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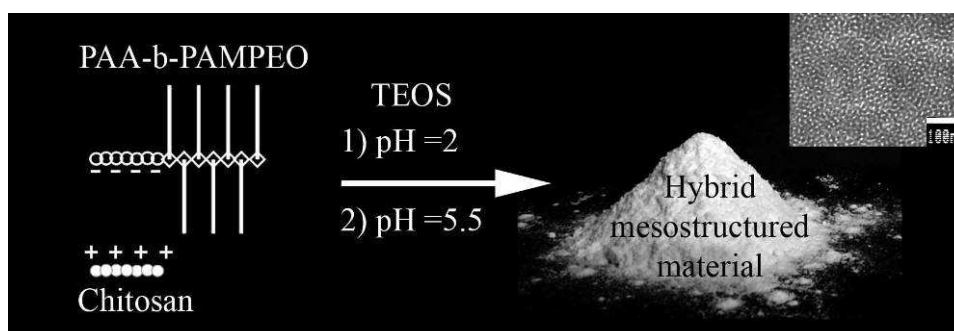
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Graphical abstract:

An original way to synthesize nanostructured materials is the use of new structuring agents constituted of induced and reversible micelles of Double Hydrophilic Block Copolymers (DHBC). The present paper aims at showing that induced micelles can be obtained by complexation between a PAA-b-PAMPEO (DHBC) polymer containing a comb-type neutral block and a polyamine, that the micellization process is reversible as a function of the pH and finally, that the obtained polyion complex micelles can be successfully used in the preparation of well organized mesostructured silica materials.



Nanostructured silica templated by double hydrophilic block copolymers with a comb-like architecture

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Abstract

An original way to synthesize nanostructured materials is to use new structuring agents constituted of Double Hydrophilic Block Copolymers (DHBC). The originality of these structuring agents is multiple: in water, the hydrosoluble DHBC copolymers can become amphiphilic and form micelles in specific conditions, i.e. after addition of other molecules or after a change of a physicochemical parameter (pH), which selectively makes one of the blocks insoluble in water. The addition of a silica precursor to a micelle suspension can lead to the formation of hybrid mesostructured materials, precursors for mesoporous silica. The micellization process may be reversible and the micelles can then be removed from

the silica materials in aqueous solution at room temperature after application of a dissociation stimulus, leading to the mesoporous materials. A new original DHBC is used here for silica structuring: instead of a classical linear diblock copolymer, it is a diblock copolymer with a linear polyacid block (PAA) and a polyethylenoxide based neutral block (PAMPEO) with a comb-type architecture. It is synthesized by controlled radical polymerization (RAFT method) which permits a control of the block lengths. It is shown here that these new DHBC polymers can form polyion complex micelles by complexation with a natural polyamine and that the micellization is reversible as a function of the pH. It is also shown that the new pH sensitive micelles can act as structuring agents in the preparation of mesoporous silica materials.

Keywords: block copolymers, micelles, silica and mesoporous materials

1. Introduction

The chemistry of nanostructured materials strongly developed since the discovery in 1992 by Mobil of materials with organized porosity (MPO)[1]. The interest in those materials is due to their remarkable properties (high surface area, regular pore size and organization of the porosity) useful in catalysis, sensing and drug delivery applications[2]. Contrary to microporous materials synthesized around isolated molecules, the MPO are elaborated around supramolecular assemblies of autoassociative molecules. The first structures of MPO, of MCM-41 type, were obtained by using micelles of surfactants made up of an alkyl chain and a cationic polar head[3]. Those materials have a limited thickness of the walls, pore sizes lower than 10 nm and have a low thermal stability. Since 1995, the use of another type of autoassociative molecules, the neutral surfactants, made it possible to increase the thickness of the walls and to improve the stability of the porous materials [4-6]. In 1998, a significant development took place with the use of amphiphilic block copolymers of

poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) PEO-PPO-PEO type [7, 8] and materials whose pore sizes were increased to approximately 30 nm could be prepared.

Today, a large set of functional mesoporous materials shaped as monoliths, thin films or powders have been synthesized. However, many of them remain within the academic field because some of their limitations effectively close the door to the real market, among them: cost, unsustainable solvents, energy-consuming process for template calcination, toxicity of some structuring agents and their non-recyclability. Some interesting procedures, using physical methods have been proposed for template removing but without a real impact on the market [9-11]. It appears essential to seek alternative solutions making it possible to avoid the combustion of the organic matter and to work out these materials under conditions as soft as possible.

Our recent studies (Figure 1) showed that it is possible to prepare MPO in soft conditions and to recover and recycle the structuring agent [12]. The new strategy consists in replacing the classical amphiphilic template by an induced and reversible assembly of water-soluble block copolymers (WSBC) [13-15], which allows to recover the template in aqueous solution. The micellization [16-18] process results from electrostatic interactions between two oppositely charged polymers in aqueous solution, a hydrophilic polyelectrolyte-neutral diblock copolymer and a homopolyelectrolyte. Electrostatic complexation leads to an associative phase separation, known as complex coacervation[19], provided certain requirements meet; such as proximity to charge neutrality. The presence of the neutral block ensures that the insoluble electrostatic complex is sterically stabilized in solution as a micellar assembly. A great advantage of such polyion complex (PIC) systems is that the phenomenon of phase separation is tunable in water with parameters influencing the electrostatic interaction between the two macromolecules such as the ionic strength, the temperature, the mixing fraction and the pH in the case where weak acids and bases are used.

The first results that we reported [12] showed that this new green strategy has yet to be improved since the template recovering is not complete: about 40% of the diblock copolymer (PEO-b-PAA, poly(ethylene oxide)-b-poly(acrylic acid) or PEO-b-PMAA poly(ethylene oxide)-b-poly(methacrylic acid)) remain in the structure, while the oppositely charged polymer (the oligochitosane polyamine) is totally removed from the material. A part of the PEO block is then probably trapped in the silica walls and prevents the PEO based block copolymer to get out of the inorganic network[20].

One of the solutions for improving the template removal could be brought by changing the interaction between the neutral PEO block and the silica structure, and one of the ideas is then to change the usual linear neutral PEO block for a block with a comb-like architecture, a poly(acrylate methoxy poly(ethyleneoxide)) PAMPEO. It is constituted of a polyacrylate backbone with PEO chains along the backbone. For a same molecular weight as that of the neutral linear part, the comb block (expected to interact with silica) is shorter and denser than the linear homologue and so, this modification should influence the organic/inorganic interactions (Figure 2). Moreover, the PAA-b-PAMPEO copolymer is here synthesized quickly by using only one polymerization technique, the RAFT (Reversible Addition Fragmentation chain Transfer) polymerization for the two polymeric blocks and it is easy to control the size of the two blocks separately [21]. In comparison, the synthesis of PAA-b-PEO block copolymers was reported in the literature by either anionic polymerization [22-24] or atom transfer radical polymerization (ATRP) [25, 26]. The anionic pathway is time consuming, because AA cannot be polymerized without protection. Poly (tert-butylacrylate) synthesis is the usual first step, and an additional step is needed to convert the poly(tert-butylacrylate) chains into PAA by hydrolysis. Moreover, the major drawback of ATRP is that it uses an organometallic catalysis, which may be the source of unacceptable contamination (transition metal) for green applications. It appeared then that the synthesis of

double hydrophilic block copolymers with a comb PEO based block, using only RAFT polymerization technique, may be simpler and advantageous, compared to linear block copolymers in the preparation of polyion complex micelles for the obtention of mesoporous materials. The present paper aims at showing that induced micelles can be obtained by complexation between a comb-type PAA-b-PAMPEO polymer and a polyamine, that the micelle formation is reversible as a function of pH, and finally that the present micelles can be successfully used in the preparation of well organized mesostructured silica materials. The effectiveness of the template removal step in soft conditions at room temperature will be studied in a forthcoming paper.

2. Experimental part

2.1 Materials

Acrylic acid (AA), α -acrylate ω -methoxy poly(ethylene oxide) (AMPEO), $M_n = 454 \text{ g mol}^{-1}$ dimethylformamide (DMF), azo-bis-isobutyronitrile (AIBN), polyamine, oligochitosan lactate (OCL) with $M_n < 5000 \text{ g mol}^{-1}$, and silica precursor, tetraethoxysilane (TEOS) were purchased from Aldrich and used as received. The transfer agent, 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) was synthesized according to Lai et al[27].

2.2 Analysis

Polymer molecular weight and polydispersity index (M_w/M_n) were determined by size exclusion chromatography (SEC), using a 25 mM solution of LiBr in DMF as the eluent at 50 °C.

The columns were calibrated with polystyrene standards. The ^1H NMR spectra were recorded with a 400 MHz Bruker spectrometer.

Dynamic light scattering measurements were carried out at 25°C using an Autosizer 4800 instrument (Malvern, U.K.) with a 50 mW laser source operating at 532 nm. Scattered light intensities were collected together with hydrodynamic diameters and polydispersity indexes (PDI) of the micellar colloids. Hydrodynamic diameters were obtained from measured diffusion coefficients using the Stokes–Einstein equation.

The materials were characterized by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and nitrogen adsorption/desorption experiments. TEM images were collected on a JEOL 1200 EX II (80-100 kV) microscope on microtomed samples. SEM micrographs were obtained on a Hitachi 4800S microscope.

Samples are calcined in an oven in air with a ramp of 2°C/min up to 500°C. N₂ adsorption/desorption experiments were performed on a Micromeritics TriStar instrument, for analysis of the specific surface area and porosity. Before adsorption measurements, the samples were outgassed under vacuum for 6h at 250°C.

2.3 Synthesis of PAA-b-PAMPEO block copolymer

The PAA-b-PAMPEO polymer with the $M_n(\text{PAA})=3000\text{g mol}^{-1}$, $M_n(\text{PAMPEO})=13000\text{g mol}^{-1}$ targeted molecular weights is synthesized as follows :

a) Synthesis of PAA first block: 0.012 g azo-bis-isobutyronitrile ($7,31\times 10^{-5}$ mol), 1.09 g DMP (3×10^{-3} mol), 15 mL of AA (1.98×10^{-1} mol) and 15 mL of DMF were mixed together in a 250mL Schlenk flask. The mixture was degassed for 30 minutes under Argon. This reaction mixture was heated in an oil bath at 70°C for 3 h. The polymer was precipitated by addition of the solution to ether, and dried under vacuum at 50°C during 48h. The molecular weight was determined by ¹H NMR in DMSO-d₆ ($M_n=3\times I_{2,44}/I_{0,8}$), where $I_{0,8}$ and $I_{2,44}$ are the intensities of the proton resonances at 0.8 ppm (terminal RAFT agent: CH₃-

$C_{11}H_{22}$, t) and 2.44 ppm ($\underline{C}H-COOH$, m), respectively. Polydispersity was measured by SEC in DMF.

b) Synthesis of PAA-b-PAMPEO: a mixture of 3 g trithiocarbonate-capped PAA (1×10^{-3} mol; M_n (NMR)= 3000 g mol^{-1} and $M_w/M_n = 1.15$), 20 g AMPEO (4.4×10^{-2} mol), 8.2×10^{-3} g AIBN (5×10^{-5} mol) and 50 mL DMF was degassed for 30 minutes under Argon and heated in an oil bath at 75°C for 2 h. The copolymer was precipitated into ether and dried under vacuum at 50°C during 48h. The copolymer is slightly yellow. The molecular weight of the second block was determined by ^1H NMR in DMSO ($M_n = 3I_{4.1}/2I_{0.8}$), where $I_{0.8}$ and $I_{4.1}$ are the intensities of the proton resonances at 0.83 ppm ($\underline{C}H_3-C_{11}H_{22}$, t) and 4.1 ppm ($\underline{C}HCOO\underline{C}H_2$, m) respectively. Polydispersity was determined by SEC in DMF.

2.4 Preparation of mesoporous materials

Typically, 204 mg of an oligochitosane salt, OCL (powder with an oligochitosan lactate unit $C_{12}H_{24}O_9N_2$, $C_3H_5O_3$) is mixed with 300 mg of PAA₃₀₀₀-b-PAMPEO₁₃₀₀₀ in 20 g of deionised water at room temperature. Equilibrium pH is about 4.25 and it is immediately reached. 0.969 ml of TEOS is then added to the stirred solution. An emulsion forms and the solution pH is lowered to about 2 for TEOS hydrolysis. The pH is kept at 2, under vigorous stirring, until the emulsion disappears and the sample looks monophasic, this is done in about 20 minutes. Then, the solution pH is brought up to 5.5. A macroscopic precipitation is observed immediately when the pH is increased, the solution is left under stirring for 24 hours at 30°C . The synthesized sample is then filtered and placed in an oven at $T = 40^\circ\text{C}$ overnight. A white powder is obtained.

3. Result and discussion

First, the DBHC (double-hydrophilic block copolymer) consisting of PAMPEO ($M_{n,NMR}=13000\text{g mol}^{-1}$) and PAA ($M_{n,NMR}=3000\text{g mol}^{-1}$) was synthesized by the sequential RAFT (Reversible Addition Fragmentation chain Transfer) polymerization of AA and AMPEO (Figure 3), according to the procedure of Aqil et al [21]. The polymer polydispersity was determined to be 1.31. This technique of controlled radical polymerization (CRP) permitted a control of each block length. The apparent pKa of the block copolymer was determined by titration, it was found at 6.1.

3.1 Behaviour in aqueous solution of the PAA-b-PAMPEO/OCL pH responsive system

The micellization process of the present polyelectrolyte/neutral DHBCs (PAA-b-PAMPEO) was induced by electrostatic complexation of an oppositely charged polyion. Herein, the weak polyacid/neutral double-hydrophilic block copolymer is studied in the presence of a weak polybase OCL, an oligochitosane lactate ($pK_a=6.5$). An electrostatic complex between the two oppositely charged polyions is expected to form, it should lead to the formation of core–corona micelles with a water-insoluble complex core (PAA-OCL) and a water-soluble corona (PAMPEO).

It is important to characterize the structuring agent in details first in solution, and to determine the pH domain of micelle formation before adding the silica precursor. The dynamic light scattering technique allows monitoring the formation of micellar objects between OCL and the water-soluble block copolymer as a function of the pH. The measurements of the scattered light intensity of the DHBC/OCL mixture (Figure 4) indicate that micelles form between pH 4 and 7: A sharp increase of the scattered light intensity corresponds to aggregation of both polymers and then, to micelle formation, while a strong decrease of the intensity reveals that micelles dissociate, below pH 4 and above pH 7. At pH 5, the micelles have a hydrodynamic diameter of 42 nm, and the polydispersity index equals 0.31.

It is then shown that the micelle formation can be driven by the pH, this is possible since the charges of the polyacid and polybase blocks are pH-dependent. Micellization of DHBCs, and more specifically formation of polyion complex (PIC) micelles [22, 28-35], has been extensively studied in the literature. The present DHBCs/polybase complex system only involves weak electrostatic interactions; the energy demand for disassembly is then quite low in comparison with breaking covalent bonds and so micellization presents here the considerable advantage of a switchable assembly/disassembly process. This advantage will be used later for generation of the material porosity at room temperature in water.

Finally, the light scattering results suggest that the material structuring step can be performed at pH 5.5, within the pH range of PIC micelle stability.

3.2 Obtention of polymeric/ inorganic hybrid materials and characterization of the materials

The synthesis of the hybrid materials using the structuring complex systems occurs in two steps [36, 37]. First the PAA-b-PAMPEO and the OCL are dissolved in an aqueous solution; TEOS is then added, leading to a diphasic system and the pH is adjusted at a value of 2 for TEOS hydrolysis. The pH is kept at 2 until the system becomes monophasic, ie. after about 20 minutes. Secondly the hybrid material is synthesized at room temperature by increasing the pH value of the mixture to 5.5, a pH value at which micelles are formed. This is done by adding small amounts of a NaOH solution. After 24 h, a precipitate is recovered and dried at 40°C overnight. The possibility of structuring silica with PAA-b-PAMPEO/OCL PIC micelles is revealed by the TEM pictures (Figure 5). They show that, like in the case of the linear diblock copolymer-based systems (PEO-b-PMAA/OCL and PEO-b-PAA/OCL)[12], hybrid mesostructured materials can be obtained with the present original diblock copolymer with a comb-like architecture. The TEM micrographs of the hybrid material synthesized at pH

5.5 reveals ordered mesostructures viewed with different orientations, and presenting a wormlike arrangement of the micelles. This result suggests that the comb PAMPEO block is able to interact with silica precursors in a similar way as linear PEO blocks, leading to precipitation of hybrid micelle-silica mesophases. The N₂ adsorption/desorption isotherms (Figure 6) of the hybrid material calcined at 500°C (with a ramp of 2°C/min) exhibit a hysteresis loop in the range 0.6 < P/P₀ < 0.9. They are type IV isotherms in the IUPAC classification, characteristic of mesoporous materials. The triangular hysteresis loop is a H2 type hysteresis according to the IUPAC classification, it shows a desorption branch which is significantly steeper than the adsorption branch, which is attributed to a pore-blocking or percolation effect. Then, the pore size distribution was calculated by using the adsorption branch, it is found to be centered at 6.8 nm. The specific surface area amounts to 505 m²/g. The average pore size is smaller than the hydrodynamic diameter D_h of the micelle (42 nm), which is expected, since D_h values include the core size (PAA/OCL complex) and the size of the large and hydrated polymer corona in a good solvent (water). Furthermore, the N₂ adsorption analysis is performed on the calcined material; during the calcination step up to 500°C, the silanol groups in the walls continue to condense, which leads to decreasing of the pore diameter and also to the structure reinforcement.

Figure 7 shows SEM images of the hybrid mesostructured silica materials synthesized through the two-step pathway at a final pH of 5.5. The morphology of the sample is not well defined; the sample presents agglomerated particles of varying shapes, with some tendency to form spheres. The observation of a distribution of morphologies from spheres to ill-defined shapes may be explained by the rate of phase separation as described in the colloidal phase separation mechanism [38]. In the present synthesis pathway, the pH of the synthesis medium is adjusted at 5.5 when the formation of the hybrid material occurs by precipitation. It is relatively high and then, it is known that it is not so favourable to the formation of spherical

particles. Moreover, we should consider the fact that the increase in the pH from the first to the second step of the synthesis (variation from pH = 2 to pH = 5.5) is not instantaneous, it is done by successive additions of minor amounts of a NaOH solution (0.5M). Then, it is probable that a part of the material is not formed at pH = 5.5 but at a lower pH (which is more favourable to the spherical morphology). A lower pH value (between 2 and 5.5) results in a lower condensation rate of silica, and then to a slower rate of phase separation. The surface free energy determines the material morphology; the spherical morphology with a high curvature is generated in order to minimize the surface energy. As a result, the spherical morphology is obtained only in the case where silica syntheses are performed in acidic medium, where condensation is as slow as possible. In conclusion, the ill-defined morphology observed here, which contains some spherical parts, is the result of a precipitation phenomenon occurring on a range of pHs from pH 2 to pH 5.5.

4. Conclusion

We showed here that the PAA-b-PAMPEO block copolymer with a comb-like architecture behaves, in a first approximation, like the linear PEO-b-PAA diblock in what concerns the micellization process and the material structuring process: (i) the micellar behaviour is the same, revealing the formation of well defined polyion complex micelles between pH 4 and 7 and the polymer disassembly outside of this pH domain. (ii) mesostructured silica materials can be prepared with the present comb-type diblock polymer, in the same way as with the homologue PAA-b-PEO polymer. It was also possible to prepare mesoporous silica when the hybrid material was calcined. Finally, the success of the nanostructuring step will permit to investigate the impact of the neutral block architecture on the washing step for template removing in aqueous solution at a well chosen pH. It is envisaged to study the influence of the copolymer architecture on the template recycling

procedure. The influence of other parameters, on the template removal step, like the synthesis temperature will also be tested: indeed, an increase of the temperature affects the PEO behaviour in water, it makes it less hydrophilic, which should decrease the interaction between the organic and the inorganic networks.

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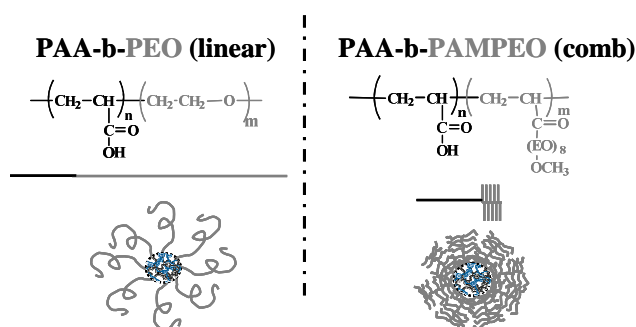


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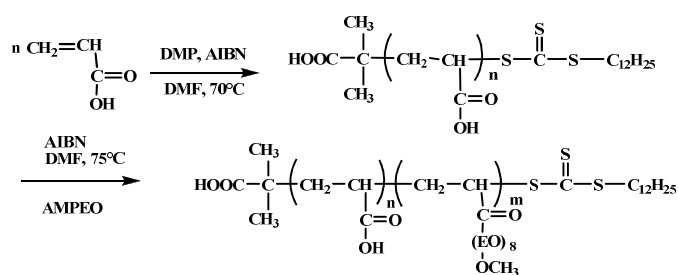


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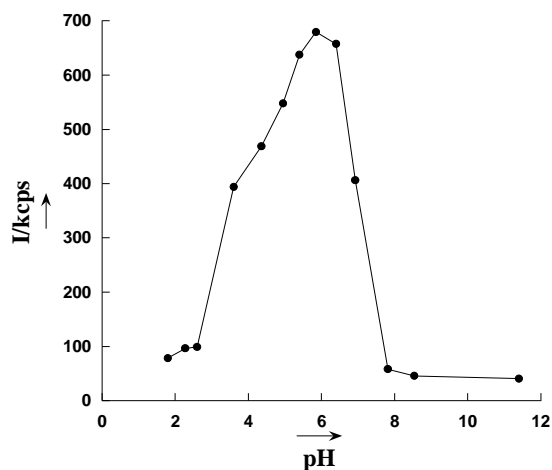


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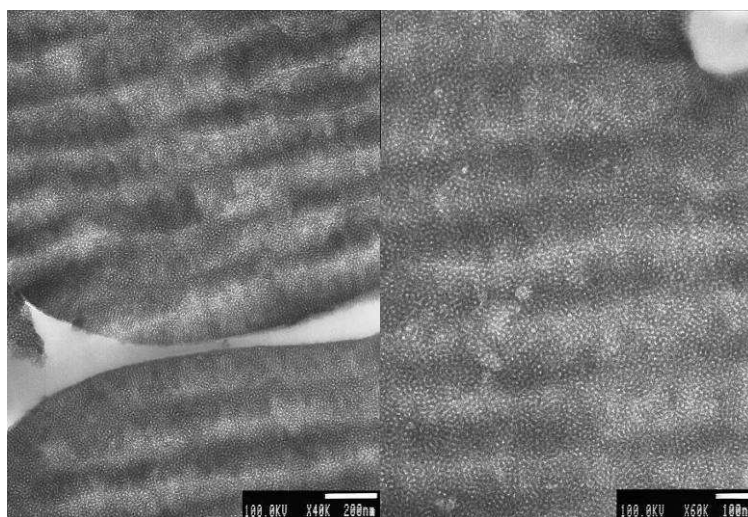


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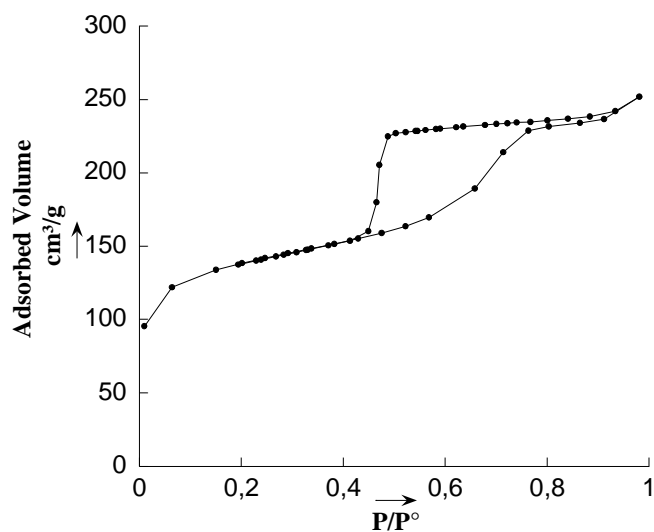


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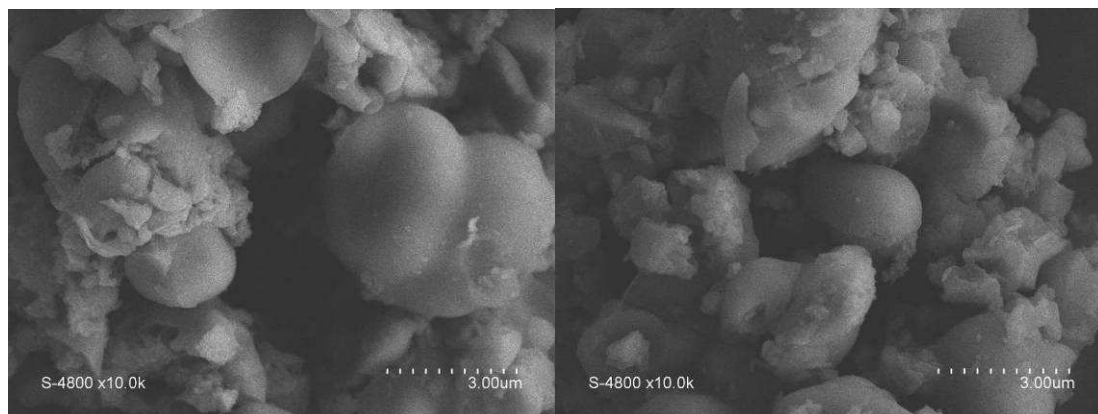


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