.

2. Theoretical framework

The new roles of the teacher and the student imply changes in the traditional ways of teaching and learning; In this context, teaching methodologies characterized by the protagonist role of the student in the challenge of learning are becoming important [Barba et al., 2007]. Hence the need to plate methodologies focused on the student, in order to foster critical reflection and lifelong learning.

Project Based Learning (PBL) has its roots in constructivism (Galena, 2006), which allows teaching to take action, where the learner, based on his previous knowledge, will build new knowledge that enriches and enhances his personal growth (Diaz & Hernández, 1999). The PBL is an educational strategy that exceeds the limits of the models of rote learning, proposes to work with groups of people and be strengthened from the differences in their learning styles and abilities.

The objective of the PBL is to develop competencies, by increasing knowledge, skills and values in an area of interdisciplinary content. The evidence of learning in this educational model is the design, development and dissemination of the product. ICT facilitate the creation, dissemination, evaluation and collaboration among users (Rosario, 2005). In addition, you can create digital journals since there are platforms or special software for it on the web. Digital journals allow savings in printing and publishing costs, include elements of high added value, have a high speed of publication and accessibility is very high (Torres, 2010).

For the aforementioned, this work addresses the construction of the school digital journal as a learning product that is shared on the web and where the participation of students is possible.

3. Research Methodology

It was proposed as a learning project the creation of a digital journal for students who took the subject of veterinary bacteriology, which is taught at the University Center of Agricultural Biological Sciences, University of Guadalajara. The product was developed in a collaborative way, integrating teams of three people and using the Canva design program with the accompaniment of the teacher. The strategy began with orientation to the students about the PBL, the design of a journal and the contents.

By consensus of the group the journal was named, the contents of the four articles that would conform according to the preferences of the members of the team were agreed, taking into account science, culture, sports and entertainment. The journals were evaluated through a rubric and shared on Facebook in a closed group for analysis and feedback.

A survey was conducted on the experience lived in order to know the influence of the design, development and dissemination of the journal on student learning.

4. Results

89.83% of the work teams completed their project on time and shared it. It was observed that 71.19% followed an order in the development of the work, 67.79% of the developed articles show a clear and pertinent content based on the information of the investigated topic, 64.40% have developed skills to work in a team, 42.37% of the journals were elaborated attractive and interesting .

The results of the survey showed that 10.17% mentioned that the responsibility among the members of the team was not shared, 37.28% identified and used the skills of each member of the team, 84.74% satisfied the work by projects. Regarding the CANVA program, 100% did not know it, 28.81% said they do not consider it friendly.

Some of the opinions expressed by the students after designing, elaborating, exhibiting and receiving feedback from their work were: developing their creativity with freedom (88.13%), increasing their knowledge and skills (71.18%), promoting participation and work in team (84.74%), the product was laborious, dynamic and enriching (81.35%), was fun (35.59%), allowed the development of tolerance (22.03%).

5. Discussion

The ABP encouraged a high percentage of students mainly because it allowed them an active participation with freedom to include other areas of knowledge. Escudero (2009) says that students are given a certain freedom to be creative, to introduce new changes, to plan for tastes and preferences.

According to the self-assessment, the students deliberated that the project of elaboration of the digital journal allowed to increase their knowledge and skills in veterinary bacteriology in one and in other interdisciplinary areas of interest (71.18%). The results of the research agree with those of Rodríguez et al (2010) with respect to the research process carried out by 30% of the students reporting that they had learned well and 60% very well.

6. Conclusions

The use of the ABP methodology was positive, since the students were involved in research, planning, organization and teamwork processes. Project work allowed students to build knowledge, develop skills and promote the strengthening of their values. In addition to strengthening their relationships to meet the goal and tasks entrusted.

The journals reflected a level of learning and a degree of creativity of the student in its creation. From the experience of the use of the Canva technological tool, it is clear that there was interaction between the participants both in its execution and in its dissemination. Using the social network Facebook for the dissemination of the journal allowed each student to receive feedback.

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Effect of the inclusion of banana peels (*Roatan or Tabasco bananas*) in feeding New Zealand fryers rabbits

DE LA CRUZ-MORENO, Carlos Omar*†, PEÑA-PARRA, Bladimir, BENÍTEZ MEZA, José Alfredo and BORRAYO-GÓNZALEZ, Juan José Fernando

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Abstract

This study was with the objective to assess the inclusion of banana fresh peels in the feeding of growing and finishing rabbits and its effect over weight gain and carcass performance. 27 New Zealand rabbits were used in this study, males and females rabbits were included, these with an age of 45 ± 1 days, with a live weight of $1,600 \pm 300$ grams. The rabbits were grouped in numbers of nine rabbits picked up at random, and were 3 groups, these were housed individually in three-compartments American style cages. An adjustment period of seven days feeding banana peels was allowed to the rabbits; later three trials were carried out, these with different level of inclusion of banana peels as replacement of comercial feed; trial #1 was 0%, trial #2 was 20% and trial #3 with 40% of banana peels. The study lasted four weeks, and the rabbits were weight-ed weekly to measure total weight gain, daily weight gain and carcass performance. 5 rabbits from each trial group were slaughtered to assess the performance variable in carcass. About the data, to identify possible differents about the initial weight among the trials; were used variance analysis ($p < 0.05$) with the minitab 16 statistic package and with at random method as a whole (unidirectional anova). In the obtained results were not found significative differences among the analysed variables, so it can be concluded that inclusión of banana fresh peels in the feeding of rabbits is feasible and this could lower significantly the economic cost of rabbits production and, the environment impact that banana peels have as industrial and household waste.

Feed, Peels, Banana, Rabbits

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Introduction

Rabbit breeding has been widespread in recent years, excelling over other productive species by having different characteristics that distinguish such as: meat quality with high nutritional value, low cost of infrastructure that can be used in the same , demand little space, its short reproductive cycle, as well as its easy handling and high productivity. All these aspects make the production of rabbits a possibility of animal production system both family and industrial, as well as being able to take advantage of other by-products such as hair, skin and organic fertilizer (López and Montaña, 2015).

Rabbit meat is a white meat of good taste, lean, easily digestible, low in calories, with high levels in proteins and low in cholesterol, sodium and lipids, with a higher proportion of unsaturated fatty acids. It also possesses a characteristic other attractive to its consumers: it does not contain uric acid (Malavé et al., 2013). In this order of ideas, compared to other meats of other species, rabbit meat is richer in proteins, in certain vitamins, in minerals, being a white meat (Calvache, 2010, Malavé et al., 2013). López and Montaña, (2015), report the nutritional content of banana peel; including values of dietary fiber, potential fatty acids and potassium, proteins, essential amino acids, antioxidants and carotenoids among other substances.

Taking into account the consumption of meat from different species, more than 90% of the meat consumed in the world is pork, beef and poultry, of which only 0.5% corresponds to rabbit. While in Italy there is a preference and per capita consumption of 5.3 kilos per year, in Mexico it only reaches around 40 grams. Mexico occupies the fourteenth place in the world as a producer, with 4,200 tons, much lower than China (500 thousand) and Italy (225 thousand) (FAO, 2007).

However, the progress of this activity in our country has been very limited, mainly due to lack of planning and the lack of consideration of this activity in official support, lack of sanitary policies that avoid epizootics, little knowledge and interest in educational institutions and research, problems of consanguinity (and therefore absence of genetically improved animals), little diffusion of the nutritional characteristics and consumption of this meat and poor organization among producers (García et al., 1998).

However, this is not a general situation, since in some states subsidies have been channeled to promote production, organization and creation of marketing structures, which will be mitigated little by little (Olivares et al., 2009). Due to its digestive characteristics as a herbivore it gives a guideline to the possibility of feeding it with different strategies that allow that there is no competition with the human species.

On the other hand, plantain is the second most important fruit tree in Mexico, 95% goes to national consumption and the remaining 5% to export (Pérez, 2010). If we take into account that waste is one of the greatest environmental problems faced by human beings, a problem that increasingly takes on a special gravity and therefore special attention in the so-called developed world, these cumulative effects due to the intense and much the subsequent irrational exploitation of natural resources, directly impacting the contamination of soil, water and air, triggers the interest of using these by-products (Fernandez et al., 2013).

There are reports that it has been used in the form of silage for the feeding of birds and snails, as well as the use in the form of flour for the fattening of chickens (Mosquera et al, 2013). Also, for the elaboration of feed for cattle and as raw material for the elaboration of flour (Vásquez et al., 2008).

With great possibilities of use we find the banana peel (Tabasco or Roatán), as already mentioned is a byproduct in abundance in our state and country, without use and that can therefore become waste and be part of environmental pollution since this by-product represents around 30 to 40% of the total weight of the fruit (Mosquera et al., 2013). The objective was to evaluate the effect of the inclusion of fresh peel of fresh banana in the diet of rabbits in fattening on weight gain and performance of the carcass.

Materials and methods

The research was carried out in the Academic Unit of Veterinary Medicine and Zootechnics of the Autonomous University of Nayarit, located at Compostela-Chapalilla km 3.5, in the municipality of Compostela, Nayarit, from April to May 2017. 27 rabbits of the New Zealand breed with an average life of 45 ± 1 days and weighing $1,600 \pm 300$ grams, they underwent a period of adaptation to the consumption of fresh banana peel for seven days in combination with pelleted food. A commercial feed was used with a guaranteed analysis of: 14% crude protein, 3.5% fat, 8% crude fiber, 8% ash, 12% humidity and 54.5% ELN.

The animals were housed in American type cages divided into three spaces each, three groups of nine rabbits were composed of five males and four females each, forming three treatments: for the three treatments, the basic food was the commercial formula, replacing the 0%, 20% and 40% of the total daily ration for banana peel for treatments 1, 2 and 3, respectively.

The rabbits were fed once a day, weighing daily the amount offered with a Tefal digital scale (model BC5113VO) with a maximum capacity of 5 kg. Five weighings of the rabbits were carried out weekly with a Tor-rey scale (model MFQ-40).

After the feeding or fattening period (28 days), five animals of each treatment were slaughtered, this was done by stripping and slaughtering, considering what the official Mexican standard NOM-033-SAG / ZOO-2014 indicates. Prior to slaughter, the animals were weighed and afterwards the channels were weighed individually (without skin, legs and guts) to measure the variables of the hot carcass weight and carcass yield..

The results obtained were analyzed by Analysis of variance ($P < 0.05$) with the Minitab Statistical Package 16, with a Completely Randomized Design (Unidirectional Anova) between the treatments with respect to the initial weight to the study and sacrifice weight to identify possible differences between these.

Results and Discussion

Table 1 shows the results obtained for variables under study. It can be observed that there were no statistical differences ($P < 0.05$) for the variables between the different treatments. It should be noted that treatment two (T2) shows slight numerical differences in their favor, but not statistics, while T1 offered the lowest values. It is important to mention that the total of the experimental animals were apparently healthy during the study time, at slaughter and post mortem. In a report by Valdivié et al., (2008) mention maximum values of inclusion of banana peel meal in the diet for rabbits in different stages from 25 to 30 percent. In another study, Palacios and Córdoba (2009) used with good results 15% of banana peel meal in broiler feed and found that this level can be used without detriment to the production characteristics.

Table 1. Mean values and standard deviation for the variables under study.

	n	T1 = 0 %	D.E.	T2 = 20 %	D.E.	T3 = 40 %	D.E.
PI (gr)	9	1,642	110	1,702	207	1,644	103
PF (gr)	9	2,436	200	2,612	334	2,472	120
GTP (gr)	9	793 ^a	140	911 ^a	176	828 ^a	85
GDP (gr)	9	28.3 ^a	4.9	32.5 ^a	6.2	29.5 ^a	3.0
PS (gr)	5	2,387 ^a	206	2,550 ^a	342	2,450 ^a	148
PCC (gr)	5	1,333 ^a	141	1,430 ^a	236	1,375 ^a	115
RC (%)	5	55.84 ^a	1.62	56.08 ^a	6.90	56.12 ^a	2.03

^a Equal literals between rows indicate statistical similarity ($P > 0.05$); D.E. = standard deviation; PI = initial weight; PF = final weight; GTP = total weight gain; GDP = daily weight gain; PS = weight at sacrifice; PCC = hot channel weight; RC = channel performance.

Conclusion

The analysis of variance did not show an effect of the main factor (treatment), not finding significant statistical difference between treatments ($P > 0.05$). Concluding that the use or inclusion of banana peel in the feeding of rabbits in fattening is a viable alternative for the use of an unconventional by-product, little used in animal feed, in addition to being able to considerably reduce production costs and the impact environmental.

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ACTN3 genotypes and their association with athletes somatotype: Results of a pilot study

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Abstract

The genotypes RR, RX and XX of the alpha-actinin-3 gene (ACTN3), are related to the physical-sports abilities and body composition, however, there were not found studies that relate the genotypes with the somatotype. The purpose of this study was to know if the ACTN3 genotypes are associated with the somatotype in athletes regardless of the sport they practice. In a cross sectional study 31 athletes from different sports were evaluated. DNA from white blood cells in peripheral blood were obtained. Anthropometric measurements were taken and so the fat mass, muscle mass, and somatotype were calculated. Both men and women, carriers of the RR genotype presented greater mesomorphy, followed by the RX genotype carriers. In the case of men, carriers of genotype XX presented greater ectomorphy. Men with RR and RX genotypes exhibit a mesomorph-balanced somatotype, women with the same genotypes, present an endomorph-mesomorphic somatotype. Men with genotype XX exhibit an ecto-mesomorphic genotype, females an endo-mesomorphic somatotype. The mesomorphy is the main component of the somatotype that defines the athletes carrying the RR genotype, while the ectomorphism to the XX genotype carriers.

Sports Genetics, Alpha-Actinin-3, Body Composition

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1. Introduction

The human body form is genetically determined, however, it can be modified by external factors generally referred to as environmental factors, such as physical activity and diet (Huygens et al., 2004). The somatotype developed by Sheldon (1954), is a representation of the body form, where the main components endo (fat), meso (muscle) and ectomorphy (linearity) characterize the subject. Johnson et al. (2015), reported that indicators of adiposity as percentage of fat and fat mass, express less variability to greater cardiovascular conditioning; that is, physical activity exerts in each subject a suppressive effect on the variability of fat tissue, caused by external factors. With regard to lean mass, its variability is influenced more by genetic factors than by environmental influences (Johnson et al., 2015).

Product of these effects, genetic and environmental, the dispersion in the endomorphic component is greater in sedentary subjects, than among athletes (Rivera-Sosa, 2016), when its somatotype is graphed in the somatocarta. On the other hand, in studies of heritability in the somatotype, it has been documented that mesomorphy is determined up to 59% by additive genetic factors, ectomorphy by 45% (Jelenkovic et al., 2011) and endomorphy by 40%. (Saranga et al., 2008). Therefore, checking the influence of genes related to muscle function and their participation in the development of muscle mass, body composition or body shape is one of the areas to be investigated.

That is, to analyze whether the genotypes associated with aerobic and anaerobic capacity, strength or muscular endurance (Oliveira et al., 2016), are also involved in the corporal form. Recently, one of the most studied genes in the field of sports performance and physical abilities has been alpha-actinin-3 (ACTN3).

This gene has two alleles: the R allele, which functionally encodes the alpha-actinin-3 protein, while the X allele encodes it non-functionally (MacArthur and North, 2004). Alpha-actinin-3 is one of the main structural proteins of the sarcomere Z line at the muscle level and is expressed only in skeletal muscle fast fibers (Beggs et al., 1992). The genotypes of ACTN3 (RR, RX and XX) have been associated with sports performance: aerobic (Ahmetov et al., 2010; Pimenta et al., 2013) or anaerobic (Mikami et al., 2014; Papadimitriou et al., 2016). In this sense, Yang et al. (2003), reported that genotype XX favors aerobic capacity activities; while the RR genotype favors anaerobic capacity activities, such as the speed of movement and the generation of muscular strength.

The literature published in the main scientific bases, does not show up to the present, reports on the associations between the genotypes of ACTN3 and the somatotype. The athlete population represents a population group where the lower variability of the fat component could allow detecting the influence of the ACTN3 gene on the somatotype components. To establish if: 1) the carriers of the RR and RX genotypes vs. XX, present greater mesomorphy, and if 2) the carriers of the genotype XX vs. RR and RX, present greater ectomorphy. Therefore, the purpose of the present work was to determine the possible associations between the genotypes of ACTN3 and the somatotype in Mexican university athletes.

2. Materials and methods

Subjects

Under a cross-sectional design and for convenience, 31 athletes of competitive university and national level (18 men and 13 women) were recruited. The inclusion criteria were: male and female athletes participating in national and local competitive events, age 18 to 30 years.

We excluded athletes with less than 2 years of practicing their sport, with the presence of any disease, who were under medical treatment or muscle injury. The athletes agreed to participate voluntarily in the study and signed the informed consent letter. The study was approved by the ethics committee of the Autonomous University of Ciudad Juárez, based on the recommendations of the Helsinki Declaration.

Genotypes

A blood sample was obtained through a puncture in the middle ulnar vein; subsequently, Genu Puregene Blood Kit commercial kit (Gentra, Minneapolis, USA) was used to obtain leukocyte genomic DNA. A segment of 291 base pairs (bp) of the ACTN3 gene was amplified using the polymerase chain reaction (PCR) technique, using the following primers: forward primer: 5'-CTGTTGCCTGTGGTAAGTGGG-3', on the other hand used the reverse primer: 5'-TGGTCACAGTATGCAGGAGGG-3'. The following amplification conditions were applied: initial denaturation at 95 ° C for 10 min, followed by 35 cycles of denaturation at 95 ° C for 1 min, an alignment at 60 ° C for 30 s, elongation at 72 ° C for 1 min .

The PCR product was visualized on 1% agarose gels. For the determination of ACTN3 genotypes, the PCR amplification and the DdeI enzyme (*Desulfovibrio desulfuricans*) (BioLabs, Inc. Beverly, USA) were combined and incubated at 37 ° C in humid heat for 4 h, then the enzyme it was inactivated at 65 ° C for 20 min. The digestion products were observed in 2% agarose gels and visualized through a UV transilluminator (Bio-Rad, Hercules, USA). For the RR genotype the following bands were obtained: 205 bp and 86 bp, while for the RX genotype: 205 bp, 108 bp, 97 bp and 86 bp, finally, for the genotype XX: 108 bp, 97 bp and 86 pb.

Anthropometric measurements

All these measurements were made following the methodology standardized by the International Society for the Advancement of Cineanthropometry (ISAK for its acronym in English), registering the weight, height, 9 skinfolds, 13 perimeters, 10 lengths and 6 body diameters (Kevin and Olds, 1996). The weight was recorded in kilograms with a digital scale (SECA 876, Hamburg, Germany), taking care that the athlete's feet were in a central position and symmetrical on the scale, which was handled on a flat, horizontal and smooth surface.

The size was recorded in centimeters using a stadiometer (SECA 206, Hamburg, Germany), with an approximation of 1 mm. For the stature it was taken care of that the person was barefoot, the feet together and kept his head in the Frankfort plane; this measurement was recorded at the end of a deep inhalation, asking the person to maintain a right posture during the measurements. The BMI was calculated by weight / height². For the other measurements an anthropometric equipment was used (Rosscraft Tom Kit, Surrey, Canada). The software LifeSize 2.0 (Lifesize 2.0, Sydney, Australia) was used to determine the components of the somatotype (Olds and Norton, 2000).

Statistic analysis

To determine the differences in the genotypic frequencies, a Chi square was performed (χ^2). To find differences between genotypes and between each variable studied, a one-way ANOVA was performed with the Tukey post hoc test. To find differences between genotypes and between sex, a two-way ANOVA was performed. To know the independent participation of the genotype (RR, RX and XX) and sex (independent variables) in the determination of endomorphy and muscle mass (dependent variables) of the athletes, a multiple regression analysis was performed by the method of successive steps.

A level of significance of 0.05 was established. The data was analyzed with the SPSS 22.0 program.

3. Results

The athletes practiced the following sports: speed and throws ($n = 11$), weightlifting ($n = 1$), physical-bodybuilding ($n = 3$), swimming ($n = 1$), soccer ($n = 3$), judo ($n = 1$), baseball ($n = 5$) and handball ($n = 6$).

The frequency of ACTN3 genotypes is shown in Table 1. The total population is in Hardy-Weinberg equilibrium ($\chi^2 = 0.00$, $P = 0.97$). In the present study, it is shown that in both sexes, the carriers with RR genotype are more mesomorphic than the XX. Men with RR and RX genotypes exhibit a mesomorfo-balanced somatotype, whereas women with the same genotypes have an endomorph-mesomorphic somatotype. Men with genotype XX exhibit an ectomorphic-mesomorphic genotype, and women an endo-mesomorphic somatotype (Figure 1). The men compared with the women had greater muscle mass and greater ectomorphy, on the contrary lower fat mass and lower endomorphy ($P < 0.05$) (Table 2).

Genotype and sex independently determined 41.4% of the differences in mesomorphy ($R^2 = 0.41$, $P < 0.01$).

Mesomorphy = $4.9 + (0.86 \times \text{sex}) - (0.73 \times \text{genotype})$. For sex, 0 = women and 1 = men. For the genotypes, 1 = RR, 2 = RX and 3 = XX.

Sex independently determined 59.2% of the differences in the percentage of muscle mass ($R^2 = 0.59$, $P < 0.01$). The genotype was excluded in the model.

Muscle mass (%) = $37.2 + (8.8 \times \text{sex})$. Where 0 = women, 1 = men.

4. Discussion

The present study groups the athletes by their genotype and analyzes their somatotype regardless of the sport they were practicing. It was found in both genders that, the mesomorphy is higher in the athletes with the RR genotype, followed by the RX genotype. In contrast, ectomorphy was greater in athletes with the XX genotype. The above, agrees with what reported by Yang et al. (2003); Pimenta et al. (2013); Orysiak et al. (2014), who report that RR and RX genotypes are associated with an improvement in anaerobic sport performance.

In this same sense, genotype XX has been associated with a possible improvement in performance in sports activities with aerobic characteristics (Ahmetov et al., 2010, Pimenta et al., 2013); Athletes who practice these sports usually have a more ecto-mesomorphic somatotype (Bale et al., 1986). The population group of athletes practiced sports of both aerobic and anaerobic characteristics. In them, the training promotes optimal muscle development and minimizes endomorphic variability, which independent athletes could develop (Johnson et al., 2015). Normally, anaerobic-type athletes have greater muscle mass than aerobic-type athletes, indicating a greater mesomorphy (Poblano-Alcalá and Braun-Zawosnik, 2014).

The development of muscle mass associated with the genotype could be attributed to the fact that the RR and RX genotypes vs. XX have higher concentrations of testosterone (Ahmetov et al., 2014). This hormone has anabolic effects, increasing or promoting the development of muscle mass. In the same sense, it has recently been reported that the possessors of the RR vs. XX genotypes, their muscle fibers IIa and IIx have a greater cross sectional area (Broos et al., 2016), which allows them to develop greater power (Orysiak and col., 2014), strength (Broos et al., 2015) and speed (Mikami et al., 2014), aspects related to mesomorphy.

In contrast, carriers of genotype XX have a higher proportion of slow fibers type I, compared to the genotype RR and RX (Ahmetov et al., 2011), favoring aerobic endurance activities (Yang et al., 2003). Among the athletes studied, a genotype distribution of 35% was found for the RR genotype, similar to that reported in Spanish swimmers (Ruiz et al., 2013), and in Israeli athletes (Eynon et al., 2009). For allelic distribution, 41% was found in the X allele, similar to what was previously reported in the Hispanic and European population (Mills et al., 2001), as well as in elite Lithuanian athletes (Ginevičiene et al., 2011).

The similarity in the allelic and genotypic frequencies with the European population, could be due in part to crosses between indigenous people with Spaniards, occurred during and after the Spanish conquest (Rangel-Villalobos et al., 2009), or to the high conservation of the ACTN3 gene that it has remained in the population for a long time (Mills et al., 2001, MacArthur and North, 2004).

The allelic frequencies of this gene (R and X) and its genotype (RR, RX and XX) are very different among the population (Mills et al., 2001). In this sense, Yang et al. (2007), have found high prevalences of the RR genotype in African black athletes (40% to 87%), however, low prevalences in white athletes (17% to 30%). Regarding the genotype XX, Yang et al. (2007), found very low or absent prevalences in African black athletes (0% to 12%), whereas low prevalences in white athletes (18% to 25%).

The results of this study, although they were not done with a population interest, are the first report of its prevalence in a Mexican population of athletes at the university level. On the other hand, it was also obtained that besides having sex, having a certain genotype favors partially, also the presence of a certain somatotype (41% of the variance observed).

To our knowledge, this is the first work that reports an association between genotypes of the ACTN3 gene and the somatotype. However, being a pilot study, the results obtained need confirmation in a larger study.

5. Conclusions

As a main result, it was observed that mesomorphy is the main component of the somatotype that defines the athletes carrying the RR genotype, however, ectomorphy is the main component of the somatotype that defines the carriers of the XX genotype. Between 41% and 59.2% of differences found in mesomorphy and ectomorphy were determined by differences in genotype and sex

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Anexo

Sample	Genotypic frequency n (%)			Allelic frequency %	
	RR	RX	XX	R	X
Total athletes (31)	11 (35.6)	15 (48.1)	5 (16.2)	59.7	40.3
Men (18)	7 (37.3)	8 (47.5)	3 (15.1)	61.1	38.9
Women (13)	4 (33.2)	7 (48.8)	2 (17.9)	57.7	42.3

$\chi^2 = 0.00$; $P = 0.97$.

Table 1 Genotypic and allelic frequencies of the *ACTN3* gene

	Men			Women		
	RR (n= 7)	RX (n= 8)	XX (n= 3)	RR (n= 4)	RX (n= 7)	XX (n= 2)
Weight (kg)	77.7 ± 8.4	71.3 ± 11.4	72.10 ± 6.2	60.9 ± 6.1	63.5 ± 12.8	72.6 ± 8.8
Height (m)	1.81 ± 0.03	1.76 ± 0.05	1.83 ± 0.09	1.61 ± 0.08 ^a	1.66 ± 0.09 ^a	1.71 ± 0.02 ^a
BMI (kg / m ²)	23.7 ± 2.2	23.0 ± 2.8	21.5 ± 0.8	23.6 ± 0.8	23.0 ± 2.7	24.8 ± 3.5
Body fat (%)	14.4 ± 7.2	11.5 ± 3.9	9.2 ± 2.4	16.4 ± 4.0 ^a	16.2 ± 4.0 ^a	19.1 ± 2.3 ^a
Muscle mass (%)	48.8 ± 4.2	44.2 ± 3.0	44.7 ± 1.7	37.4 ± 3.9 ^a	37.6 ± 3.9 ^a	35.6 ± 2.0 ^a
Endomorphy	2.9 ± 1.5	2.7 ± 1.4	1.9 ± 0.4	4.2 ± 1.1 ^a	3.7 ± 1.2 ^a	4.8 ± 1.1 ^a
Mesomorphy	5.0 ± 0.7	4.6 ± 1.0	3.1 ± 1.1 ^b	4.2 ± 0.4	3.3 ± 0.9	3.2 ± 0.9 ^b
Ectomorphy	2.5 ± 1.0	2.7 ± 1.1	3.6 ± 0.8	1.4 ± 0.6 ^a	2.0 ± 1.0 ^a	1.6 ± 1.3 ^a

Values are presented in averages ± DE. ^a differences between sex. ^b differences between genotype RR vs XX. $P < 0.05$.

Table 2 Anthropometric characteristics between sex and genotypes of *ACTN3*

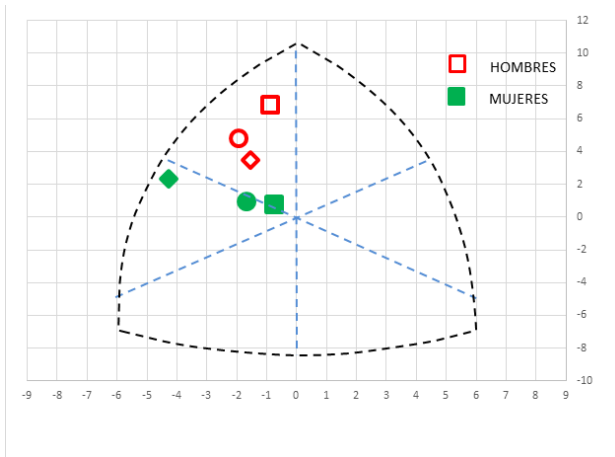


Figure 1 Average somatotype in men and women athletes with different genotypes of ACTN3. Figures without filling correspond to men, figures with fill correspond to women. Squares: RR genotype, Circles: RX genotype, Rhombos: genotype XX. Significant difference was found in the carriers of the RR vs. XX genotype ($P < 0.05$).

Synthesis and characterization of ZnO nanoparticles prepared by pulsed laser ablation in different liquid medium

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Abstract

Zinc oxide nanoparticles were prepared by pulsed laser ablation of zinc metal target using different liquid medium, distilled water and 2-propanol. Ablation was carried out using 532 nm and 1064 nm output from a pulsed (10 ns, 10 Hz) Nd:YAG, separately. Analysis of the morphology, crystalline phase, elemental composition and optical properties were done using Transmission Electron Microscopy (TEM), X-Ray Photoelectron Spectroscopy (XPS) and UV-Visible absorption. TEM analysis showed that a change in liquid medium and laser wavelength resulted in ZnO and Zn(OH)₂ nanoparticles with different sizes and morphologies. XPS results confirmed the compositions and chemical states of these nanoparticles. The results of this work demonstrated that by varying the liquid medium, the structure, composition, morphology and optical properties of the nanomaterials could be modified during pulsed laser ablation in liquid.

Pulsed Laser Ablation, Semiconductor, Nanomaterials, Zinc Oxide

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1. Introduction

Zinc oxide is a semiconducting material with optical energy band gap of 3.3 eV, also it is considered as an important material due its optical properties, electrical conductivity and piezoelectricity (Djurisic & Leung, 2006; Singh, Swarnkar, & Gopal, 2010). ZnO have been investigated due its applications in photovoltaics, photonics, light emitting devices, photo detectors, transparent conductive films, etc. (Francis B. Dejene, 2011). Nanostructures of ZnO have been synthesized by different chemical methods, such as solvothermal (Dev, Kar, Chakrabarti, & Chaudhuri, 2006), thermal evaporation (Pan, Dai, & Wang, 2001), sol-gel synthesis (Haase, Weller, & Henglein, 1988), chemical vapor deposition (Gorla et al., 1999; Song et al., 2013).

However, chemical methods involve the generation of chemical by-products, so, an alternative synthesis method to produce NPs colloids without impurities is Pulsed Laser Ablation in Liquid (PLAL) (Amendola & Meneghetti, 2009). In PLAL, a solid target is submerged into liquid medium; a high energy laser beam interacts with the solid target surface forming a plasma plume.

The chemical species inside of plasma plume are subjected to a nucleation and condensation processes which occur in the expanding plasma plume allowing nanoparticles growth in the liquid (Zeng et al., 2012). Nanorings of SiC have been synthesized by PLAL irradiating a Si target in ethanol. The proposed growth mechanisms are based on the plasma formation following by the reaction between the high active species and the carbon species from ethanol molecules allowing the nucleation and growth of SiC rings nanostructures (Yang et al., 2012).

However, the proposed mechanisms are under investigation because they are strongly depend of the experimental conditions, target and liquid medium properties, such as pulse duration, laser beam energy pulse, laser beam focusing, repetition rate, the presence of surfactant molecules in the liquid medium, the optical properties of the target, etc. (Itina, 2011).

Therefore, the present work takes into account the pulsed laser ablation of a Zn target in distilled water and 2-propanol using two laser wavelength from a Nd: YAG output to study the effect of liquid as well as laser wavelength on the size, morphology and structure of the laser ablation products. TEM analysis showed that a change in the liquid medium resulted in different morphologies and sizes of the zinc nanomaterials. XPS results confirmed that the NPs obtained were that of ZnO and Zn(OH)₂ for the laser ablation.

1.1 Justification

The advantages of using PLAL as synthesis method for semiconductor nanomaterials are that it is a simple experimental technique without the use of toxic chemical precursors to control the growth of the colloids and it can be applied in pure water or in a biologically compatible aqueous solution. However, there are some limitations such as controlling the average size distribution and the rate of ablation, also, the start-up costs due to the laser equipment, materials and optics supplies can be excessive.

Therefore, considering that the high costs are presented at the initial step, and the laser device, optical and raw materials supplies are available, the synthesis of nanomaterials by PLAL could be improved by the systematic studies on the effect of the adjustment of laser processing and experimental ablation parameters, resulting in an affordable synthesis method.

1.2 Problem

Up to date, there have been substantial interests in the preparation, characterization and application of semiconductor materials at the nanometer scale. As a consequence, the physical and chemical properties of semiconductor nanomaterials are intensively studied looking for their application in new technologies, such as photovoltaics, optoelectronics, sensors, light emitting devices, etc.

There are chemical methods which are reliable and cost effective, allowing better control on the shape and size of the semiconductor nanoparticles by functionalization with different organic capping ligands. However, a huge disadvantage is the use of toxic chemical precursors, because the disposal of them implies that chemical methods represent an eco-unfriendly synthesis route. So, it is needed simpler and clean technologies for the preparation of nanostructures of metals, metallic alloys, semiconductors and polymers.

1.3 Hypothesis

The pulsed laser ablation of zinc metal target in distilled water and 2-propanol allows the production of ZnO nanomaterials having different size and properties.

1.4 Objectives

1.4.1 General Objective

The main objective is to synthesize and characterize nanomaterials of ZnO using pulsed laser ablation in liquid.

1.4.2 Specific Objectives

- To study the effects of laser ablation parameters (fluence and wavelength) on the formation and properties of the nanomaterials of ZnO by PLAL.

- To investigate the behavior of different liquid media (distilled water and 2-propanol) on the production of the nanomaterials as well as their structure, size distribution and morphology.
- To characterize the structure, morphology, composition and chemical states of these nanomaterials using various characterization techniques.
- To evaluate the optical absorption properties of these nanomaterial colloids.

2. Background

An alternative to synthesize ZnO nanostructures with different morphology, size, structure and optical properties is PLAL, a simple environmental friendly method. It is possible to vary some ablation conditions, such as liquid medium, pulse width and energy fluence in order to study the final properties of the as-prepared ZnO nanomaterials.

Zn metal and ZnO powders targets have been ablated in different liquid media, SDS, distilled water and 2-propanol (Hu et al., 2011; Liang, Tian, Tsuruoka, Cai, & Koshizaki, 2011; Shoutarou et al., 2010; Singh et al., 2010; Thareja & Shukla, 2007; Zeng, Cai, Li, Hu, & Liu, 2005; Zeng et al., 2010; Zeng et al., 2007) synthesizing ZnO nanomaterials with different morphologies.

Rods and flakes shaped ZnO nanoparticles, were formed by ablation of Zn metal and ZnO pellet in distilled water, respectively, showing both UV and visible emissions (Hu et al., 2011). Also, ZnO spherical nanoparticles have been obtained by ablation with 355 nm laser beam in distilled water and 2-propanol (Thareja & Shukla, 2007) and by ablation of ZnO chemical precursors in 2-propanol with a continuous laser (Shoutarou et al., 2010).

Zn/ZnO nanoparticles were synthesized by ablation of Zn metal target in tetrahydrofuran using a high-power (25 W) picosecond-pulsed laser system, to achieve a control in their size and in the ablation efficiency by varying the repetition rate and laser fluence (Wagener, Faramarzi, Schwenke, Rosenfeld, & Barcikowski, 2011; Wagener, Schwenke, Chichkov, & Barcikowski, 2010). Moreover, a wavelength of 248 nm from a KrF excimer laser was used to irradiate a ZnO target in distilled water resulting in ZnO nanoparticles with ferromagnetic properties (Zhao, Huang, & Abiade, 2012).

ZnO quantum dots (1-8 nm) were synthesized through the size reduction by laser irradiation of ZnO hollow nanospheres (30 nm) originally prepared by PLAL and dispersed in distilled water. As the laser irradiation time was increased, the size of the ZnO hollow nanospheres was decreased, due to the laser fragmentation mechanism (Hu et al., 2012).

Laser parameters such as the laser wavelength, output power and fluence can be varied in order to study their effects on the size, morphology, structure and optical properties of the as-prepared ZnO nanostructures. In this way, w-ZnO and ϵ -Zn(OH)₂ composite nanoparticles (500 nm) with spherical and hexagonal shapes synthesized by pulsed laser ablation in water at different laser power outputs (800 mJ/pulse of 1064 nm and 400 mJ/pulse of 532 nm Nd:YAG), possessed an optical band gap of 3.1 eV (Lin, Shen, & Chen, 2011). Also ZnO nanoparticles were synthesized by PLAL in distilled water using the 1064 nm and 532 nm outputs from a Nd:YAG laser system at different fluences (Dorranian, Solati, & Dejam, 2012), where ZnO nanoparticles with smaller sizes by ablation with 532 nm and photoluminescence emissions at 335 nm and 375-377 nm.

3. Experimental Methodology

PLAL was the experimental technique used for the synthesis of ZnO nanomaterials. As described earlier, it is based on the pulsed laser ablation of a solid target in a liquid medium. In this study Nd:YAG pulsed laser system (Model LQ 929, Solar Laser System) having 10 ns of pulse width and 10 Hz of repetition rate, was used to irradiate a highly pure (99.99%) zinc metal plate as is shown in Figure 1.

3.1 Experimental design

The experimental parameters varied for the pulsed laser ablation were the energy per unit of area (energy fluence) and the liquid medium. The laser beam was focused using a convergent lens of suitable focal length. The energy fluence was estimated at different focusing conditions. Also, the liquid medium was changed in the present work.

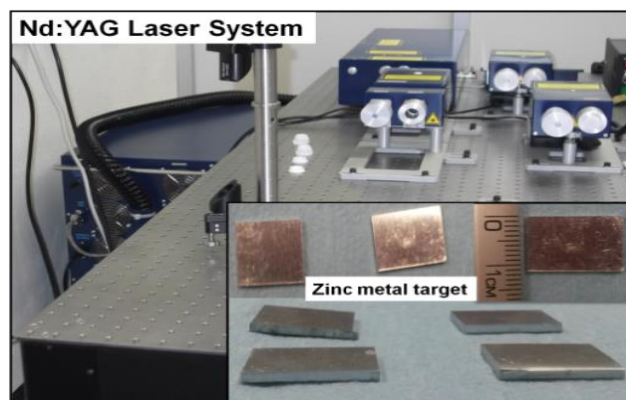


Figure 1 Nd:YAG laser and the Zn target used of the PLAL

Colloidal solutions of ZnO nanomaterials were synthesized through pulsed laser ablation of a highly pure (99.99%) zinc metal target, first in distilled water and after that in 2-propanol. The target was kept at the bottom of a glass vessel filled with 15 ml of liquid medium, 3 cm below the solution surface and was ablated during 5 minutes by the second harmonic (532 nm), and after, fundamental (1064 nm) of a Nd:YAG laser operated at 10 Hz with a pulse width of 10 ns.

A laser energy meter (Model PM100D, Thorlabs Inc.) was used to monitor the output energy of the 532 and 1064 nm laser; they were 230 and 300 mJ/pulse, respectively. The laser beam was focused on the metal plate using a lens with a focal length of 20 cm and the estimated fluences were 3.9 J/cm² (532 nm) and 6.1 J/cm² (1064 nm).

3.2 Characterization

Drops of all of the colloidal solutions prepared at different ablation conditions were dried separately on carbon-copper grids to characterize their morphology, size and structure using Transmission Electron Microscopy (TEM, Model FEI Tital G2 80-300). All the samples were dried on conducting copper tapes to perform X-ray photoelectron (XPS) analysis (Thermo Scientific Inc. Model K-Alpha).

The analysis was done with monochromatized Al K α radiation ($E=1486.68$ eV). The colloidal NPs solutions were subjected to UV-Visible absorption analysis by a UV-Visible Spectrophotometer (Shimadzu UV-1800) in the wavelength range of 250-1000 nm. The results on morphology, structure, chemical composition and optical properties of nanomaterials obtained by pulsed laser ablation of zinc metal in different liquid medium were analyzed.

4. Results and Discussion

4.1 TEM Analysis

TEM images of the nanomaterials obtained by ablation using 532 nm and 1064 nm, at 3.9 and 6.1 J/cm², are shown in Figure 2 and Figure 3, respectively.

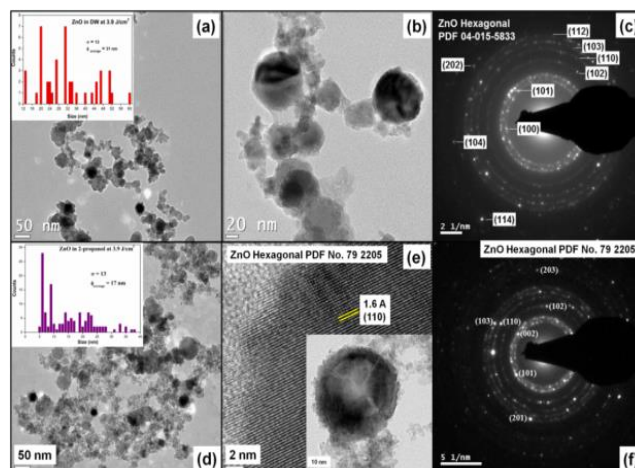


Figure 2 (a, b) TEM images and (c) SAED of ZnO colloids obtained by ablation in distilled water (532 nm, 3.9 J/cm²). (d) TEM images, (e) HRTEM image and (c) SAED of ZnO colloids prepared by ablation in 2-propanol (532 nm, 3.9 J/cm²)

Spherical and quasi-spherical nanoparticles which are linked as a chain (Figure 2a and 2b) were prepared in distilled water at 3.9 J/cm². These nanoparticles do not follow a normal size distribution and their average size is 31 ± 13 nm (inset of Figure a). By ablation in 2-propanol at 3.9 J/cm² smaller spherical nanoparticles (17 ± 13 nm) are obtained which are agglomerated, as shown in Figure 2d.

The morphology of the products from the ablation at 6.1 J/cm² in distilled water is quasi-spherical (Figure 3a and 3b) and they are smaller than those synthesized by ablation using 532 nm (10 ± 5 nm). Larger spherical nanoparticles were produced by ablation in 2-propanol using 1064 nm, as observed in Figure 3d and 3e.

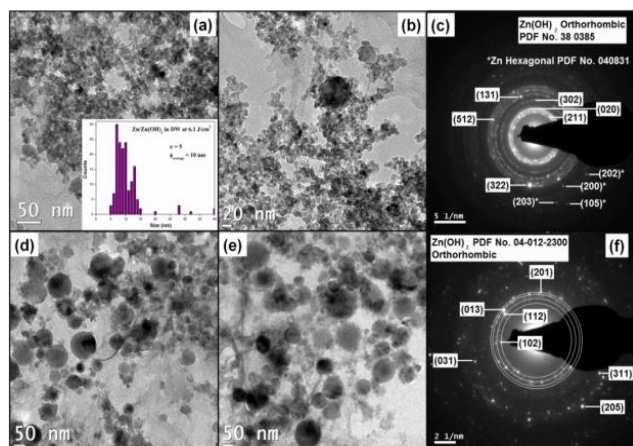


Figure 3 (a,b) TEM images and (c) SAED of Zn/Zn(OH)₂ nanoparticles obtained by ablation in distilled water (1064 nm, 6.1 J/cm²). (d,e) TEM images and (c) SAED of Zn(OH)₂ nanoparticles obtained by ablation in 2-propanol (1064 nm, 6.1 J/cm²).

The SAED (Selected Area Electron Diffraction) patterns of spherical nanoparticles prepared at 3.9 J/cm² are included in Figure 2c and 2f; the electron diffraction spots were indexed and the estimated lattice parameters 'd' are in agreement with the diffraction planes of ZnO Hexagonal phase (PDF #04-015-5833 and 79-2205, respectively). Zn(OH)₂ crystal phase was identified in the products from ablation at 6.1 J/cm² in distilled water and 2-propanol, as shown in Figure 3c and 3f. Also, the indexed diffraction rings of the nanoparticles obtained in distilled water correspond to Zn Hexagonal (PDF # 04-0831).

For both laser ablation products an EDX (Energy Dispersive X-Ray) analysis was done. A spherical nanoparticle from the ablation in distilled water at 3.9 J/cm² is composed of 56.7 % and 43.3 % of zinc and oxygen, respectively (Figure 4a). Similarly, Figure 4b, shows that spherical nanoparticles in 2-propanol are composed of 37.6% zinc and 60.8 % oxygen.

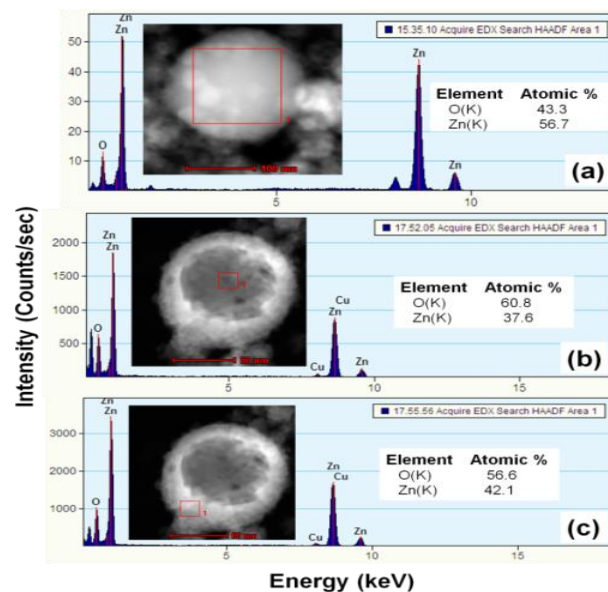


Figure 4 EDX analysis of ZnO colloids obtained by ablation in (a) distilled water and (b,c) 2-propanol (3.9 J/cm², 532 nm)

Figure 5a and 5b show that spherical nanoparticles obtained by the ablation using 1064 nm in distilled water were composed of 44.2% of zinc and 55.8% of oxygen.

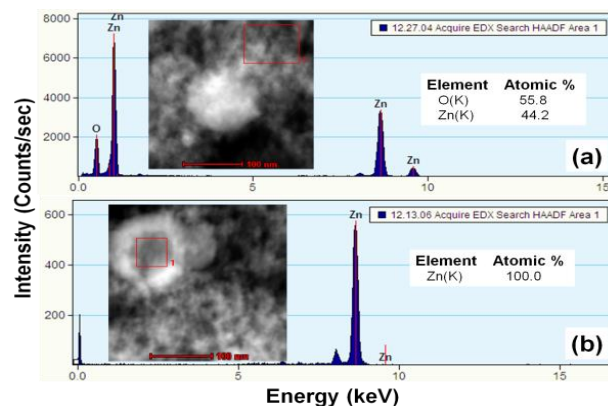
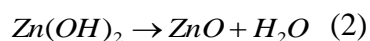
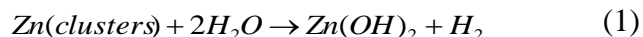


Figure 5 EDX analysis of Zn/Zn(OH)₂ nanoparticles prepared by ablation in distilled water at 1064 nm (6.1 J/cm²)

The proposed laser ablation mechanism is thermal evaporation and the liquid media has an important role in determining the size or shape of the synthesized ablated particles.

Due to the temperature gradient on both sides of the plasma-liquid interface, the highly active zinc clusters reacts with distilled water, leading to the nucleation and condensation of initial $\text{Zn}(\text{OH})_2$, which can be decomposed to ZnO on the basis of the reactions (Liang et al., 2011; Zeng et al., 2005):



As 2-propanol, $(\text{CH}_3)_2\text{CHOH}$, has an alcohol carbon atom and $-(\text{OH})$ functional group, attached to two other carbon atoms, it also tends to oxidize the highly reactive zinc ablated clusters. So, $\text{Zn}(\text{OH})_2$ and ZnO nanomaterials can be produced by ablation of Zn metal target in both liquid media. Moreover, when the zinc clusters mix with the surrounding the initial parameters of the medium such as zinc cluster concentration chemical and physical properties, determine its following evolution.

As the distilled water has higher dipole moment than 2-propanol, their molecules tend to form a layer on the charged nanospheres, inducing an electrostatic repulsive force, which can prevent the aggregation of the as-produced nanoparticles (Lin et al., 2011; Rao, Podagatlapalli, & Hamad, 2014; Thareja & Shukla, 2007). Hence less agglomerated ZnO nanoparticles are produced by ablation of Zn target with 532 nm in distilled water.

Perhaps, the morphology, size and structure of ablated products also depend on the laser ablation wavelength and energy. The higher power density ($6.11 \times 10^8 \text{ W/cm}^2 - 1064 \text{ nm}$ at 300 mJ) promotes the formation of smaller and agglomerated quasi-spherical Zn-Zn(OH)₂ nanoparticles and at low power density ($4.02 \times 10^8 \text{ W/cm}^2 - 532 \text{ nm}$ at 230 mJ) larger spherical ZnO nanoparticles.

It was reported that an increase in the laser energy lead to increase in the kinetic energy of ablated particles, in the plasma plume generated on the surface of target during ablation, to form smaller particles (Solati, Dejam, & Dorrnian, 2014). Also, ZnO and $\epsilon\text{-Zn}(\text{OH})_2$ nanomaterials with different size and morphology were obtained by changing the laser ablation wavelength from 1064 nm to 532 nm (Lin et al., 2011).

4.2 XPS Analysis

Figure 6 shows the survey XPS spectra from the spherical ZnO nanoparticles prepared by ablation in 2-propanol using the 532 nm output laser beam (3.9 J/cm^2), indicating the presence Zn, O and adventitious C. No contaminants were detected on the sample surface. The high intensity showed by the C1s peak is due to the liquid media, which are composed of carbon other than from the environmental contamination when the samples were dried.

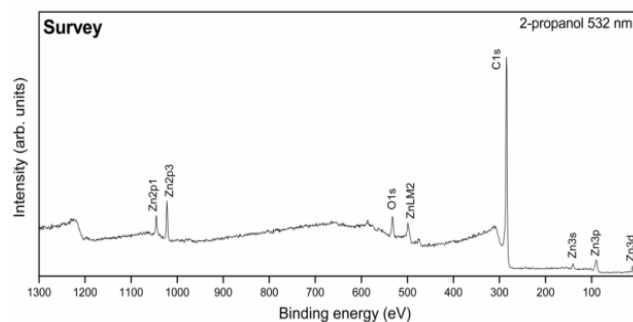


Figure 6 Survey analysis of the ZnO nanoparticles synthesis by ablation in 2-propanol (532 nm, 3.9 J/cm^2), made by XPS

Figure 7a shows the high resolution core level spectra Zn2p for the bulk zinc metal target and for the ZnO/Zn(OH)₂ nanomaterials obtained by ablation in distilled water and 2-propanol using the 532 and the 1064 nm output laser beam at 3.9 and 6.1 J/cm^2 , respectively. Also, the O1s high resolution spectra of the as-synthesized nanomaterials by ablation are presented in Figure 7b.

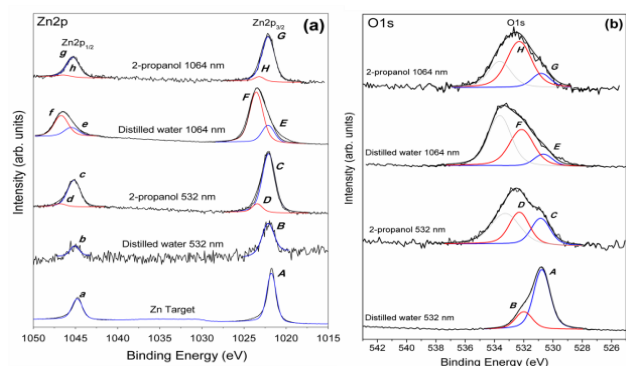


Figure 7 Zn2p and O1s high resolution core level spectra of the as-synthesized zinc nanomaterials by ablation in distilled water and 2-propanol using the 532 nm and 1064 nm output laser beam (3.9 and 6.1 J/cm², respectively)

All the recorded binding energy data were corrected using C1s binding energy from adventitious carbon at 284.6 eV. Background (using Shirley method) and deconvolution of the spectra was done in the software of the XPS equipment (Avantage). All the recorded Zn2p and O1s binding energies are described in the Table 1 and Table 2, respectively.

The reported binding energy of elemental Zn is 1021.8 eV for Zn2p_{3/2} and the doublet separation (ΔE) is 22.97 eV (Moulder, Stickle, Sobol, & Bomben, 1992). The Zn2p_{3/2} peaks located at the binding energy of 1022.1 and 1023.4 eV, are reported for Zn⁺² in ZnO and Zn(OH)₂ phases, respectively.

The ZnO and Zn(OH)₂ nanoparticles are produced by ablation in distilled water and 2-propanol using the both laser wavelengths, and this is in agreement with the SAED pattern reported in . Figure 2 and Figure 3.

The O1s spectra were deconvoluted in 2-3 peaks as shown in Figure b, binding energies 530.8 eV and 532.0 eV correspond to O⁻² in ZnO and in Zn(OH)₂ respectively.

Peak	Binding Energy (eV)	Compound
A	1021.8	Zn ⁰
a	1044.8	Zn ⁰
B	1022.1	ZnO
b	1045.1	ZnO
C	1022.1	ZnO
c	1045.2	ZnO
D	1023.4	Zn(OH) ₂
d	1046.6	Zn(OH) ₂
E	1022.1	ZnO
e	1045.3	ZnO
F	1023.5	Zn(OH) ₂
f	1046.7	Zn(OH) ₂
G	1022.1	ZnO
g	1045.3	ZnO
H	1023.2	Zn(OH) ₂
h	1046.4	Zn(OH) ₂

Table 1 Binding energies of the Zn2p core level spectra for the zinc nanomaterials synthesized by ablation in distilled water and 2-propanol, using the 532 nm and 1064 nm.

Peak	Binding Energy (eV)	Compound
A	530.8	ZnO
B	532.0	Zn(OH) ₂
C	530.8	ZnO
D	532.3	Zn(OH) ₂
E	530.7	ZnO
F	532.1	Zn(OH) ₂
G	530.8	ZnO
H	532.3	Zn(OH) ₂

Table 2 Binding energies of the O1s core level spectra for the zinc nanomaterials synthesized by ablation in distilled water and 2-propanol, using the 532 nm and 1064 nm

Hilon Hu et al. (Hu et al., 2011) reported the binding energy at 530.6 eV which was attributed to O²⁻ ions in wurtzite structure of hexagonal Zn²⁺ ion array. Also, they reported a peak at the binding energy of 531.2 eV and it was associated with O²⁻ ions in the oxygen-deficient regions within the matrix of ZnO. Fazio et al. (Fazio, Patanè, D'Urso, Compagnini, & Neri, 2012) reported XPS spectrum for a ZnO film on a silicon substrate obtained by spraying a colloidal solution of ZnO NPs prepared at two laser energies (20 and 150 mJ) of the second harmonic (532 nm) of a Nd:YAG laser operating at 10 Hz repetition rate with a pulse width of 5 ns.

They reported the core line $Zn2p_{3/2}$ at 1021.8 eV for zinc in ZnO. The O1s structures for the two energies showed the presence of two distinct components at 530.3 eV (O^{2-} on normal wurtzite structure of ZnO single crystal) and 531.9 eV (O-H bonds). XPS spectral analysis confirmed that the ablation in both liquid mediums resulted in ZnO and $Zn(OH)_2$ phases.

4.3 UV-Visible Spectroscopy analysis

The different optical behavior of the samples is identified by the change in the slope of their optical absorbance in the visible region. The optical band gap is evaluated by extrapolating the Tauc plot for direct band gap materials. The influence of nanocrystal size on the electronic structure of semiconducting material is represented by the band gap increasing with decreasing of the particle size, which is attributed to the so-called quantum confinement effect (Dorranian & Eskandari, 2015; Kuncser & Miu, 2014; YU & Cardona, 2010). The optical absorbance spectra and the estimated optical band gap for the colloids prepared by ablation in distilled water and 2-propanol using the 532 nm and 1064 nm output laser beam are shown in Figure 8

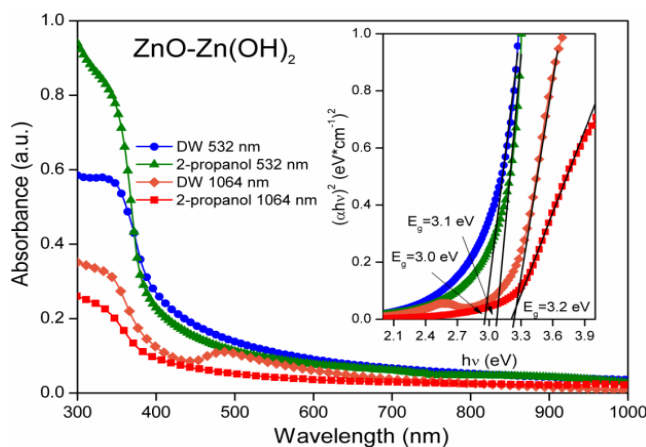


Figure 8 Absorption spectra and optical band gap (inset) of the Zn nanomaterials obtained by ablation in distilled water and 2-propanol (532 nm – 3.9 J/cm² and 1064 nm – 6.1 J/cm²)

All the absorption edges and band gap energies are included in Table 3. There is a change in the optical band gap value to higher energies when the ablation is done with the 1064 nm output laser beam. By ablation in distilled water, smaller nanoparticles are synthesized and well dispersed spherical nanoparticles are prepared by ablation in 2-propanol, as shown in Figure 3

However, these optical band gaps are lower than the reported value for ZnO bulk semiconductor (3.3 eV) (Rodnyi & Khodyuk, 2011), and represent a red shift in the absorption spectra, which can be due to the presence of a broad size distribution of ZnO nanoparticles, or by the observed agglomeration (Kumar, Venkateswarlu, Rao, & Rao, 2013). An absorption edge at 380 nm and a broad absorption edge from 400 to 600 nm have been observed for ZnO nanoparticles prepared by PLALM of Zn metal target in distilled water and SDS, respectively. The absorption edges were indicative of the presence of a broad size distribution or relatively severe aggregation of the as-prepared ZnO nanoparticles (Hu et al., 2011).

5. Conclusions

ZnO and $Zn(OH)_2$ nanomaterials having different morphologies were synthesized by PLALM, changing the liquid medium and the laser ablation wavelength (532 nm, 1064 nm). The morphology, size, size distribution, crystalline structure and elemental composition of the zinc nanomaterials were analyzed using TEM, SAED and EDX. The elemental composition and chemical states of all the as-synthesized ZnO and $Zn(OH)_2$ nanomaterials were confirmed by XPS analysis. It was synthesized ZnO spherical nanoparticles (31 ± 13 nm) by ablation in distilled water using 532 nm, however, by changing the laser ablation wavelength to 1064 nm, more agglomerated and smaller $Zn(OH)_2$ nanoparticles (10 ± 5 nm) were obtained. Their size was dependant of the optical and chemical liquid medium properties and the laser wavelength used.

6. Acknowledgments

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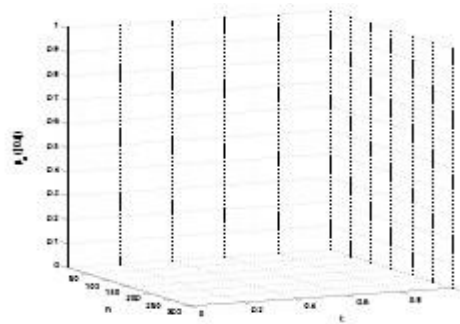
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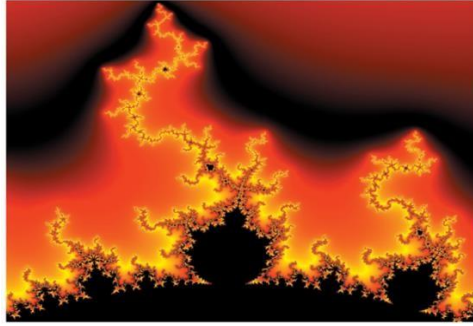


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