World Academy of Science, Engineering and Technology
International Journal of Educational and Pedagogical Sciences
Vol:11, No:5, 2017

Lab Activities for Introducing Nanoscience to Teachers and Students

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Abstract**—**Nanoscience has become one of the main science fields in the world; its importance is reflected in both society and industry; therefore, it is very important to intensify educational programs among teachers and students that aim to introduce "Nano Concepts" to them. Two different lab activities were developed for demonstrating the importance of nanoscale materials using unique points of view. In the first, electrical conductive films made of silver nanoparticles were fabricated. The silver nanoparticles were protected against aggregation using electrical conductive polypyrrole, which acts also as conductive bridge between them. The experiments show a simpler way for fabricating conductive thin film than the much more complicated and costly conventional method. In the second part, the participants could produce emulsions of liposome structures using Phosphatidylcholine as a surfactant, and following by minimizing the size of it from micro-scale to nanometer scale (400 nm), using simple apparatus called Mini-Extruder, in that way the participants could realize the change in solution transparency, and the effect of Tyndall when the size of the liposomes is reduced. Freshmen students from the Academic Arab College for Education in Haifa, Israel, who are studying to become science teachers, participated in this lab activity as part of the course "Chemistry in the Lab". These experiments are appropriate for teachers, high school and college students.

Keywords**—**Case study, colloid, emulsion, liposome, surfactant.

I. Introduction

NANOSCIENCE is a field that deals with materials and systems at a very small scale. A nanometer is one millionth of a millimeter; one millimeter is the smallest measurement visible on a 30 cm ruler. Where the nanoscience deals with a scale 1000 times smaller than anything that can be seen with an optical microscope, nanotechnology is the application and development of nano-scale systems across various science fields such as chemistry, biology, physics, medicine, and engineering. Nowadays, it has a significant importance which extends from the industry of technology to the medical one. Nanotechnology will impact virtually every industry in the future. In practice, the words "nanoscience" and "nanotechnology" are used interchangeably [1]. The great importance of nanotechnology and its "fingerprint" on our life increases the demand to raise awareness with students and teachers. This paper presents two different lab activities, which offer a great opportunity for participants to learn and develop an interesting knowledge about nanoscience, and became familiar with concepts of scale, particularly at the nanoscale and be able to "taste" slightly by a curious experiment how nanomaterials and nano-systems could be applied. In the first experiment, the participants prepared different aqueous solutions of silver nanoparticles using standard laboratory equipment and procedure that based on simple reduction of silver ions [2]. To prevent clustering the nanoparticles together and precipitation, conductive polypyrrole, and poly-diallyldimethylammonium chloride (PDAC) were used to stabilize the silver colloid [3]. Polypyrrole (PPy) is a typical electro-conductive polymer which combines polymeric and metallic properties [4]. The conductivity of PPy is derived from its structure, which is distinguished by alternating single and double bonds called conjugated bonds between carbon atoms in the doped polymer backbone; each bond contains a localized "sigma" bond which forms a strong chemical one; in addition, every double bond contains a less strongly localized "pi" bond. Fig. 1 depicts the chemical structure of PDAC, and electrical conductive PPy. By preparing these solutions, the participants could realize the unexpected chemical and physical properties that are different from the properties of bulk materials. The optical properties of silver behave differently at the nanoscale compared to macroscale, while silver at the macroscale is a light grey color; silver at the nanoscale could appear yellow and green. Moreover, the participants could determine the colloidal silver particles by detecting the effect of Tyndall compared with aqueous solution of silver ions. According to this effect [5], when a beam of light is allowed to pass through a colloidal solution, the path of light gets illuminated. This phenomenon is known as Tyndall Effect. It occurs because light is scattered when it hits the particles in the colloid solution, when the solute particles in the solution are less than 1nm the light passes without scattering.

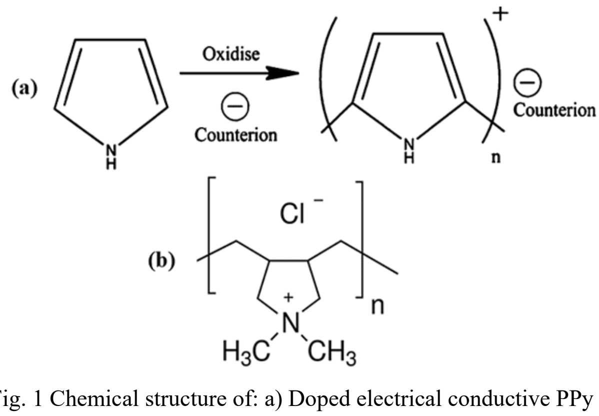

Fig. 1 Chemical structure of: a) Doped electrical conductive PPy b) PDAC

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The preparing of nanoparticles of silver solutions and detecting different properties of it was followed by a very intriguing activity, which arouses the curiosity of the participants. This experiment gives the participants a “taste” one of the possible applications of these solutions by fabricating very thin and electrical conductive film based on silver nanoparticles. The manufacture of thin conductive films is considered very important for various electronic devices; the conventional method is very complicated, with high cost [6]. Nowadays, very simple alternative methods were developed based on metal nanoparticles [7], which exhibit easy, rapid processing techniques to fabricate such films.

The second lab activity presents an experiment in which the students explore the areas of possible impact of nanomaterials and nano-systems in biology and medical science. Here, the students produced aqueous solutions of nano-liposome structures that are extremely close to the structure of cell membrane, making them highly compatible with the biological milieu. The procedure for preparation is based on using phosphatidylcholine as a surfactant, its structure incorporates choline as a “head” group, while two fatty acyl groups are the “tail” groups, as seen in Fig. 2. It can be physically extracted from natural materials like egg yolk and soybeans.

In order to reduce the size of liposome structures from microscale to nanometer scale, we have exploited the very cheap and simple apparatus called “Mini-Extruder” (by passing the liposome solutions through 400 nm membrane in it). Nano-liposome structures are considered as an effective drug delivery system and more than 10 types of liposomal drugs have been already approved and commercialized [8]. By this activity, the participants could explore the structure of liposomes, which are similar to the structure of cell membrane, and “design” a drug carrier, using hydrophilic dye (Amaranth) and hydrophobic red dye (1-([4-(Xylyl Azo)xylyl]azo)- 2-naphthol) in order to detect the different chemical parts of the liposomes.

II. Experimental Procedure

A. The Preparation of Colloid Solutions of Silver Nanoparticles

Ag nanoparticles were synthesized by silver salt ($AgNO_3$) reduction with sodium citrate [2], using either PPy or PDAC to prevent precipitation and disperse the nanoparticles of silver in water.

Two milliliters of trisodium citrate solution in (1%, 0.34M) were added dropwise to a heated (94-95 ^oC) solution of $AgNO_3$ (0.18 g in 100 ml of aqueous PPy or PDAC solutions of 1%, 0.8%, 0.5%, 0.3%, and 0.1% w/w), while stirring. Each mixture was kept heated for 10 min, and the resulting solutions were cooled to room temperature.

B. Formation of Thin Conductive Films

Thin electrical conductive films made of silver nanoparticles were prepared very simply: the PPy-silver colloid solutions were deposited on a microscope glass substrates using regular pipette, creating films of 4 cm length and 0.5 cm width, consisting of 12 layers of silver solution. Each layer was prepared by spreading 2 ml of solution on the glass substrate, letting it dry, and then spreading another layer. This process was repeated until the 12 layers were formed.

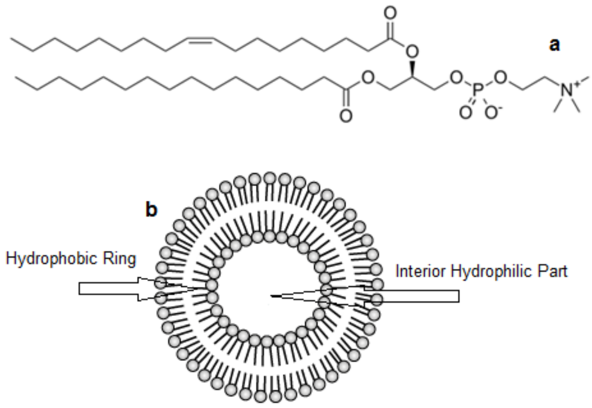

Fig. 2 (a) Chemical structure of phosphatidylcholine (b) Structure of liposome produced by phosphatidylcholine in water

A Digimatic Micrometer-APB-1D was used to measure the resistivity of the dry films.

The measurement of electrical conductivity (σ) was done by using the simple equations as (1) and (2):

$$\sigma = 1/\rho \quad (1)$$

$$\rho = R \cdot A / L \quad (2)$$

where, ρ = Resistivity (constant value), [ρ]= Ωcm, R= Film's resistance, [R]= Ω. A= Film's cross-sectional area, [A]= cm2, L= Film length, [L]= cm , [σ] = 1/ Ωcm= S/cm.

C. Producing Different Solutions of Liposome Structures

1. Producing Aqueous Solutions of Liposome Structures

Phosphatidylcholine of 1 g and isopropanol of 25 ml were added to 50 ml round bottom flask equipped with magnetic stir bar, and stirred for a 1-2 minutes in order to dissolve all the Phosphatidylcholine. The solvent was removed by evaporation under vacuum at 50^{o}C to yield transparent lipid film on the surface of the flask, followed by adding 100 ml of double-distilled water into the flask and stirring vigorously for 1 hour using a magnetic stir bar and stirring plate.

2. Producing Aqueous Solutions of Liposome Structures with Hydrophilic Dye

This procedure consist from two steps, in the first, a phospholipid films were produced by a similar way which described in Section I, namely, a mixture of 1 g of phosphatidylcholine and 25 ml isopropanol were added to a 50 ml round bottom flask, and stirred for 2 minutes. This was followed by solvent evaporation under vacuum at 50^{o}C. In the second step, the phospholipid films were dissolved in 100 ml aqueous solution of hydrophilic red dye (10 mg red dye in 100 ml double-distilled water), and stirred vigorously for 1 hour.

3. Producing Aqueous Solutions of Liposome Structures with Hydrophobic Dye

A solution of 1 mg hydrophobic red dye and 25 ml isopropanol was prepared. This solution was added to a 50 ml round bottom flask containing 1 g of phosphatidylcholine. The mixture was stirred for two minutes. The solvent was evaporated under vacuum at 50 °C, resulting in obtaining colored lipid films on the surface of the flask. The lipid films were dissolved in 100 ml double-distilled water and stirred for 1 hour using magnetic stir bar and stirring plate.

The solutions were sized by multiple extrusions through a stacked membrane of pore size of 400 nm using a medium pressure extruder, as seen in Fig. 3. This apparatus allows us to minimize the size of liposome structures to colloidal dimensions. The liposome size distribution is considered as a function of the number of passes through the Extruder membrane. A minimum of 11 passes through the Extruder membrane is recommended for most lipids. This allowed the students could understand that minimizing the size of the aggregate droplets was reflected through obtaining more transparence solutions. All the solutions were viewed through an optical microscope.

Fig. 3 Mini-Extruder Apparatus

III. Results

Part 1. Two basic solutions of silver nanoparticles were prepared, one with PDAC as stabilizer and the other by using electrical conductive PPy. Polymer layers served as a barrier against the attraction between the nanoparticles by adsorbing on the surface of it and impart electric charge, as seen in Fig. 4. Yellow-brown solutions were obtained by using PDAC as a stabilizer, while black stable solutions of silver nanoparticles were obtained with PPy as an electrically conductive stabilizer, as seen in Fig. 5. In order to distinguish between a regular aqueous solution of silver ions and aqueous colloid of silver nanoparticles, an inexpensive and simple method was used based on the Tyndall Effect, the phenomenon of scattering light by particles larger than 1 nm, whereas, light passes without scattering with particles less than 1nm as in the case of silver ions. Fig. 6 presents the images of passing laser light through the two solutions; the participants could detect easily the line of laser beam inside the colloid solution, unlike the solution of silver ions.

The mechanism of stabilization against precipitation is based on acquiring the nanoparticles cationic electrical charge by adsorbing the polymer layers either PPy or PDAC. The students could realize very simply the charged silver nanoparticles without the use of any sophisticated apparatus. This method is based on naturalization the negative charge of the silver nanoparticles by adding a solution of positively charged polymer. Because of the spontaneous attraction force between positive and negative charges, the added positively charged polymer will be attracted directly to the surface of silver nanoparticles, causing the reduction of the negative charge of it. This process will enhance the attraction between the silver nanoparticles, and finally precipitation of it. The minimal concentration needed for getting precipitation of the nanoparticles is called Critical Coagulation Concentration (CCC). During this part of lab activity, the participants were very curious to see the process of destroying the nano-structured silver particles. Fig. 7 presents a schematic illustration of the different steps of the precipitation process. For this purpose, we use the anionic carboxymethyl cellulose solution in order to naturalize the cationic charge of the silver nanoparticles. For colloid solutions of 0.01M $AgNO_3$ and 0.5wt% of PDAC we needed to add a solution of 0.02wt% of carboxymethyl cellulose; whereas, 0.05wt% of it was needed for the same colloid solution stabilized by PPy. These simple detecting methods were followed by exploring one of the possible applications of silver colloid solutions, namely, the fabrication of electrical conductive thin films. Despite the high electrical conductivity of silver, the films fabricated from nanoparticles of PDAC stabilized silver nanoparticles were insulator. Whereas, an electrical conductivity was measured by films produced by colloid solutions of PPy stabilized silver nanoparticles. The PPy layers act as a conductive "bridge" between the disconnected silver nanoparticles. Fig. 8 depicts the conductivity values of different films made of silver nanoparticles. Three solutions of silver nanoparticles stabilized by PPy were compared with three other solutions stabilized with non-conductive PDAC.

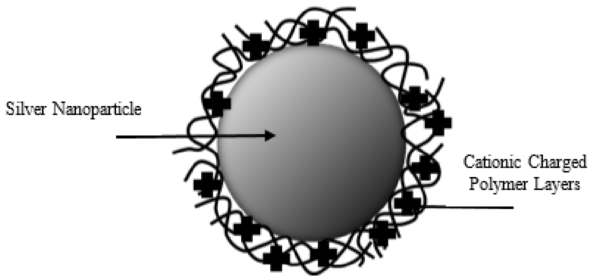

Fig. 4 Schematic illustration of silver nanoparticle stabilized by charged polymer layer

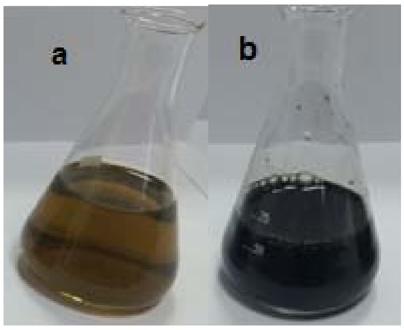

Fig. 5 (a) Silver colloid stabilized by PDAC (b) Silver colloid stabilized by PPy

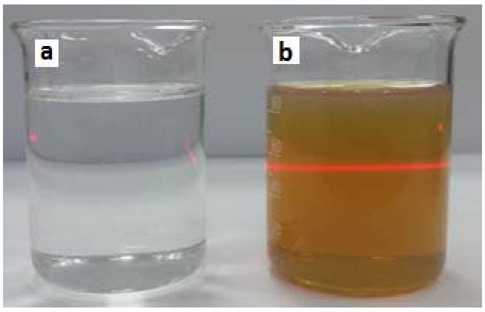

Fig. 6 Laser beam passing through (a) aqueous solution of silver ions, (b) colloid solution of silver nanoparticles

Part 2. Three solutions were prepared. The first is the aqueous solution of liposome structures, and the two other solutions were supplemented with either hydrophobic or hydrophilic red dye. The participants reveal the fascinating structures and the way the red dyes "organize" themselves either outside or inside the liposome structures by viewing the images of these solutions with the aid of optical microscope, as seen in Fig. 9.

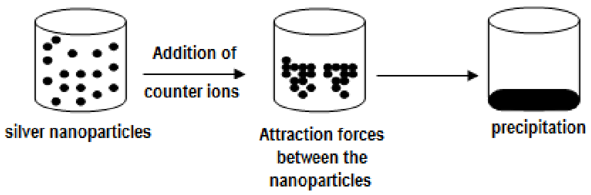

Fig. 7 Schematic illustration of precipitation process of stable charged nanoparticles by adding a solution containing counter ions

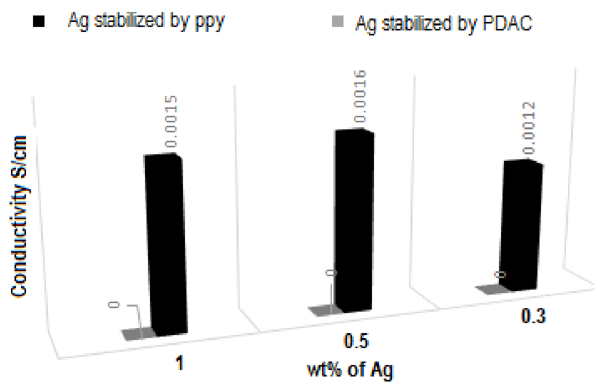

Fig. 8 Conductivity values of silver nanoparticles films stabilized with PPy and PDAC

According to Fig. 9, uncolored micro-liposome structures were detected by optical microscope, whereas, the using of hydrophilic dye (Amaranth) enabled the participants to distinguish between the hydrophilic and the hydrophobic parts of the liposomes. They were able to see clearly that the Amaranth dye penetrated into the interior hydrophilic part of the liposome, and in addition, its distribution in the aqueous dispersion medium. Seemingly, uncolored images were detected when hydrophobic dye was used; in fact, the dark hydrophobic ring of these structures was colored, but we could not detect it because of its dark black coloring. This point fascinated the participants because they could not see the dye despite their use of it. In addition, one can clearly observe the reduction of the liposome's size when passed through 400 nm membranes, as seen in Fig. 10. The participants could easily realize that the solutions became more transparence, despite the increase of the number of liposome structures when it reduced, and by viewing inside these solutions, they could detect the relation between the size of it and the solution transparency. This part of experiment, enabled the participants to design nano-liposomes, which are used as a drug deliver, and could imagine that using a similar method that we could penetrate a hydrophilic drug into the interior part of the liposomes. The reaction of the participants was amazing.

IV. Educational Section

College freshmen from the Academic Arab College for Education in Haifa, Israel, who are studying to be science teachers, participated in this lab activity as a part of the course "Chemistry in the Lab". Following the lab activity, the researchers asked the participants to fill in a survey to examine their impressions of the lab activities, their previous knowledge about the topic of nanoparticles, and their predictions of the benefits to their students through the implementation of this activity in their classrooms in the future.

An analysis of the survey revealed the following:

The students were asked if they learned about nano-science in their classrooms. The majority stated that they had learned about nanoparticles using high-cost materials and apparatuses.

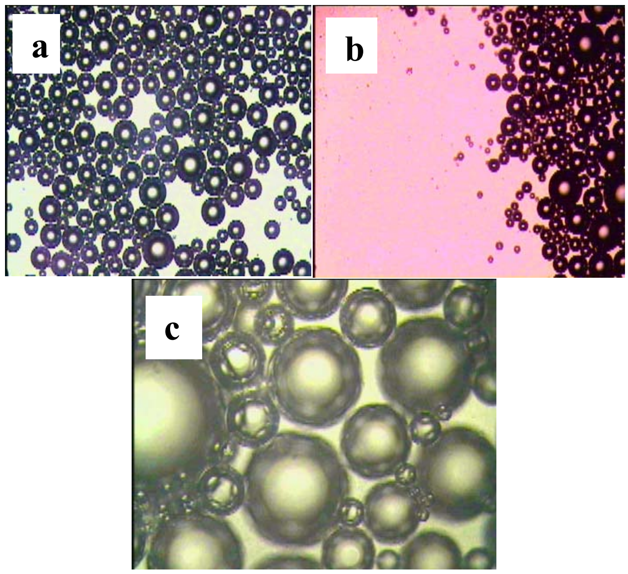

Fig. 9 Optical microscope images with a 100 X magnification of (a) liposome structures, (b) liposome with a hydrophilic dye, and (c) liposomes with a hydrophobic dye

They were then asked to describe briefly whether the experiments presented in this lab activity helped them to understand the process of nano-systems and its possible applications in a better way. Most of them answered that after the lab activity, the concept of nano-science became much clearer to them and that they would now be able to explain it clearly in their classroom in the future. In an anecdotal remark one of the students stated that at the beginning of the lab activity she had a very little knowledge on the subject, but after completing these experiments knows enough to be able to present the topic to her students in the future. The students commented that these low cost experiments were presented in a way that was easy to implement and did not need a complicated science laboratory. Some of them also showed a clear gain in substantive knowledge, by using specific language to explain what occurred in the electrically conductive thin films made of silver nanoparticles, and nano-liposomes for drug delivery.

When asked about whether they think they would implement this kind of activity in the future when they become science teachers, the students expressed their intentions to carry out some of these activities in their classroom, especially the low cost experiments.

The participants expressed their positive reaction with higher motivation and were looking forward to employing new methods of teaching which aim to the expand horizons toward the pupils.

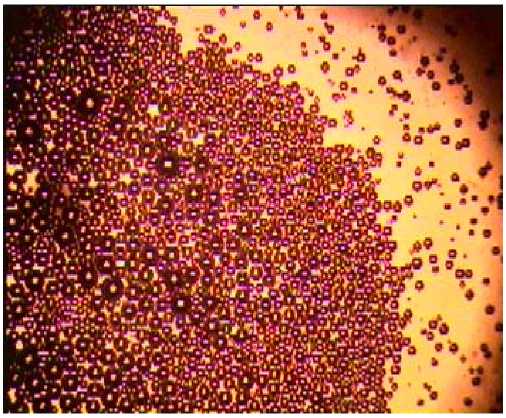

Fig. 10 Optical microscope images with a 100 X magnification of liposomes with a hydrophilic dye after passing through a stacked membrane of pore size of 400 nm

V. Conclusion

Two different lab activities were conducted that aim to highlight the concept of nano-systems and nano-materials. In the first one, aqueous solutions of liposome structures were prepared; this was followed by reducing the size of it to nano-meter scales. In the second part, producing thin films with electrical conductivity was an interesting idea for highlighting the concept of nano materials among students. The fabrication procedure of silver nanoparticles and the production of electrical conductive films could be considered a very useful teaching model for metal colloids and their applications. We believe that such experiments affect student attitudes to science and can encourage them to perform similar experiments when teaching in the future, and this in turn will lead to a significant change in the way the subject of nano materials is taught in science classes.

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