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# Hybride Nanomaterials Based on Silica Coated $C_{60}$ Clusters Obtained by Microemulsion Technique

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*Currently, there is a major trend to produce nanostructures of a wide variety of materials by understanding their properties and their functionality in order to develop future nanotechnologies. In this article the silica coated fullerene $C_{60}$ clusters have been produced by microemulsion technique. Firstly, the ternary phase diagrams in water/TX-114/tetraethylorthosilicate (TEOS) system at different temperatures were constructed, followed by establishing the influence of clusterization and solubilization agents in choosing the pseudoternary system. By using the phase diagram specific working conditions have been selected, in order to facilitate nanostructured templates for preparation of the silica coated fullerene nanoclusters.*

**Keywords:** nanoparticles; O/W microemulsions; silica coated $C_{60}$ clusters; thin film



## INTRODUCTION

The incorporation of different dopant agents and particles (organic/inorganic) into porous or layered materials is a highly challenging task in the field of nanomaterials, and the study of these composites represents an important step in the utilisation of these materials for potential applications [1–4].

An alternative method with huge potential in soft nanotechnology not exploited enough is the use of microemulsions based on a deeper

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understanding of thermodynamic equilibrium within phase diagrams of colloidal systems [6–10].

There are two main applications of microemulsions [5,8,9]:

- templates for reactions taking place in nanodrops as *nanoreactors* like precipitation of metallic oxides, covering/coating of nanoparticles with protecting nontoxic shells, functionalization of active biomolecules, encapsulation of nanoprobes like chromophores, fluorofores, etc;
- the obtaining of adequate compositions for thin film preparation by spin coating, drawing, etc.



The advantage of using these dispersed systems consists in obtaining of some nanostructures, with controlled shape and size, resulted by microemulsification within ternary system water/surfactant/oil.

The obtaining and the utilization in optimal conditions, and adequate to purpose of some nanodomains, well defined in size and shape, requires to delimit the regions of interest for water-oil-surfactant system by drawing the appropriate phase diagrams. These phase diagrams permit a rigorous selection of the preparation conditions of microemulsions of any type, and consequently the nanostructure corresponding to specific applications (Fig. 1). More precisely, if the process occurs in a polar, aqueous medium, the zones of interest are Winsor II (W/O, W) and Winsor IV (W/O), while in a nonpolar, organic medium the zones are Winsor I (O/W, O) and Winsor IV (O/W).

In this article the silica coated of controlled size and shape fullerene $C_{60}$ clusters have been performed by microemulsion technique in pseudoternary systems. In order to accomplish the purposed objectives the research was carried out in many stages. Firstly it was necessary to construct ternary phase diagrams in water/TX 114/tetraethylorthosilicate (TEOS) system at different temperatures, followed by establishing the influence of clusterization (acetonitrile) and solubilization agent (toluene) in choosing the pseudoternary system. By using the ternary phase diagram the working conditions, composition – temperature have been selected in order to find the specific domains large enough to facilitate nanostructured templates useful in preparation of nanomaterials, both inorganic and hybrid, especially to obtain the silica coated fullerene $C_{60}$ nanoclusters.

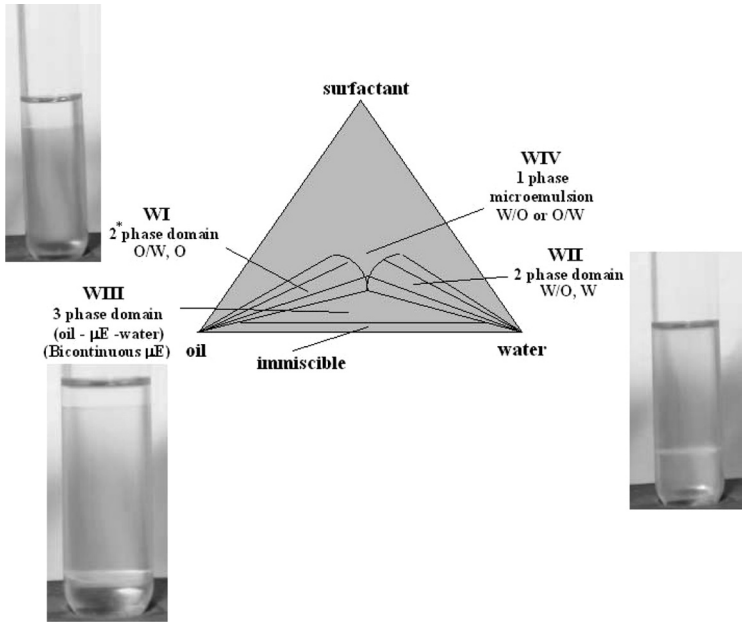



**FIGURE 1** Phase diagram in ternary system water (W)/surfactant (SF)/oil (O) associated to microemulsions. 1 phase – micellar solution (reverse or direct), microemulsion W IV, gel or liquid crystals; 2 phases* – system W I (microemulsion O/W, O); 2 phases – system W II (microemulsion W/O, W); 3 phases – system W III (W, microemulsion, O).

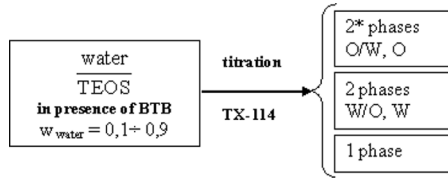
## EXPERIMENTAL

### Materials

Polyethylene glycol *tert*-octylphenyl ether (TX-114) was provided from SIGMA; bromthymolblau dye (BTB), tetraethylorthosilicat (TEOS) and acetonitrile (ACN) were purchased from MERCK; toluene was obtained from J. T. BAKER; water used was deionized and double distilled.

### Sample Characterization

- The mean particles size was determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS, Malvern, UK. Light scattering measurements have been performed at $25 \pm 0.1^{\circ}C$. Hydrodynamic measurements were made at $90^{\circ}$ angle, without dilution of samples.



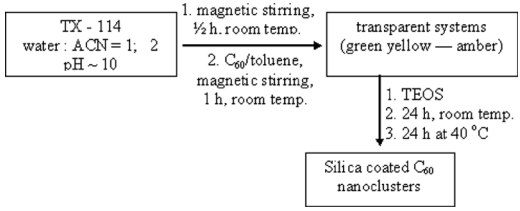

**SCHEME 1** Procedure to determine phase diagrams.



- VIS electronic spectra of samples held in 1-cm path length quartz were recorded at a wavelength between 360 and 800 nm using a Jasco double – beam V570 Spectrophotometer.
- Topographic characteristics of the samples were prepared and viewed with an NT-MDT BL222RNTE atomic force microscopy (AFM). The measurements have done operating in a contact mode, using the silicon probe (CSG10, force constant = 0.15 N/m, sensor radius = 10 nm). Dry film is scanned in ambient air. The dry film was obtained by sample spreading onto glass support and drying at 50°C during several days.

## Construction of Phase Diagram

In order to find out the region where microemulsion can be formed, ternary phase diagram were constructed using surfactant titration method at different temperatures, isotherm (26°C and 52°C) and over a temperatures range (17 ÷ 70°C) (see the Sch. 1). The samples were taken in sealed test tubes and shaken vigorously using a magnetic stirrer to ensure proper mixing and then kept in a thermostatic device at desired temperature. The phase transition was detected by direct visual inspection by using BTB as colour indicator.




**SCHEME 2** Procedure for tanoparticles preparation of silica coated fullerence $C_{60}$ clusters.

## Synthesis of Silica Coated Fullerene Clusters

The silica coated $C_{60}$ nanoclusters were prepared via O/W microemulsion using a pseudothernary composition in the water (34%), TX-114 (32.5%), toluene, ACN and TEOS (3.5%) system, following the scheme below (see the Sch. 2). The final nanomaterials contains a $C_{60}:SiO_2$ ratio of $1.2 \cdot 10^{-2}:1$.

## RESULTS AND DISCUSSION

The study of the phase equilibrium in ternary systems consisting in water, oil and a nonionic surfactant is important for the synthesis of microemulsion processes and also for enhancing the mutual solubility of water and oil under the action of a surfactant. The study has to take into consideration several variables, such as the types of oil and surfactant, the composition of the ingredients used, the effect of additives, and temperature.

In this context, the application of microemulsifying in ternary and pseudo ternary systems was studied, with the aim of preparing clusters of fullerene $C_{60}$ and their coating with silica. Microemulsions represent a suitable medium for the formation of reproducible and stable fullerene clusters, due to the tailored shape and size of the colloidal aggregates. The selection of the components of the microemulsion system is determined by the immiscibility or low solubility of fullerene $C_{60}$ in almost all common solvents. A relatively good solvent for the $C_{60}$ fullerene is toluene. Acetonitrile is also added in order to transform the fullerene in clusters. The coating of fullerene or its clusters with siliceous oxides requires the introduction in the system of the alcoxide type precursors.

### Temperature Effect on Phase Equilibrium and on the Type of Dispersions in Nonionic Ternary Systems

The studied systems contain water, alcoxide, toluene, surfactant and acetonitrile as co-solvent and clustering agent in the same time. Since the surfactant, TX-114, is nonionic, a rise in the temperature promotes a change in the water/TEOS ratio as a result of the decreasing lateral interactions between surfactant molecules because of increased amount of the amphiphiles at the interface (Figs. 2 and 3).

As for the water/TX-114/TEOS system, the increase in temperature at 40°C diminishes significantly the region corresponding to the W I microemulsion, thus favorizing the formation of a very narrow region of W III microemulsion type and also the formation of the

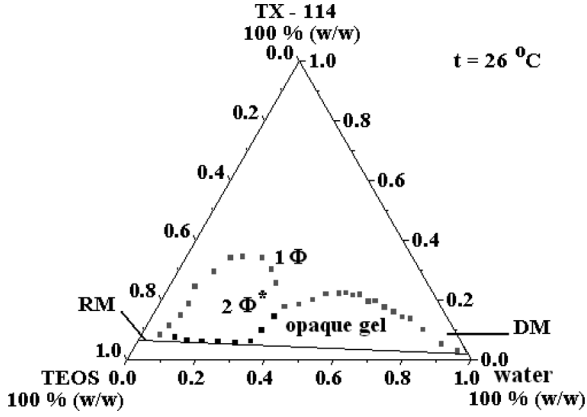



**FIGURE 2** The phase diagram of water/TX 114/TEOS at 26°C. 1Φ – one phase (direct or reverse micelles, Winsor IV system, gel or liquid crystals); 2Φ* – two phases (Winsor I system).

W II microemulsion, which is extended over a large part of the working domain, even at small concentration of surfactant.

At low surfactant concentrations, the system is separated in three phases, corresponding to the W III system. If the temperature is increased further, the oxyethylenic groups are increasingly dehydrated, thus

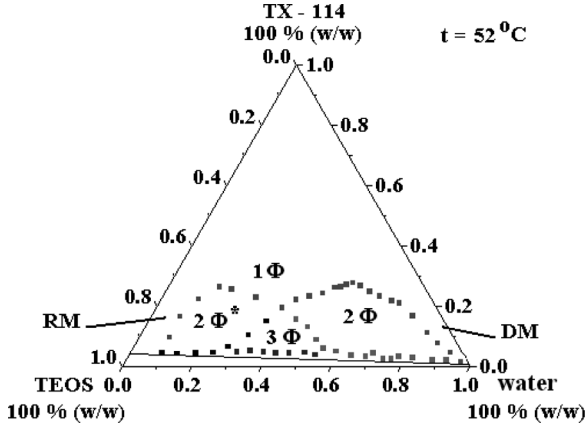



**FIGURE 3** The phase diagram of water/TX 114/TEOS at 52°C. 1Φ – one phase (direct or reverse micelles, Winsor IV system, gel or liquid crystals); 2Φ* – two phases (Winsor I system); 2Φ – two phases (Winsor II system); 3Φ – three phases (Winsor III system).

enhancing the solubility of the surfactant in the organic medium, so that in the end the inversion takes place with the formation of the water/oil microemulsion (W II).

For the presented results (Fig. 3) the behaviour of the system at 52°C could be considered at optimum corresponding at a water/oil ratio of unity and within a range of surfactant concentrations resulting to three phases (W III system, at low concentration) or one phase (WIV system, at high concentration). The microemulsion contains in this case equal proportion of water and TEOS.



## The Influence of Cosolvent

The effect of the addition of acetonitril (ACN) upon water/surfactant/alcoxide + toluene systems is presented in Figure 4.

It can be observed that the presence in the system of ACN affects the type of interaction at the interface, all systems leading to a W II microemulsion at low surfactant concentrations. Therefore, ACN requires a maximization tendency of the interfacial surface with water, while the contact surface with the alcoxidic phase is minimized. At large surfactant concentrations W IV microemulsions are formed, similar to the systems of direct micelles.

Consequently, by choosing the optimal working conditions, composition-temperature, it can be stated that there are sufficiently large domains that can be used for obtaining nanostructures with the aim of preparing both inorganic and hybrid nanomaterials.

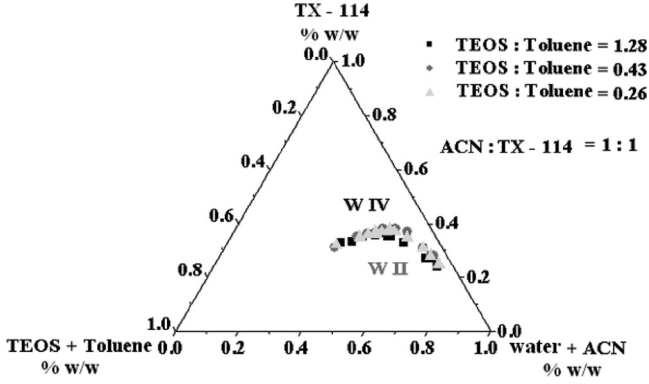



**FIGURE 4** The phase diagram of water + ACN/TX 114/TEOS + Toluene. W IV – one phase (direct or reverse micelles, gel or liquid crystals); Winsor II – two phases.

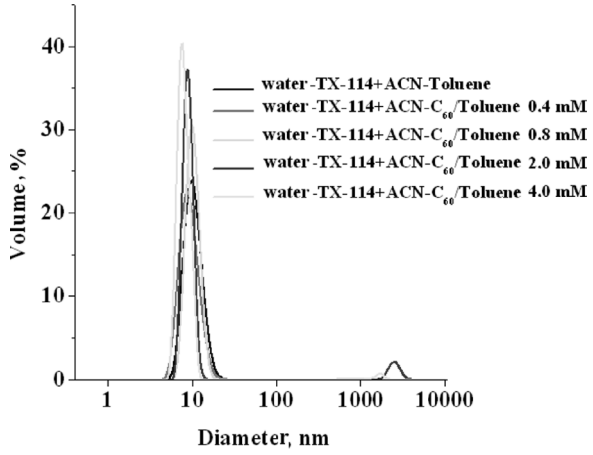



**FIGURE 5** Size estimation of the nanostructured colloidal aggregates.

## Size Estimation of $C_{60}$ Monodispersed Nanoclusters by DLS

The size of the nanostructured colloidal agregates obtained after the microemulsion process was estimated by dynamic light scattering technique (DLS) (Fig. 5, Table 1). The average hydrodynamic diameters of $C_{60}$ nanoclusters are between 7 nm and 10 nm (Table 1). The curve is single modal and the peak is rather narrow, indicating that the samples have low polydispersity.

Table 1 summarizes the effect of sample composition on the hydrodynamic diameter and their polydispersity.

## Electronic Spectra of $C_{60}$ Nanoclusters Dispersed in Microemulsion System

An indirect proof on $C_{60}$ clusters formation in microemulsion is revealed by the significant change in electronic spectra, where the

**TABLE 1** Cosolvent ACN Influence on the Nanostructured Colloidal Aggregates

| System | Water: ACN ratio | $C_{60}$ concentration [mM] | Diameter [nm] | Polydispersity |
|---|---|---|---|---|
| Water – TX 114 + ACN – $C_{60}$/Toluene | 1:1 | 0.4 | 10.1 | 0.155 |
| | 2:1 | | 8.7 | 0.206 |
| | 1:1 | 0.8 | 10.1 | 0.485 |
| | 2:1 | | 7.5 | 0.243 |

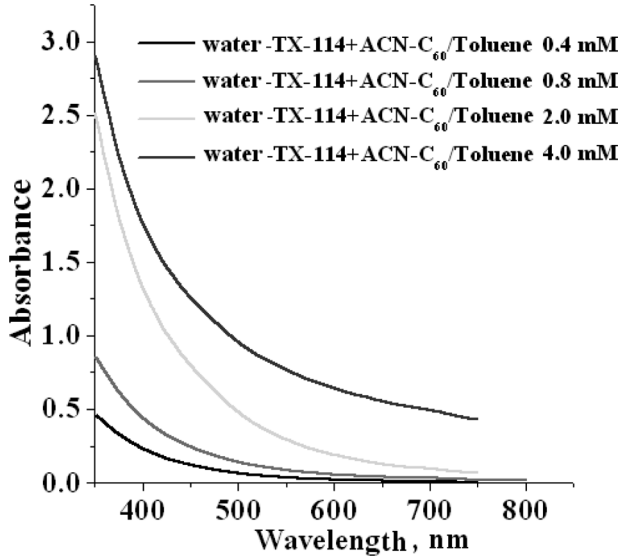



**FIGURE 6** Electronic spectra of water + ACN/TX-114/$C_{60}$/Toluen (O/W) microemulsion.

specific band of fullerene at 525–600 nm is replaced by a continuous absorption on the entire visible domain, due to the complex absorption/diffusion/fluorescence processes caused by the solid clusters in the droplets core (Fig. 6).

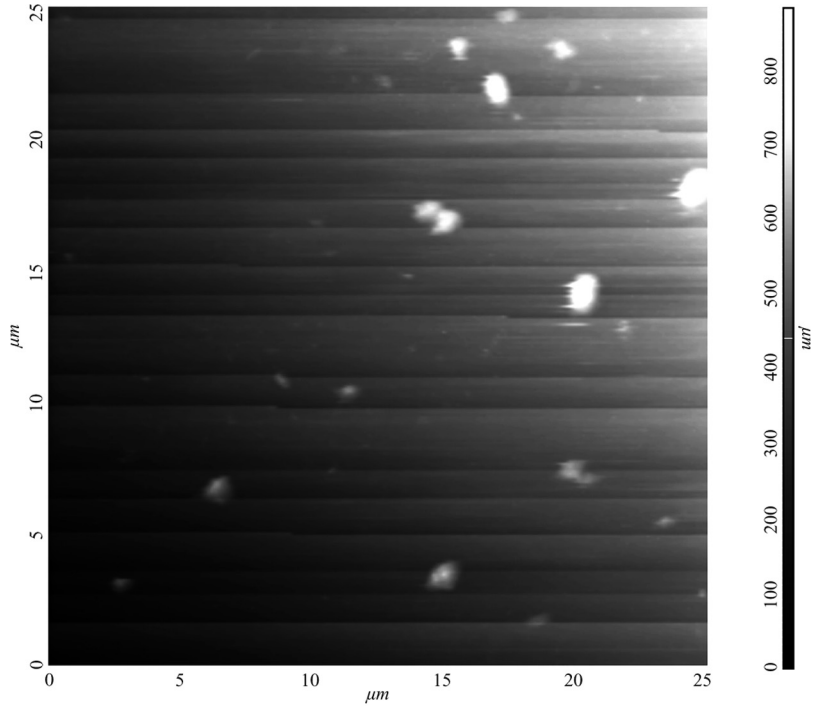
## Nanoparticles Size and Topography

The morphology and essential features of the synthesized materials have been studied using atomic force microscopy (AFM). The AFM measurements allow examining the shapes, size, and dispersion of substrate and surface texture of nanoparticles. By using the AFM individual particles and groups of particles were visualized. 3D information is incorporated in both views. They are formed as a result of drying process of microemulsion.

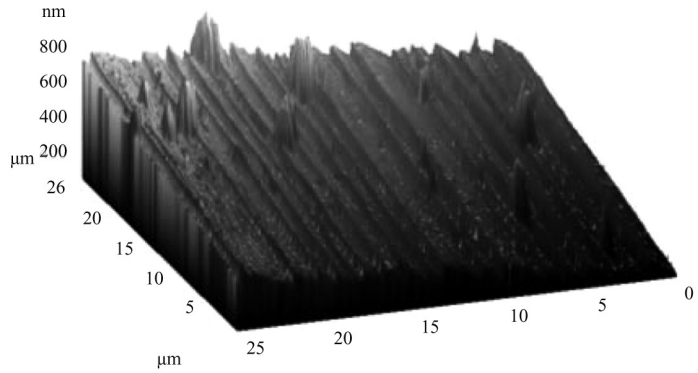
Figure 7 shows both perspective view and top view image of monodispersed and homogenous silica coated fullerene clusters with the mean diameter less than 300 nm.

The ratio of the numbers of particles at a given size is immediately apparent by visualising the 2D image (Fig. 7a).

In the 3D image (Fig. 7b), the intensity of the colour reflects the surface roughness and it can be estimated the films depth which is




(a) **2D topography image**




(b) **3D topography image**

**FIGURE 7** Topographical scan images of silica coated fullerene cluster on the glass substrate. Scan size is $25 \times 25\,\mu m$ image on thin film.

less than 300 nm which recommends these nanomaterials for the thin films deposition.

## DISCUSSION AND CONCLUSION

The phase diagrams in ternary systems water – TX-1114 – TEOS have been performed, which allowed us to select the optimum composition domain for conducting synthesis in different medium, organic and/or inorganic.

Consequently, by choosing the optimal working conditions, composition-temperature, it can be stated that there are sufficiently large regions that can be used for the obtaining of nanostructures with the final aim of both inorganic and hybrid nano materials manufacture.

The effect of the addition of amphyphilic organic compounds was proven by drawing the phase diagrams of pseudo-ternary systems. This effect consists in the widening of the microemulsions formation domain in a Water/Oil, Water system.

It can be stressed the advantage of using tetraetoxysilan (TEOS) due to a variety of microemulsion types that could be formed, allowing thus a wide pallet of applications for the nanomaterial synthesis.

The size of aggregates at nanometric scale (clusters, nanoparticles, droplets, micelles) there have been evaluated by two methods: by atomic force microscopy, as well as by performing experiments based on dynamic light scattering.

It results that microemulsification represents a method for obtaining of silica coated fullerene clusters, this being the first stage of the preparation of hybrid nanocomposites appropriate to deposition of silica based thin films.

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