ADVANCED TECHNOLOGIES FOR OBTAINING COMPOSITE "CORE-SHELL" NANOSTRUCTURES AND ENVIRONMENTAL APPLICATIONS

C. Gaidau[1], M. Simion[2], Jianzhung Ma[3], Qunna Xu[3], L. Pascu[2], D. Simion[1], M. Niculescu[2]

[1] *The National Research and Development Institute for Textile and Leather, Leather and Footwear Research Institute Division, Bucharest, Romania, tel:+40 21 3235060, e-mail:demetra.simion@ymail.com*

[2] *The National Research – Development Institute for Industrial Ecology, Bucharest, Romania, tel:+40 21 4106716, e-mail:mariussic@ymail.com*

[3] *Shaanxi University of Science &Technology, Xi'an, China, tel: 8602986268010, e-mail:majz@sust.edu.on; xxqqnn870304@163.com*

The existence of drugs, hormones, toxic substances, synthetic polymers, etc in wastewaters is a great problem for environment. In this research the technologies for obtaining biodegradable "Core-Shell" composites with shell from natural biopolymers (collagen, casein or their combination) and immobilized in core drugs (ampicillin or gentamicin) in the smallest amount were developed.

Keywords: advanced technologies, composite "Core-Shell" nanostructures, environmental applications, release mechanism of drugs in "Core-Shell" composite.

INTRODUCTION

This paper presents advanced technologies for obtaining composite "Core-Shell" nanostructures and environmental applications. Composite "Core-Shell" are structured nanoparticles which contain a core from one material (coloured, fluorescent, with magnetic properties, drug container, full or empty) and a protective shell from another material (stabilizing particles, with biorecognition, receptive and optical functions, etc.) with sizes ranging between 20 and 200 nm. Structured nanoparticles have found wide spread application in varied fields of engineering. Recently, "Core-Shell" nanostructures have been found to have improved properties when compared to their other alternatives are patented. These "Core-Shell" nanostructures interest researchers in the field of biomedical engineering, but also some potential environmental applications have been identified in this paper. The classification of "Core-Shell" nanoparticles, the technologies of obtaining this nanostructures and the environmental applications are discussed in this article. The future work points at the possibilities of improvement and the material that might be preferred for specific applications. "Small is beautiful", today we know that small is not only beautiful but also powerful. With the range of applications that nanoparticles find in varied fields of engineering and science, nanoparticles seem a promising option when compared to the conventional materials used. Nanoparticles are particles that have at least one dimension in less than 100 nm range. They have a high surface to volume ratio and thus mass transfer and heat transfer properties are better than bulk materials. Recently; "Core-Shell" nanoparticles have found widespread application. There is a class of "Core-Shell" nanoparticle that has its entire constituent in the nanometer range. "Core-Shell" nanoparticles are nanostructures that have core made of a material coated with another material. Also, composite structures with these core/shell particles embedded in a matrix material are in use. The necessity to shift to "Core-Shell" nanoparticles is the improvement in the properties. Taking into consideration the size of the nanoparticles, the shell material can be chosen such that the agglomeration of particle can be prevented. This implies that the monodispersity of the particles can be improved. "When a core nanoparticle is coated with a polymeric layer or an inorganic layer like silica because the polymeric or inorganic layer would endow the hybrid structure with an additional function/property on top of the function/property of the core hence synergistically emerged functions can be envisioned" [1]. The properties of the nanomaterials are diverse and cannot be generalized even though the particles under comparison might be made of similar material and composition. This rule is applicable to "Core-Shell" nanoparticles and hence, we try to classify them broadly based on the material with which the core and shell of the nanocomposite are made.

On these lines we can group the nanoparticles as:

- Inorganic Core/Shell Nanoparticles (metallic, semiconductors or lanthanides nanoparticles);
- Organic-Inorganic Hybrid Core/Shell Nanoparticles;
- Polymeric Core/Shell Nanoparticles.

The most common technologies for obtaining the "Core-Shell" nanoparticles have been discussed and we have tried to generalize the type of nanoparticle that can be synthesized. Though it is not a rule that is applicable to all cases but it can be applied to most cases.

1. Polymerization:

1.1. Radical Polymerization:

The polymerization could be a free radical polymerization or an atom transfer radical polymerization. The process of atom transfer radical polymerization (ATRP) is better than the free radical polymerization as control of molecular weight and size of the particle can be achieved. The coating of polymer on silica nanoparticles is generally done by ATRP. The surface of the silica particle is modified with a suitable initiator. One of the methods would be to attach a bromine group to the surface of silica and add to solution containing the monomer of the shell polymer. The polymerization occurs and is depicted by change in the optical clarity of the solution. This method of attachment of bromine group to silica and forming polymer of t-butyl acrylate has been discussed [1]. The formation of silica coated gold nanoparticles by a biomimetic approach through ATRP was presented:

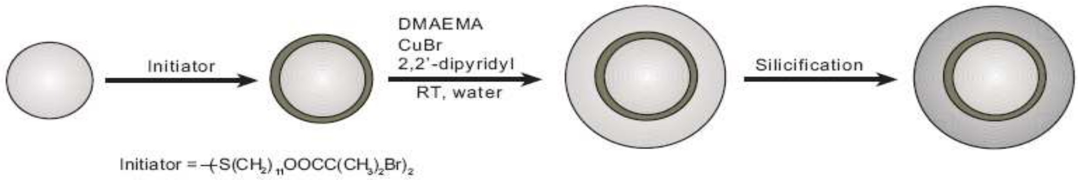


Fig. (1). Schematic Representation of Procedure [1]

1.2. Chemical Oxidation Polymerization:

The nanoparticle, if it has suitable groups attached to it allows the monomer which are generally aromatic compounds to form adduct. The monomer can be polymerized by adding suitable oxidizing agents. Generally metallic particles are given a coating of poly aromatic compounds by this method. Most metallic nanoparticles are formed by chemical reaction and then reduction. This implies there might be acidic or basic groups attached to the surface that induces modification. Such a method has been discussed by Jing et al. [2] in silver/poly aniline and silver/polypyrrole and PbS/poly pyrrole core/shell nanocomposite technology.

2. Sol Gel Technology:

This method of synthesis is used generally for the synthesis of metal/polymer core metal oxide shell nanoparticles in inorganic matrix that forms a gel, like silica. The steps can be stated in general as formation of the solution containing the salt of the metal and silica based compound. The solution is then heat treated and upon gelation, the metal salt is reduced in hydrogen atmosphere to metal nanoparticles. For polymer core and metal oxide shell the polymer nanoparticles can be added to metal salt solution and then oxidized.

3. Reverse Micelle Technology:

One of the major concerns in the synthesis of nanoparticles and in specific core/shell nanoparticles is the achievement of control over size and morphology. This can be obtained by conducting the synthesis in emulsions or in solutions that form micelles. Micelles are formed by mixing aqueous reactant with suitable surfactant. Micelles act as the center for nucleation and epitaxial growth of nanoparticles. The molar ratio of the surfactant to water (w) is the parameter that affects size and morphology of the resultant particles. These particles can be further processed to obtain core/shell structure by oxidation polymerization as discussed above. Other surfaces can be coated with other metals or silica. Polymeric particles can also be synthesized if the emulsion of the monomer is thermodynamically stable.

Jianzhong Ma and et all. [6-8], were studied casein-based silica nano-composite latex as bio-based film-forming material, synthesized from casein, caprolactam, acrylate, tetraethoxysilane and silane coupling agent via double-in situ emulsion polymerization. The objective of their study was to solve the problem of casein film deficiencies, such as hard, brittle and poorer water resistance. Morphology of resultant composite latex exhibited evident core–shell structure with the average size of around 80 nm, and the improved shell thickness indicated the encapsulation of silica on the outer layer of the particle, which was verified by TEM results. Additionally, compared with the latex film without silica, the hybrid latex film containing silica showed higher hydrophobicity, lower water absorption, enhanced tensile strength and decreased flexibility.

4. Mechanochemical Technology:

Mechanochemical technology as the name suggests involves mechanical and chemical means of nanoparticle synthesis:

- *Sonochemical Synthesis;*
- *Electrodeposition.*

Core/Shell Nanoparticles are finding wide spread applications in all fields. They are making their way into our day to day life. Things such as cabinet and car doors contain nanoparticles which improve their durability. At a large scale the industries that make most use of these materials are the chemical, electronics, biomedical, civil and mechanical Industries. They are used as catalysts, modifiers, fillers, thermal and mechanical property enhancers, sensor material due to high sensitivity to slight changes in parameter. Core/Shell structures serve a wide category of drug delivery application. The particles are biocompatible, have the ability to be conjugated to molecules without affecting the core and also can be used to encapsulate drugs. The material of choice decides the multifunctional nature of the particles. They can be structured so that they can be used for imaging and for drug delivery.

Knowing and controlling the release mechanism of drugs in “Core-Shell” composite is a protection measure for environment because they are discharged in smaller quantities in water, soil, etc.

MATERIALS AND METHODS

The experimental techniques used in the study of the release mechanisms and identification from water will consist in ultraviolet, infrared spectral methods, electronic scanning and optical microscopy, chromatography. All the analytical methods will provide proper information regarding the structure of the resulted “Core-Shell” composite and interactions with drugs.

EXPERIMENTAL

In this paper the new advanced technologies for obtaining composites “Core-Shell/ Hollow” contain two steps:

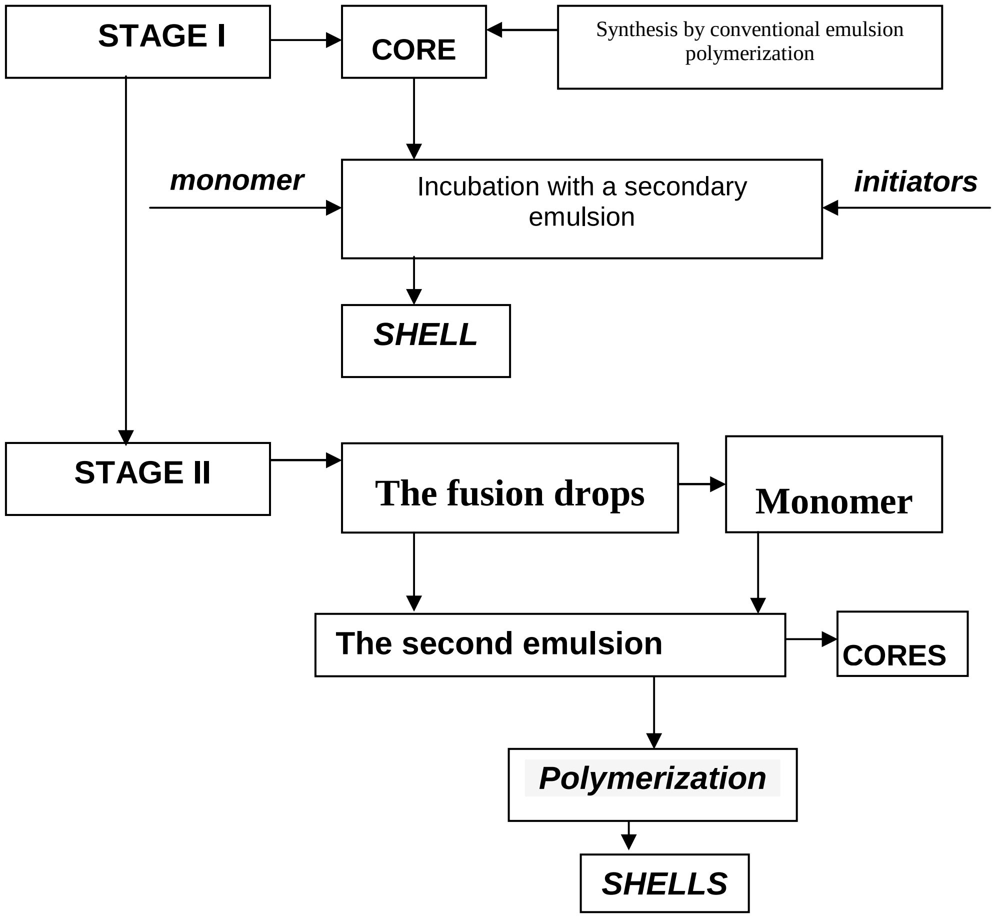


Fig. (2). Obtaining advanced technologies for "Core-Shell/Hollow" type composites

This technology is applied to obtain "Core-Shell" type composite. For structures such as "Shell-Hollow", core formation steps are missing. Multiple emulsions are complex systems in which the droplets of the dispersed phase contain a continuous phase of other dispersed droplets. The main types of multi-emulsions are water-in-oil-in water (W/O/A) and the oil-in-water-in-oil (W/A /U).

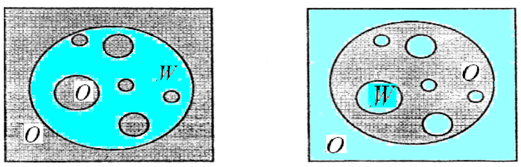


Fig. (3). Schematic representation of multiple emulsions: a) O/ W/O b) W/O/W

In most cases, multiple emulsions were prepared using a two-step emulsification process:

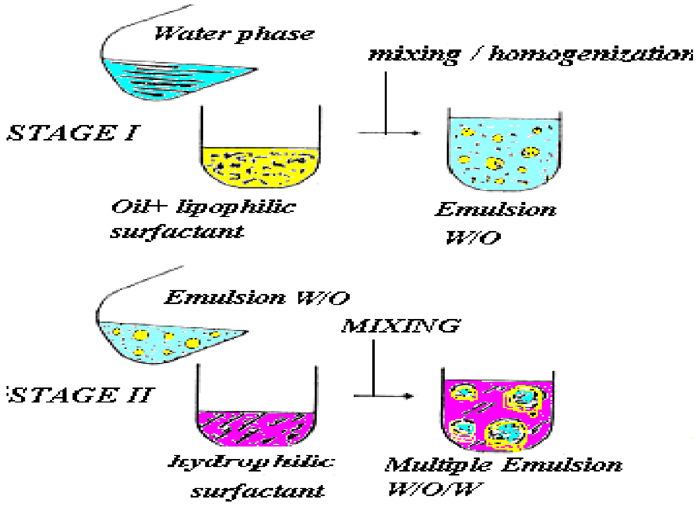


Fig. (4). Schematic illustration of the two-step emulsification process

Two types of emulsifiers are used: hydrophobic I one (for the formation of the emulsion W/O) and the other hydrophilic, II (for the emulsion O / W).

Reverse micelle technology was used for obtaining "Core-Shell" structures with polymer (collagen)/silver nanoparticles and core composed from drug (ampicillin or gentamicin). The surfactant cetyltrimethylammonium bromide (CTAB) was used and as cosurfactant, 1 -butanol.

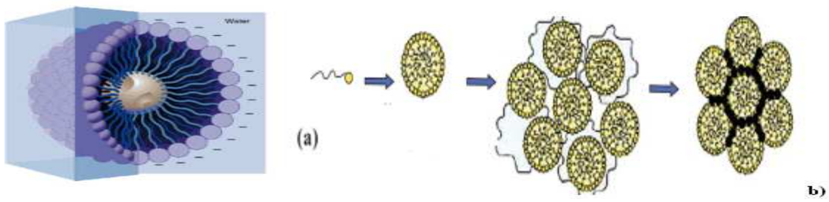


Fig. (5). Reverse micelle technology in the formation of Core-Shell" structures " (in b with nanoparticles) [2]

Technological conditions for obtaining the "Core-Shell" structures (molar ratios):

Code sample	Surfactant/ Polymer (collagen)	Surfactant/ Nanoparticles of silver	Polymer/ Nanoparticles of silver
HA1	10,4	14	1,5
HA2	2,1	14	1,8
HA3	8,2	14	7,2
HA4	8,1	14	7,1

Table 1- Technological conditions, molar rations of samples

HA1, HA2, HA3, HA4, are hydrolyzed collagen with different degrees of hydrolysis [3-5]. The drug (ampicillin or gentamycin) was introduced to the samples shown in Table 1, (fig.6):

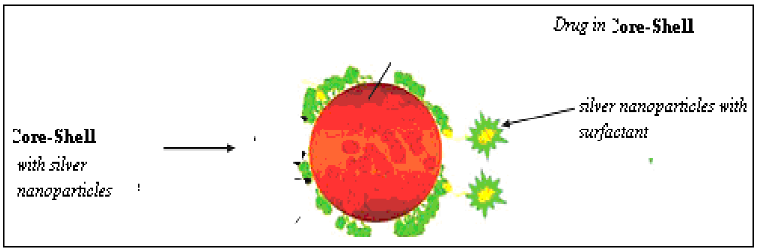


Fig. (6). The immobilization process of drugs in "Core-Shell" structures with/or without silver nanoparticles [2]

"Core-shell" samples were characterized by optical and electron microscopy. We performed electron microscopic study of "core-shell" from samples in Table 1, HA1, HA2, HA3, HA4, containing different ratios of polymer (collagen)/silver nanoparticles with or without drug (ampicillin and gentamicin).

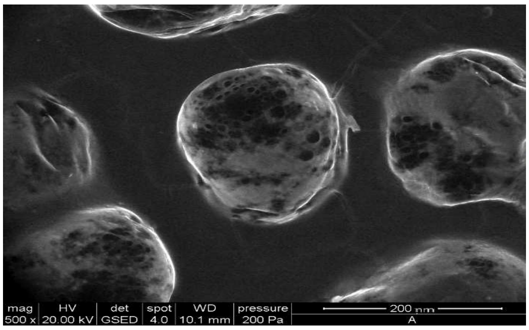


Fig. (7). SEM electron micrography detail of a "Core-Shell" structure containing polymer (collagen) and gentamicin

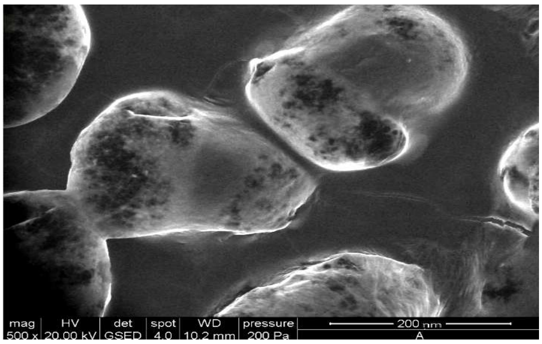
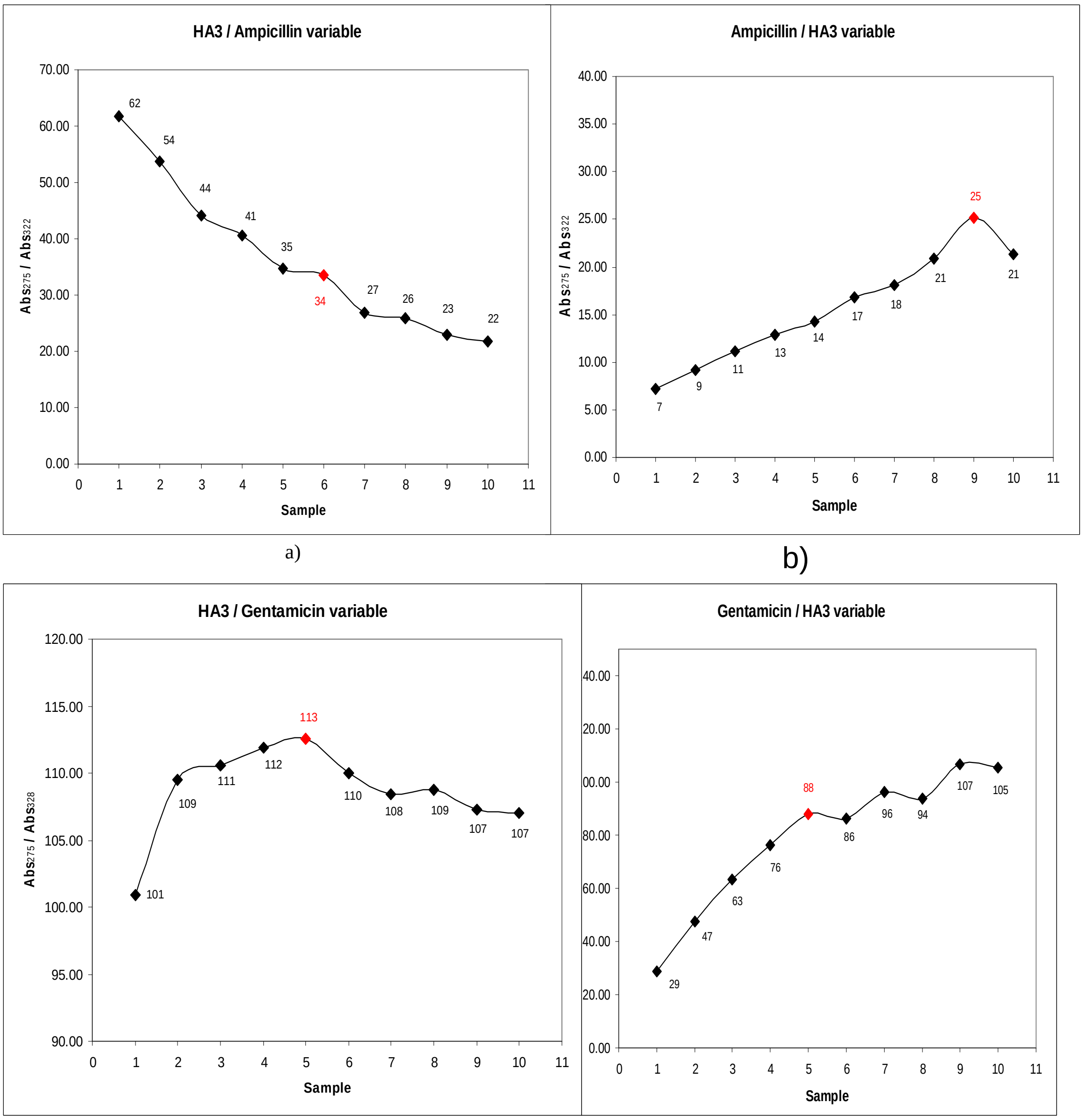


Fig. (8). SEM electron micrography detail of a "Core-Shell" structure containing polymer (collagen) and ampicillin

A UV-VIS spectrophotometric compared study, of interactions and delivery in "Core-Shell" composite structures with immobilized drugs, was carried out in this paper for samples presented in table 1, (fig.9-a, b, c, d):



c) d)

Fig. (9). Analytical UV-VIS spectrophotometric compared study for different samples (with variable ratio polymer/drug) of interactions and delivery in “Core-Shell” composite structures with immobilized drugs (ampicillin or gentamicin)

Treatment with the "core-shell" solution of silver nanoparticles obtained by the electrochemical technique, ensures the concentration of silver from 490 ppm and resistance to the important fungi and bacteria.

CONCLUSIONS

The basic composition for both the core and the shell can be changed, providing a wide range of properties and applications. Knowing and controlling the release mechanism of drugs in “Core-Shell” composite is a protection measure against assaulting the body with unnecessary amounts to be assimilated and also for environment because they are discharged in smaller quantities in water, soil, etc. The work discussed above brings forth the green aspects of the new "Smart" generation materials.

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