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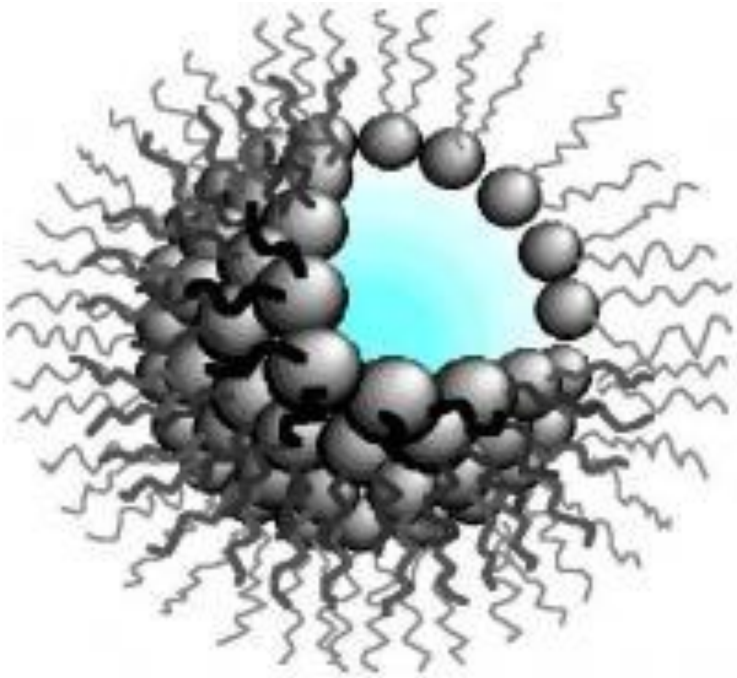

Tailor-made silver particles by microemulsion for use in catalysts

Bachelor of Science Thesis in Chemical Engineering

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Department of Chemical and Biological Engineering
Division of Applied Surface Chemistry
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden, 2012

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Cover:
A water droplet in microemulsion with a film of surfactant,
page 2

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Acknowledgements

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Abstract

Microemulsions are often used when synthesizing nanoparticles. In this thesis, silver particles of a certain size, for use in a catalytic converter in cars, were synthesized with microemulsion. The microemulsion used was the water in oil type and the chemicals used were n-heptane, Brij30, $AgNO_3$ (aq) in combination with the reducing agent $NaBH_{4.}$

Different water to surfactant molar ratios were tested and the samples were observed with a transmission electron microscope. The result shows that the size of the silver particles depends on the water to surfactant molar ratio, when the molar ratio decreases so does the radius of the silver particles'.

Keywords: microemulsion, silver particles, catalyst.

Table of Contents

1. Introduction and background

Emission control of automobile exhausts is a subject well debated in today's society. Improvement of the air we breathe is crucial and with better catalytic after-treatment of the exhaust the future emission standards can be reached.

The main components in automobile emissions are nitrogen oxides (NO_X), carbon monoxide (CO) and hydrocarbons (HC). These substances are harmful. Without any after-treatment of the exhaust the consequences would be noticeable. For example, an increase of nitrogen oxides in the atmosphere could lead to catalytic degradation of the ozone layer [2]. In the troposphere, on the other hand, nitrogen oxides and hydro carbons contribute to elevated levels of ground level ozone [3].

However through catalytic after-treatment these substances can be converted into less harmful compounds. The desired products are carbon dioxide (CO_2), water (H_20) and nitrogen (N_2). Some reactions taking place in a three-way catalyst, which usually contains noble metals such as platinum, palladium and rhodium, can be seen below [4]:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \quad (1)$$

$$H_4C_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad (2)$$

$$CO + NO_x \rightarrow CO_2 + N_2 \quad (3)$$

Even though the catalytic converter has reduced the emission considerably there is still need for improvements [5]. For example there is a need for catalysts that can work in excess oxygen (like for diesel exhaust) and at low temperatures because today's engines are so energy efficient. One reason that a catalyst needs to operate at lower temperatures is so that the catalytic reactions can be initiated earlier in the drive cycle, and thus reduce the emissions of the unwanted components [5]. This is especially important because of today's new cars with start- stop systems and hybrid cars.

The objective of this thesis is to synthesize silver particles of a certain nanosize (10^{-9} m) for use as catalysts. The properties of the metal's i.e. the catalysts change drastically with the size of the particles. Since the catalytic reaction occurs on the surface of the metal particles, a change in size affects the reactions and the catalytic processes. As the size of the particles decreases, the active surface area increases as well as the catalytic activity [1].

2. Theory

2.1 Surfactant

A surfactant is an amphiphilic molecule which means it has a hydrophilic head group and a hydrophobic tail group. This makes it suitable for mixing oil and water. Surfactants can be either ionic or nonionic and therefore have some different properties [6]. Two common surfactants used in microemulsion are Brij30 and Dioctyl sodium sulfosuccinate (AOT).

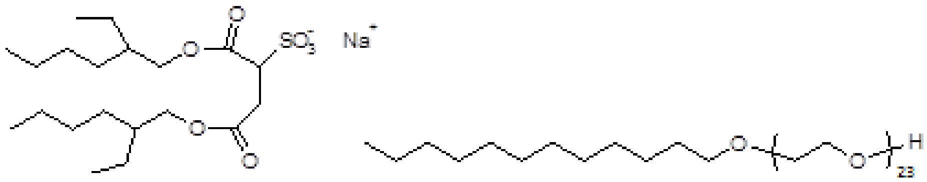


Figure 1- The picture shows two different types of surfactants, AOT and Brij30

2.2 Microemulsion

A microemulsion is a solution consisting of a mixture of water, oil and a surfactant and sometimes also a cosurfactant. The surfactant works as an active film between the water and the oil, which makes it possible to create micelles in the solution. Microemulsion is thermodynamically stable and will therefore not separate into two phases, unlike emulsion [7].

There are different types of microemulsions, water in oil-, oil in water- and bicontinuous microemulsion. For preparation of small inorganic particles the water in oil microemulsion is known to be useful [8]. This is because the metal salt is water soluble and the metal will therefore be trapped in the droplets. See section 2.2.1.

2.2.1 Microemulsion with metal particles

When synthesizing metal particles by microemulsion, the metal salt is dissolved in the water and will therefore be trapped in the droplets in the oil. To be able to obtain the metal particles the salt must be reduced by a reducing agent. Another microemulsion containing the reducing agent in the droplets is prepared. The two microemulsions are mixed together causing the metal salt to reduce and the nanoparticles are formed [9].

The water to surfactant molar ratio influences the size of the droplets and therefore the size of the particles [10]. The concentration of the metal salt also affects the size of the particles; higher concentrations provide larger particles [7].

Although this method is relatively new it is commonly used, one reason for this is because it is easy to control the size of the particles. Addition of a cosurfactant can make it even easier to control the size of the particles [10]. However, there are disadvantages with this method, for example that the large amount of surfactant needed makes is expensive and the chemicals used are often rather toxic [11, 12].

2.4 Transmission electron microscopy (TEM)

The transmission electron microscope is an instrument that allows observation of particles at Angstrom size (10^{-10}m) [13]. It consists of an electron source that beams electrons through a condenser lens, which directs the electrons straight through the sample. The electrons are then directed by an objective lens before reaching the aperture and are depicted on a fluorescent screen where the particles in the sample can be observed [13].

3. Experimental Procedure

The water to surfactant molar ratio is important because it determines the size of the particles when formed in the microemulsion. The higher water to surfactant molar ratio in the microemulsion the larger particles can be formed. However particles can only reach a certain size, approximately 15-20 nm, before the microemulsion no longer can hold the particles.

3.1 Chemicals

In this work n-heptane (C_7H_{16}) (99%), silver nitrate ($AgNO_3$) (99.5%), sodium borohydride ($NaBH_4$) (>95%) and Brij30 ($C_{58}H_{118}O_{24}$) from Sigma –Aldrich where all used as received.

3.2 Deciding oil to surfactant weight ratio

Five solutions of 50 g with different oil (n-heptane) to surfactant (Brij30) weight ratio were made; 90:10, 80:20, 70:30, 60:40 and 50:50. Each solution was tested to decide which solution was the most optimal for achieving good results. To decide which solution was the most optimal a small amount of solution where added to a vial. Then Milli-Q water was added in aliquots of 20 µL until microemulsion ceased to exist, see Figure 3. The water to surfactant molar ratio for each test where calculated and the conditions (80 wt% n-heptane) with the highest molar ratio was shown to be most suitable of the weight ratios tested.

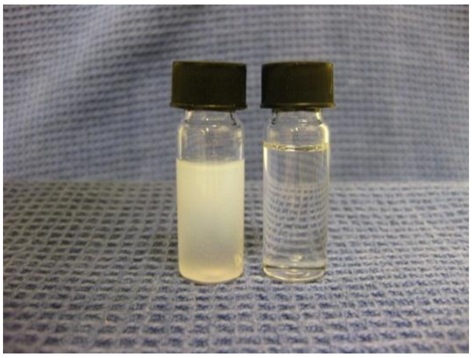


Figure 2- The vial to the right contains a solution when microemulsion exists and the vial to the left when there no longer is microemulsion

3.3 Deciding the maximum water to surfactant molar ratio

Two solutions with 0.5 wt% Ag respectively 2 wt% Ag were prepared from $AgNO_3$ and Milli-Q water. The solutions were added in aliquots of 20 µL to four vials each with oil and surfactant until microemulsion no longer existed i.e. when the solution no longer was clear. The water to surfactant molar ratio where calculated for each test. This was made to decide the maximum molar ratio when microemulsion still exists, in order to be able to prepare as wide range of silver particle sizes as possible. The maximum molar ratio was calculated to 30:1 water to surfactant.

3.4 Preparation of silver particles

Four vials with microemulsion containing silver nitrate in the water droplets were prepared, where the concentration of Ag in the aqueous solutions was 0.5 wt%. The oil to surfactant weight ratio was 80:20 with the water to surfactant molar ratio 10:1, 15:1, 20:1 and 25:1. Since the maximum molar ratio were calculated to 30:1 the maximum molar ratio used in the tests were 25:1, in order to be certain that microemulsion exists. Four other vials with the reducing agent and the same water to surfactant molar ratio and oil to surfactant weight ratio were prepared. The molar ratio between water and the reducing agent, $NaBH_4$, was 15:1 and the molar ratio between $NaBH_4$ and Ag was 4:1.

The two microemulsions, containing $AgNO_3$ and $NaBH_4$, respectively, were mixed and the $AgNO_3$ was reduced to Ag particles by the $NaBH_4$ (Figure 4). The new solution was dark brown; this indicates that silver particles have been formed.

The same procedure was made with 2 wt% Ag in the water solution.

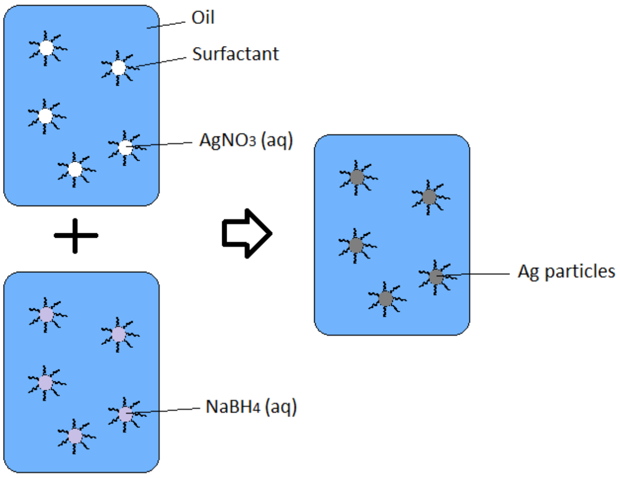


Figure 3- Reduction of silver nitrate by sodium borohydride to silver particles

3.5 Determining the size of the silver particles

The size of the silver particles was studied by transmission electron microscopy. One drop of each sample was applied on a copper grid for analysis in the transmission electron microscope (JEOL JEM-1200 EX II). In Table 1 the properties of the samples analyzed with TEM is listed.

Table 1- Data on the samples that was analyzed in the TEM

Sample:	Wt% Ag	Water/Surfactant molar ratio
1	0.5	25
2	0.5	20
3	0.5	15
4	0.5	10
5	2	15
6	2	20

The silver particles were observed and photographed by a camera attached to the transmission electron microscope. Each picture includes a scale that was used as a reference when the particles were measured by a ruler.

All images from the TEM session can be seen in the Appendix.

4. Results and Discussion

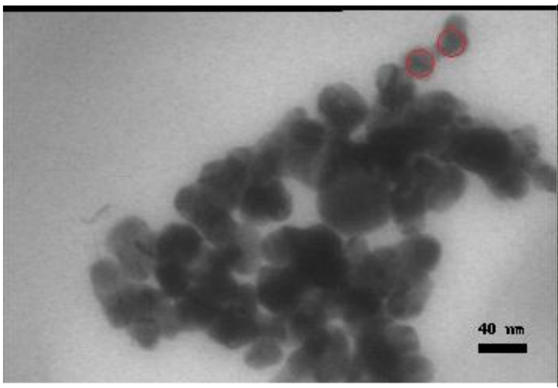
Table 2 describes the change in radius of the silver particles depending on the water to surfactant molar ratio. As expected the radius decreases with decreasing water to surfactant molar ratio, this because the size of the silver particle depends on the size of the droplets which in turn depends on the water to surfactant molar ratio.

The water to surfactant molar ratio 15:1 with 2 wt% Ag (Figure 3 F) gave the best image from the TEM to measure the particles. In the other images, it was difficult to distinguish particles from each other, which could have had an impact on the result.

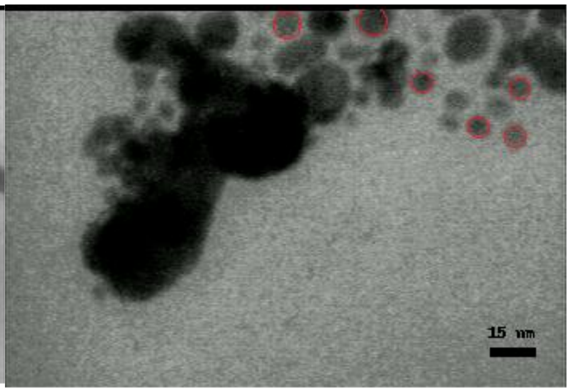
Table 2- Measured radius, from TEM images, of Ag particles prepared in microemulsions with varying water-to-surfactant molar ratio

Sample	Water/surfactant molar ratio	Wt% Ag	Radius (nm)
1	25	0.5	23
2	20	0.5	6-9.6
3	15	0.5	5-8.4
4	10	0.5	7.8
5	15	2	5.4-7.8
6	20	2	6.6-11.4

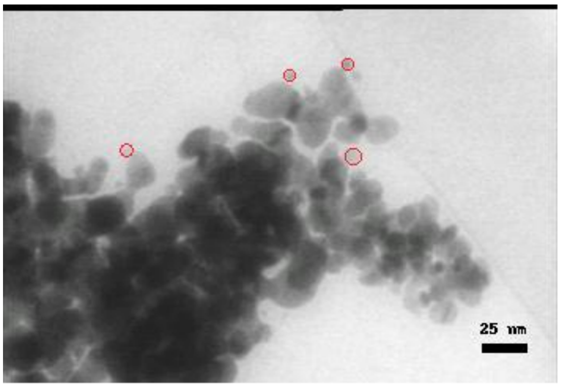
Figure 3 includes images of each sample observed in the transmission electron microscope. The red circles shows the silver particles in each sample which the radius was measured on.



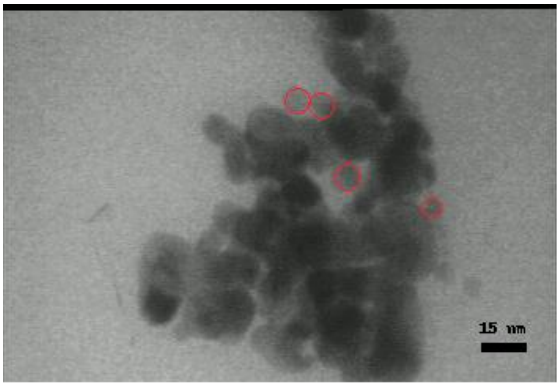
A



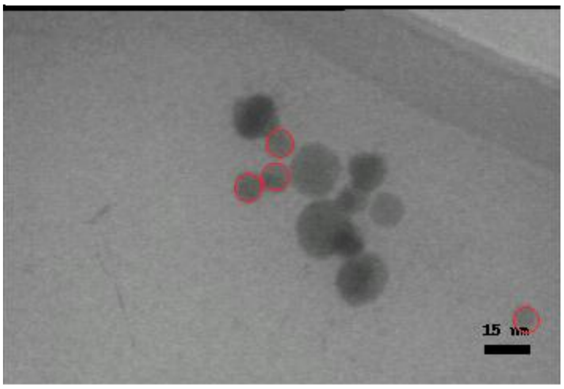
B



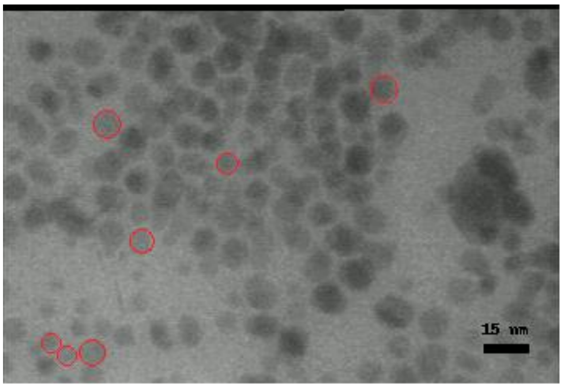
C



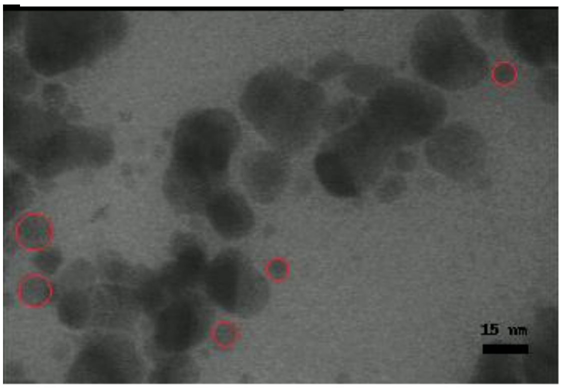
D



E



F



G

Figure 3 – TEM images of Ag particles prepared in microemulsion.

A) 0.5 wt% Ag, w/s=25,
B) 0.5 wt% Ag, w/s=20,
C, D) 0.5 wt% Ag, w/s=15,
E) 0.5 wt% Ag, w/s=10,
F) 2 wt% Ag, w/s=15,
G) 2 wt% Ag, w/s=20.

Image E in Figure 3 shows the sample with the water to surfactant molar ratio 10:1 and the silver concentration 0.5 wt%. The image shows some of the silver particles in the sample, a few of them are easy to distinguish and some of them are not. The radius of the silver particles was determined to 7.8 nm

Since it is hard to distinguish single particles in the images the result could be affected. A solution to this could be a dilution of the samples or separation of the silver particles by repulsion. Another transmission electron microscope could give better images since the one used in this thesis gave dark images at high zoom in.

Another surfactant could also affect the out coming result because different water to molar ratios would be enabled, and because different surfactants have different properties that could affect the result. Such properties are the elasticity and the length of the surfactant.

5. Conclusions

The results indicate that it is possible to influence the size of the silver particles with varying water to surfactant molar ratio. The result shows that decreasing water to molar ratio gives a decrease of the silver particles radius. However, the size of the particles differs but only within a rather small range.

6. References

[Front page] Picture available from: http://www.hybridnanocolloids.com/Research/Research-Projects

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Appendix

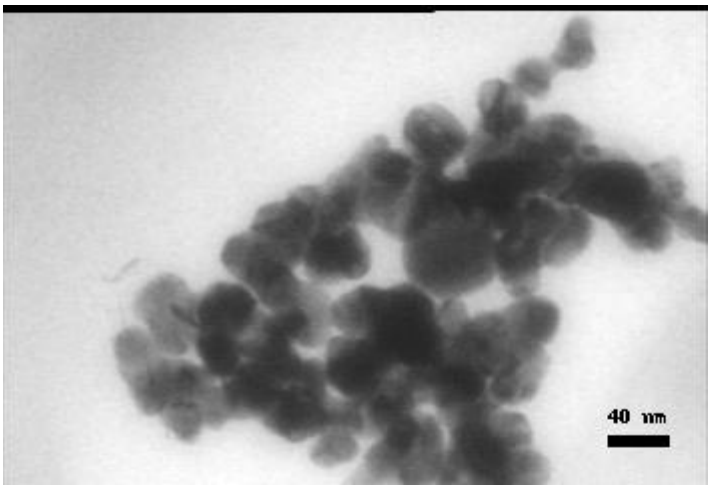

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
1	0.5	25	80K
2	0.5	25	120K
3	0.5	25	120K

Figure 1-Sample 1

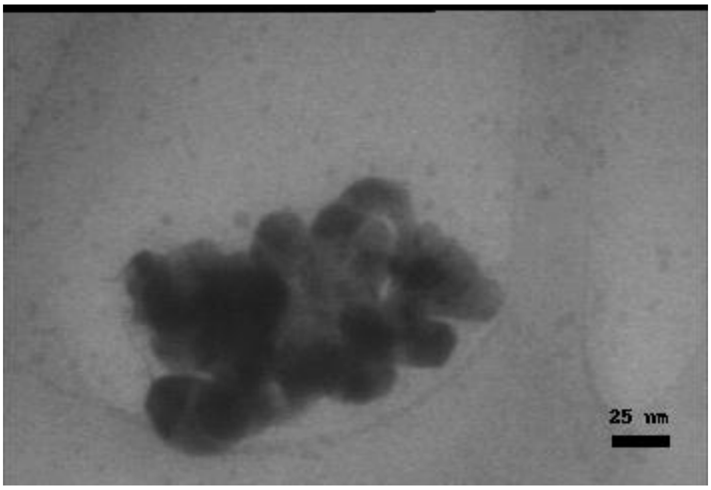

Figure 2-Sample 1

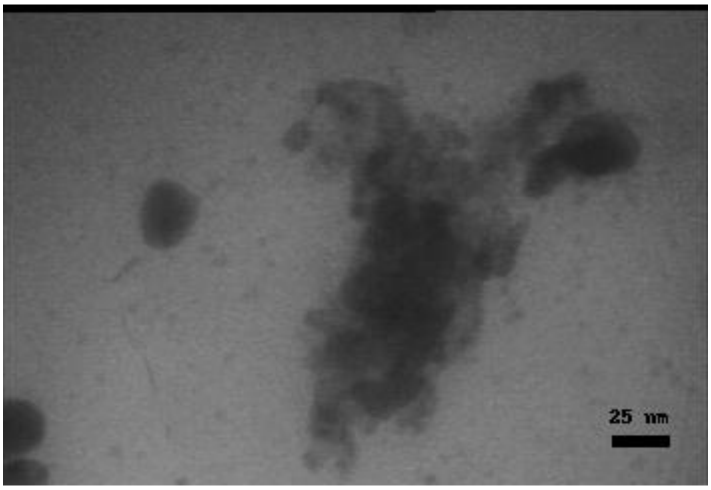

Figure 3-Sample 1

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
4	0.5	25	120K
5	0.5	25	120K
6	0.5	25	120K

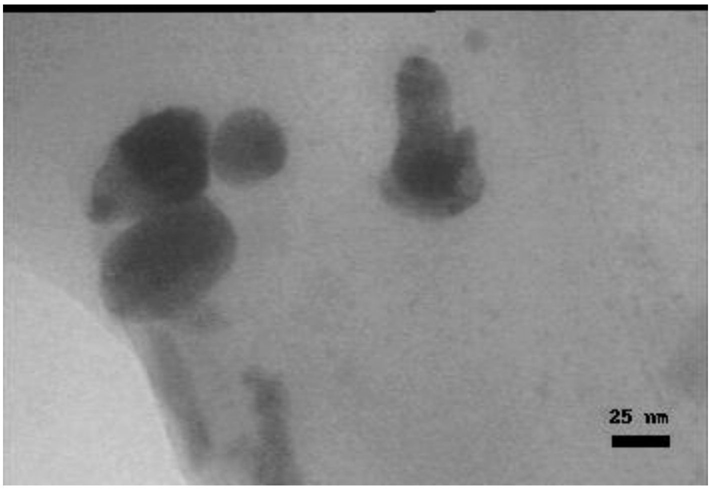

Figure 4-Sample 1

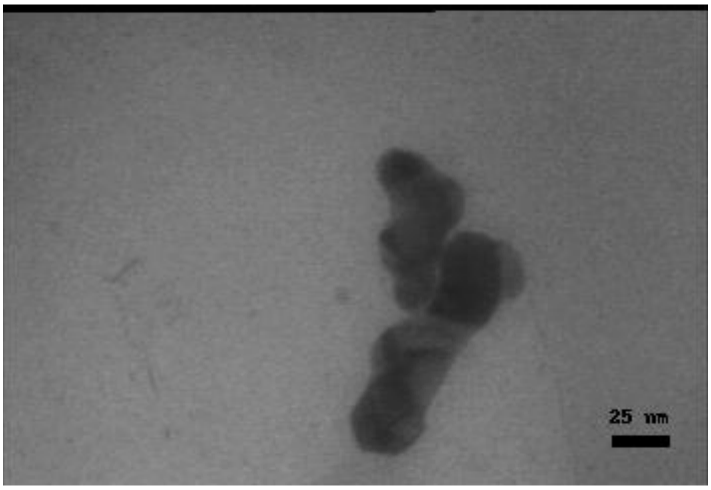

Figure 5-Sample 1

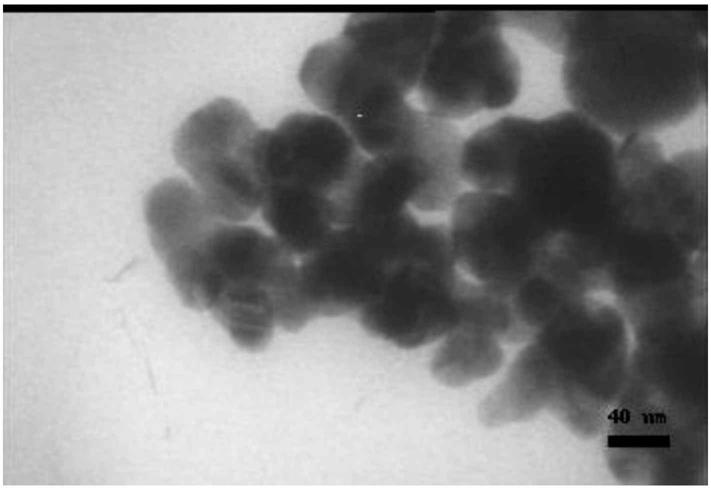

Figure 4-Sample 1

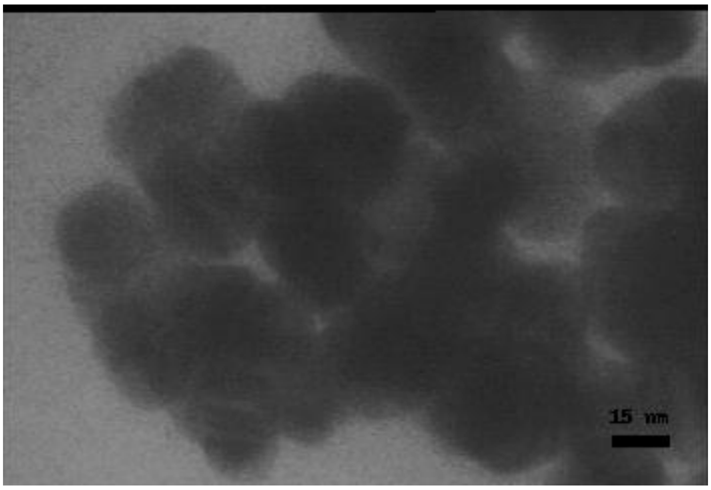

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
7	0.5	25	120K
8	0.5	20	120K
9	0.5	20	120K

Figure 7-Sample 1

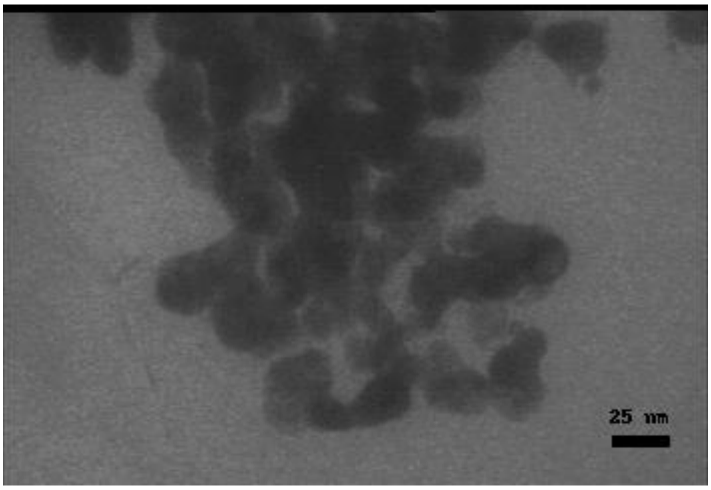

Figure 8-Sample 2

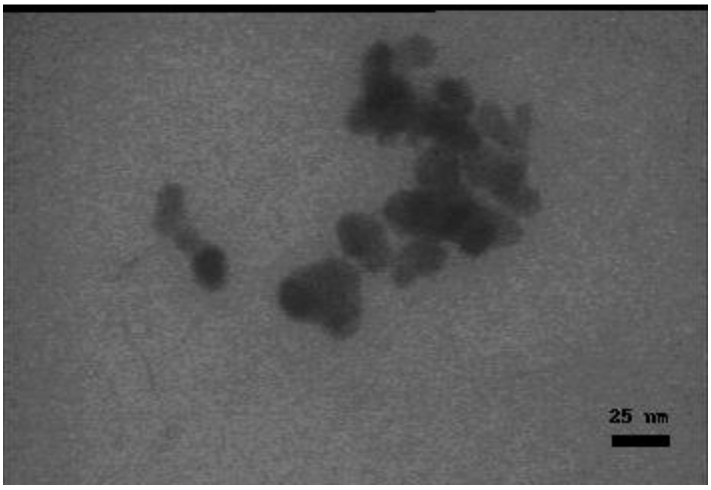

Figure 9-Sample 2

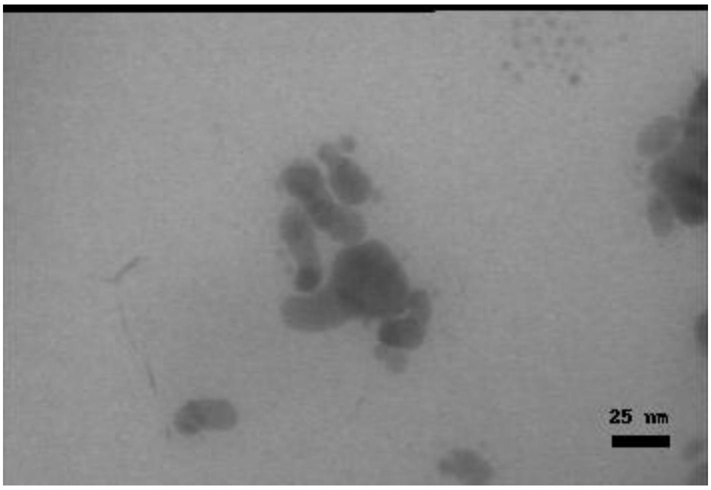

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
10	0.5	20	120K
11	0.5	20	120K
12	0.5	20	200K

Figure 10-Sample 2

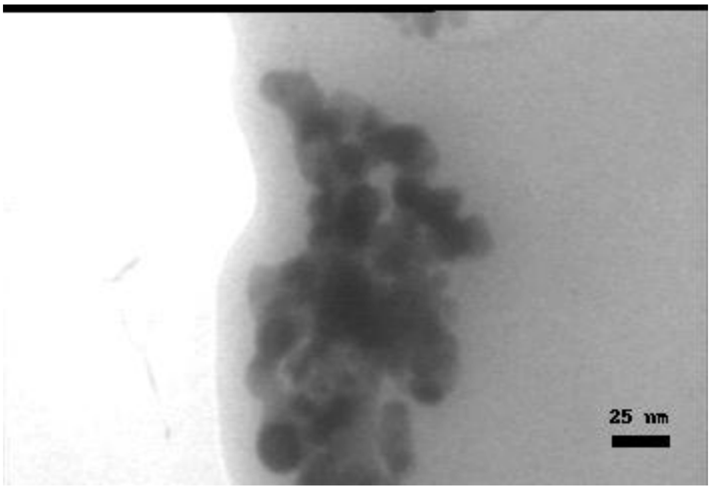

Figure 11-Sample 2

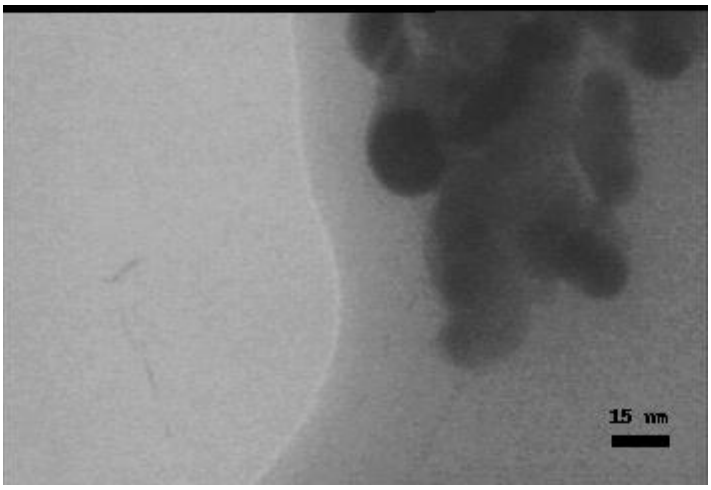

Figure 12-Sample 2

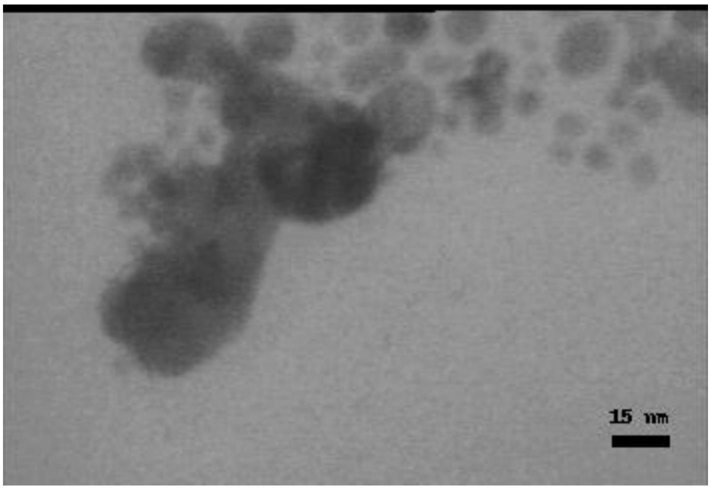

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
13	0.5	20	200K
14	0.5	15	120K
15	0.5	15	120K

Figure 13-Sample 2

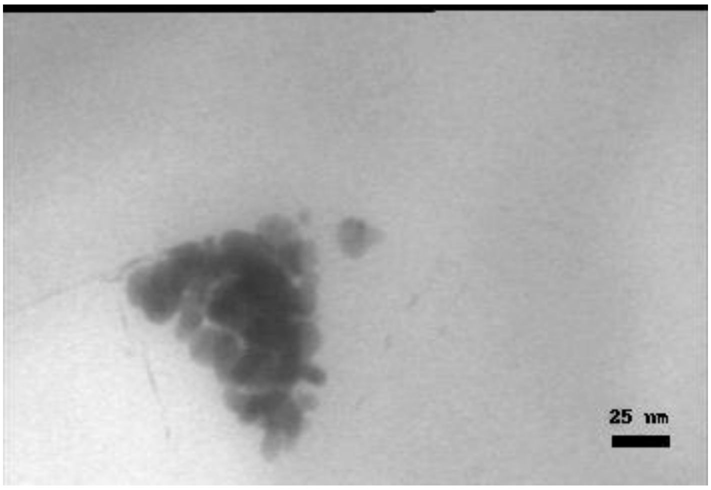

Figure 14-Sample 3

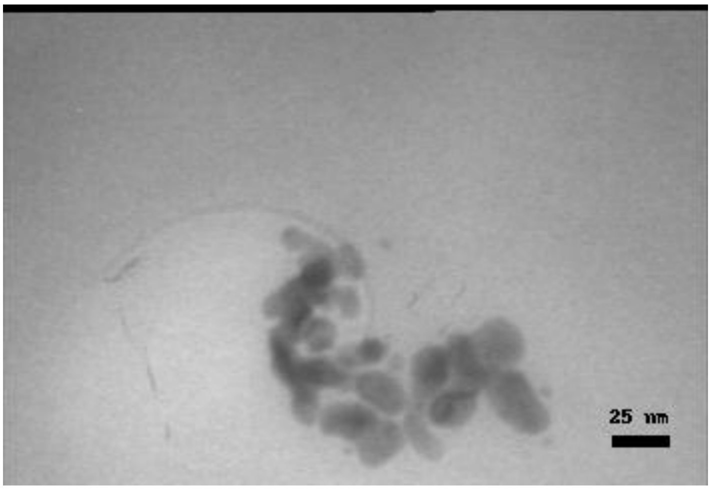

Figure 15-Sample 3

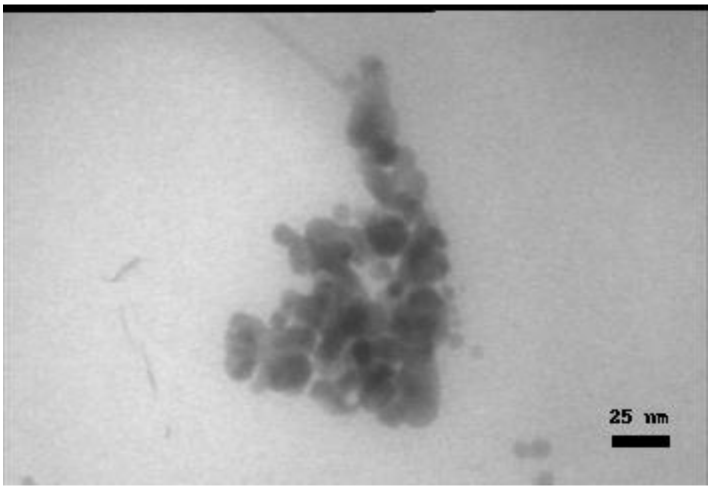

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
16	0.5	15	120K
17	0.5	15	120K
18	0.5	15	200K

Figure 16-Sample 3

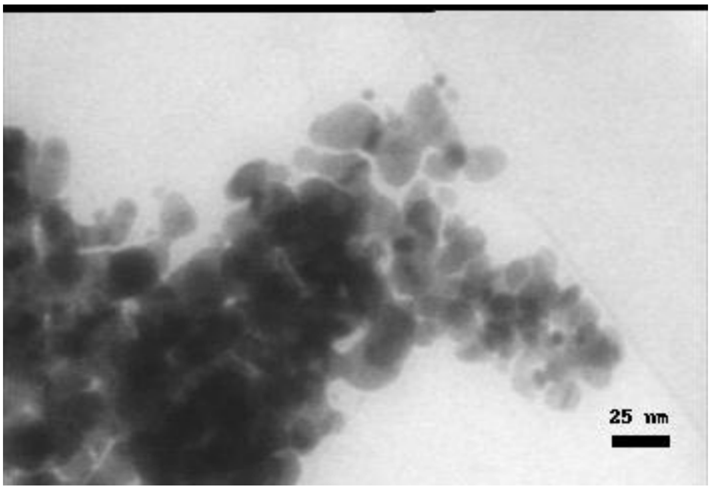

Figure 17-Sample 3

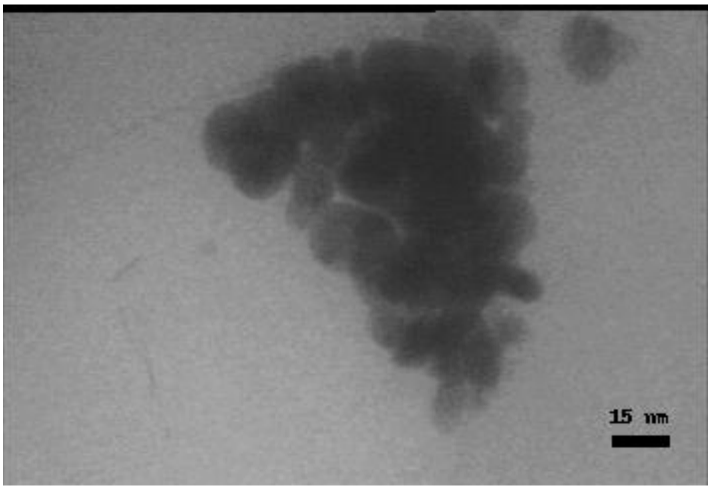

Figure 18-Sample 3

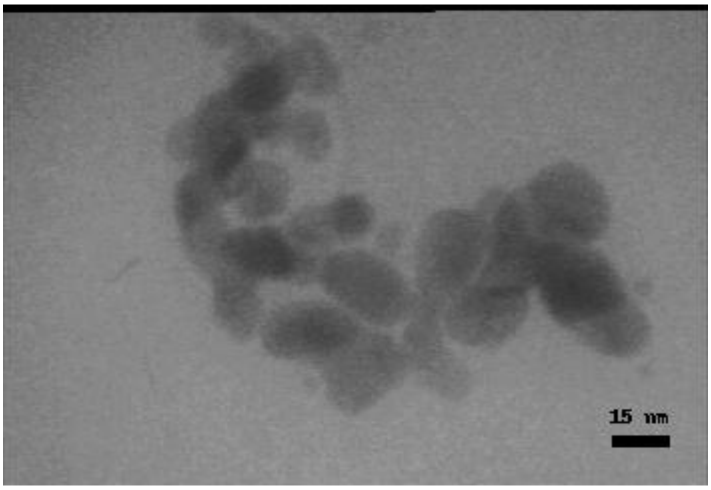

Figure 19-Sample 3

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
19	0.5	15	200K
20	0.5	15	200K
21	0.5	15	200K

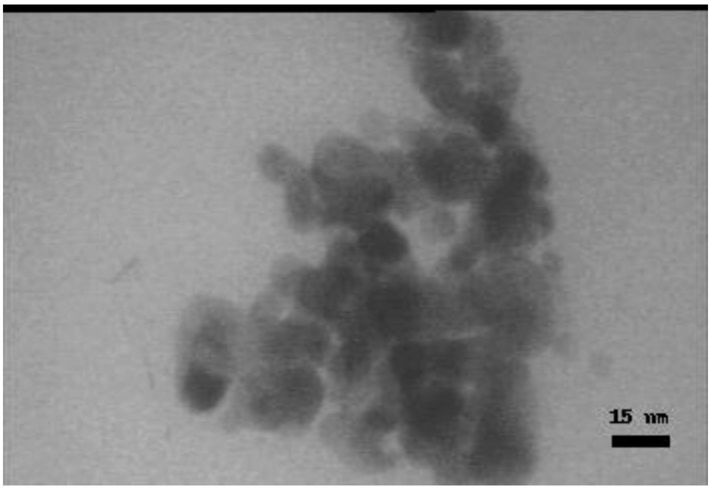

Figure 20-Sample 3

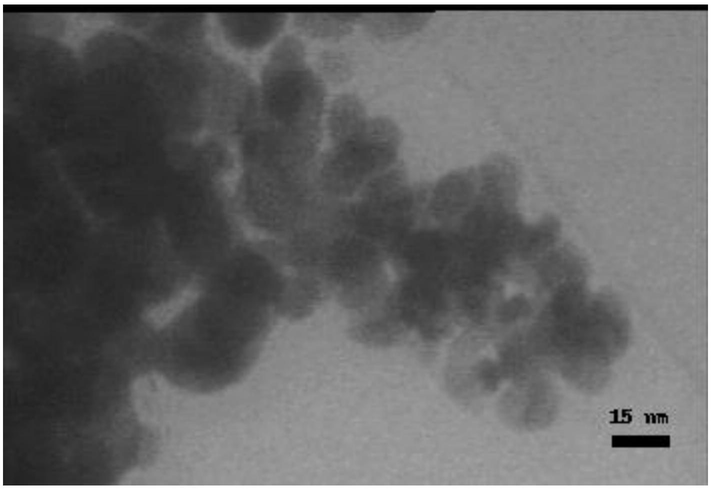

Figure 21-Sample 3

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
22	0.5	10	120K
23	0.5	10	120K
24	0.5	10	120K

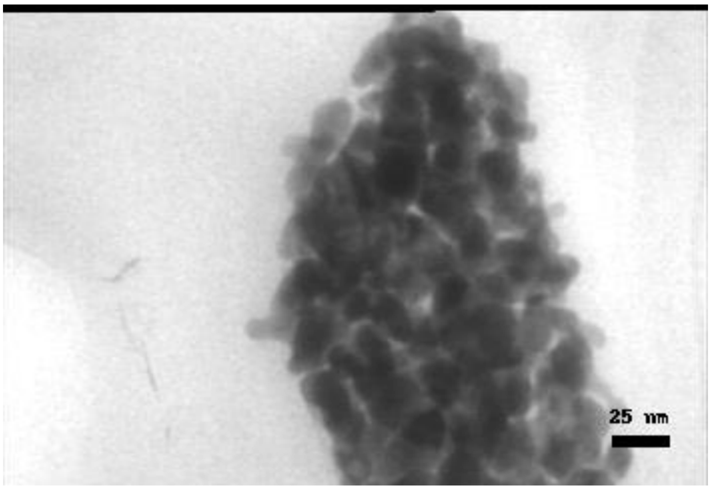

Figure 22-Sample 4

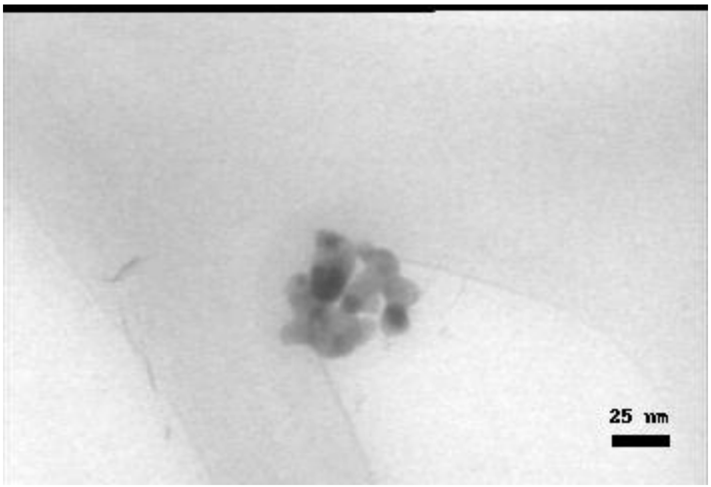

Figure 23-Sample 4

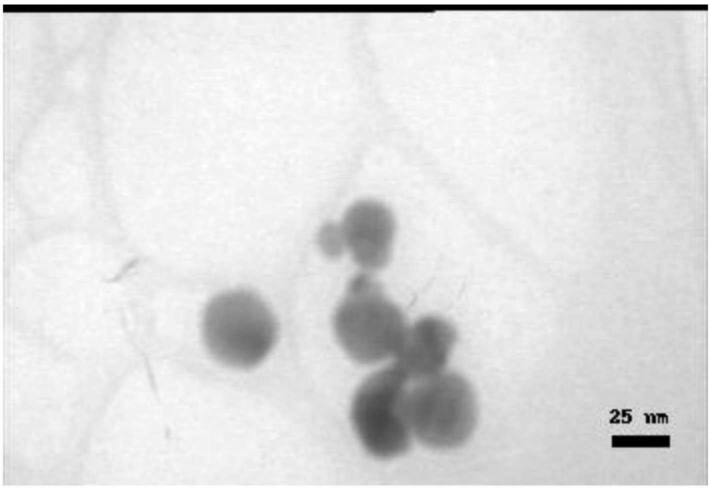

Figure 24-Sample 4

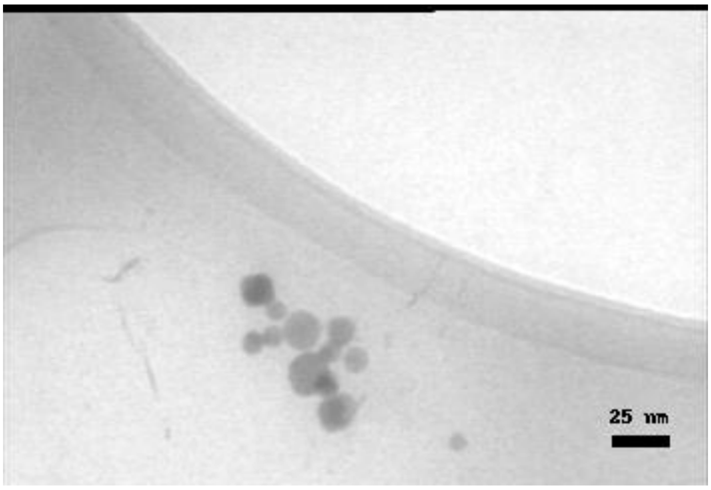

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
25	0.5	10	120K
26	0.5	10	200K
27	0.5	10	200K

Figure 25-Sample 4

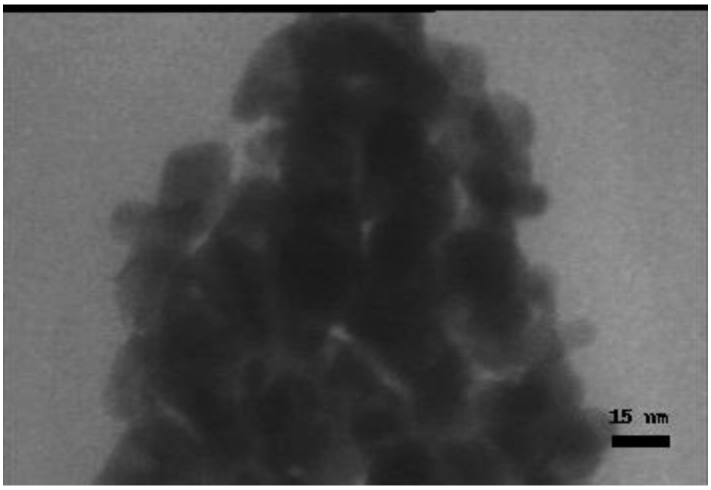

Figure 26-Sample 4

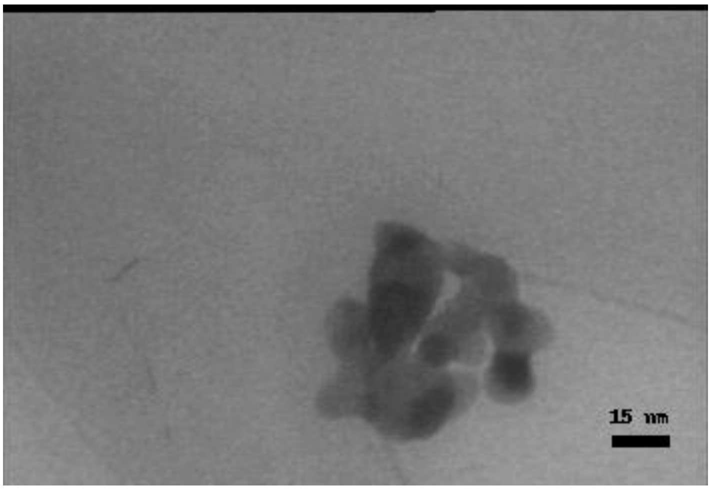

Figure 27-Sample 4

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
28	0.5	10	200K
29	0.5	10	200K
30	2	15	120K

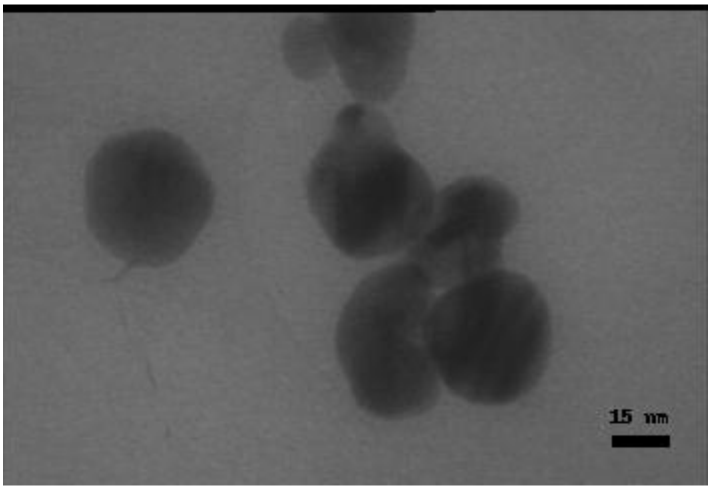

Figure 28-Sample 4

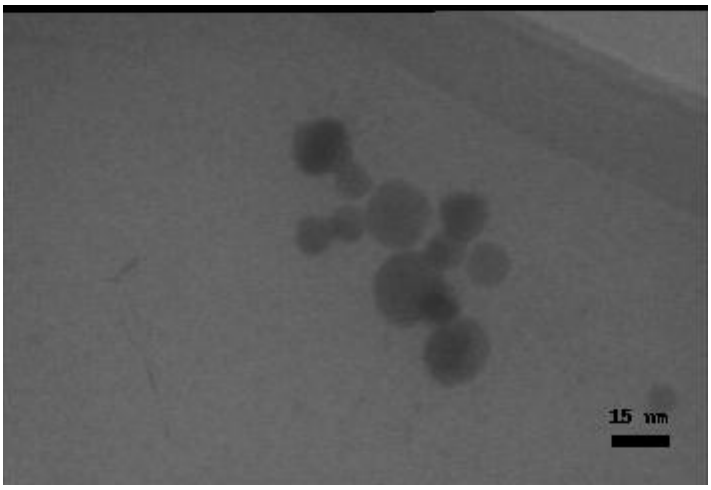

Figure 29-Sample 4

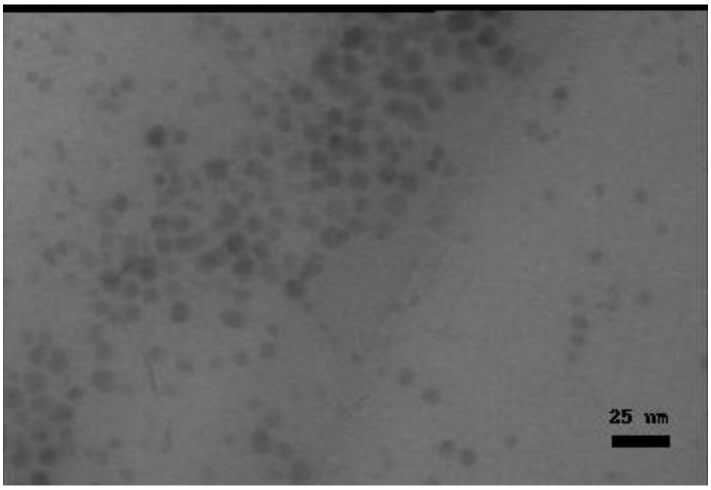

Figure 30-Sample 5

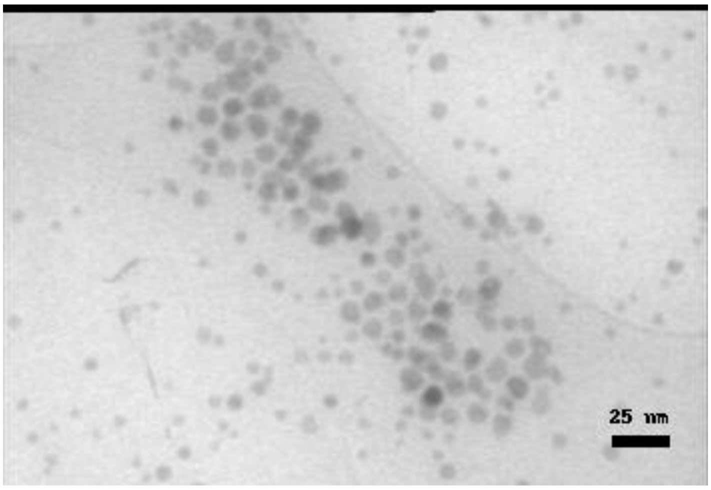

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
31	2	15	120K
32	2	15	120K
33	2	15	120K

Figure 31-Sample 5

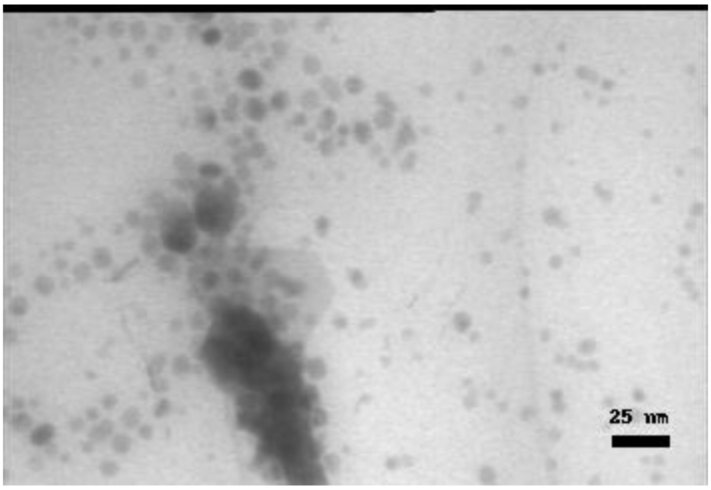

Figure 32-Sample 5

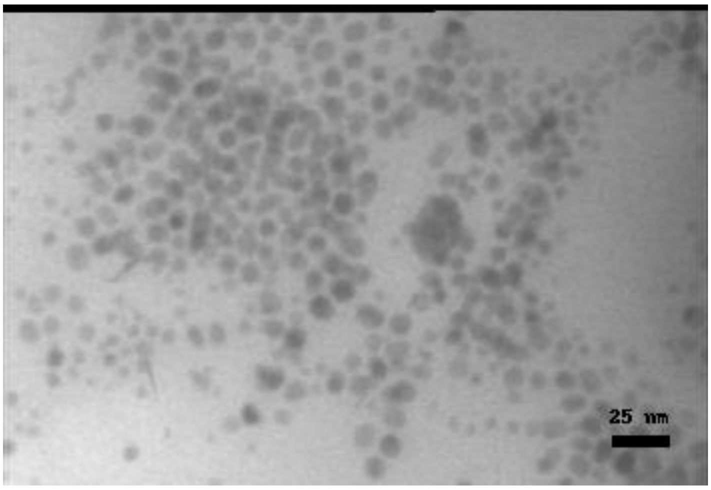

Figure 33-Sample 5

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
34	2	15	200K
35	2	15	200K
36	2	15	200K

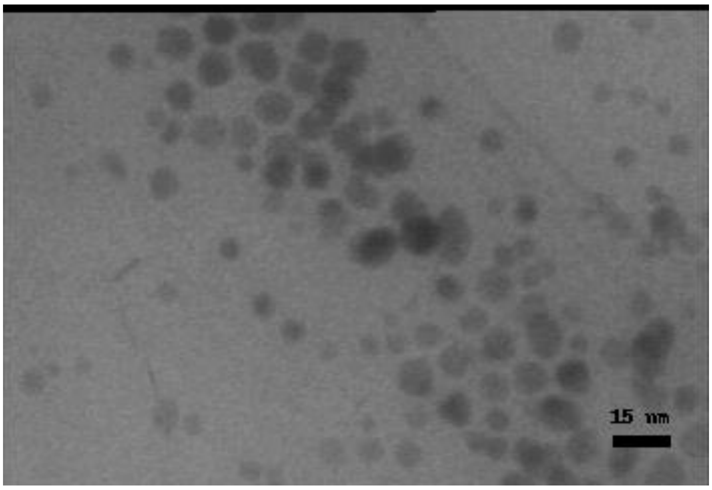

Figure 34-Sample 5

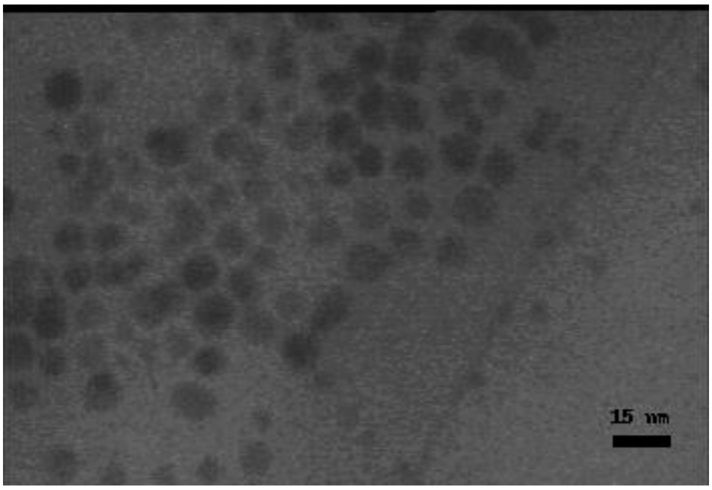

Figure 35-Sample 5

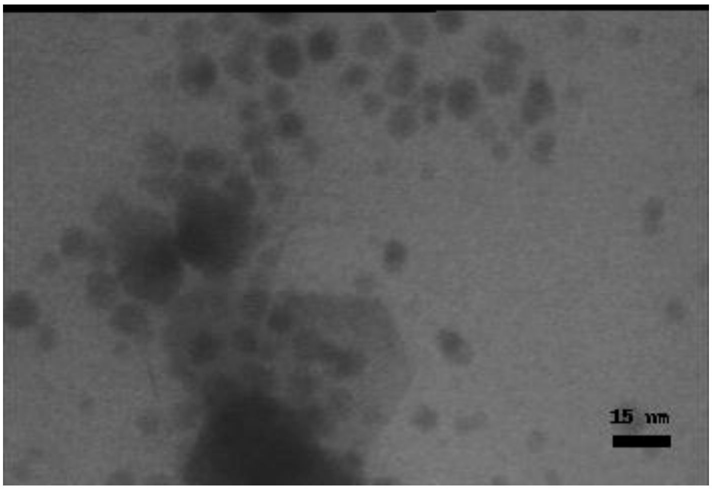

Figure 36-Sample 5

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
37	2	15	200K
38	2	20	120K
39	2	20	120K

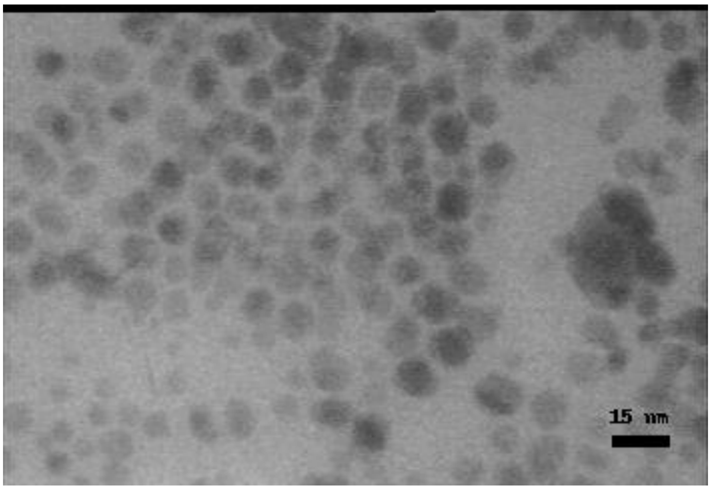

Figure 37-Sample 5

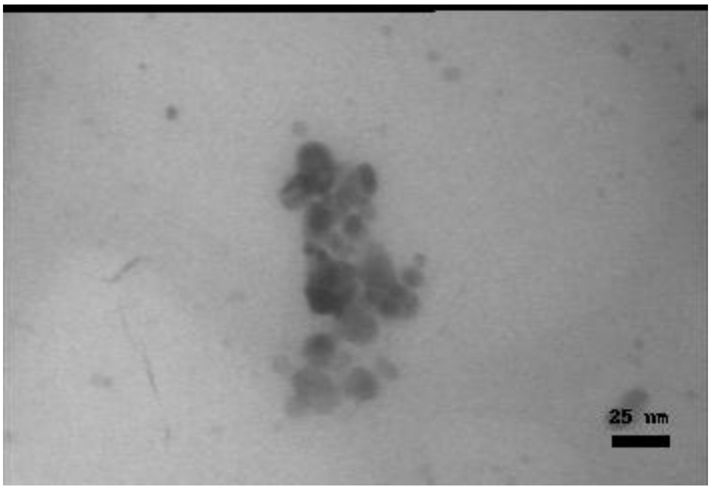

Figure 38-Sample 6

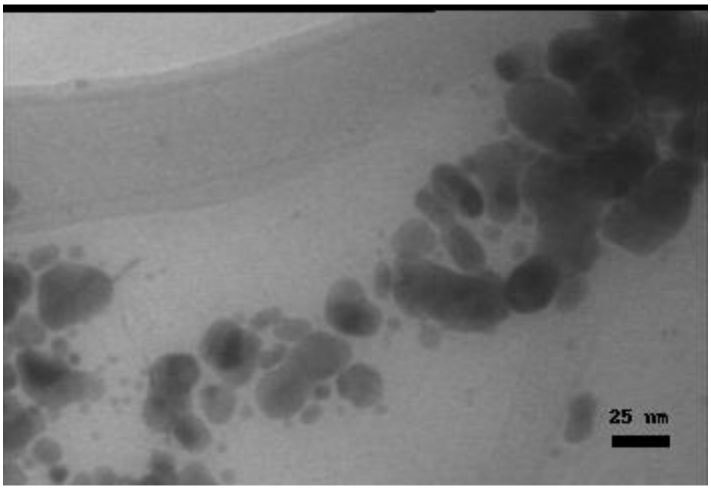

Figure 39-Sample 6

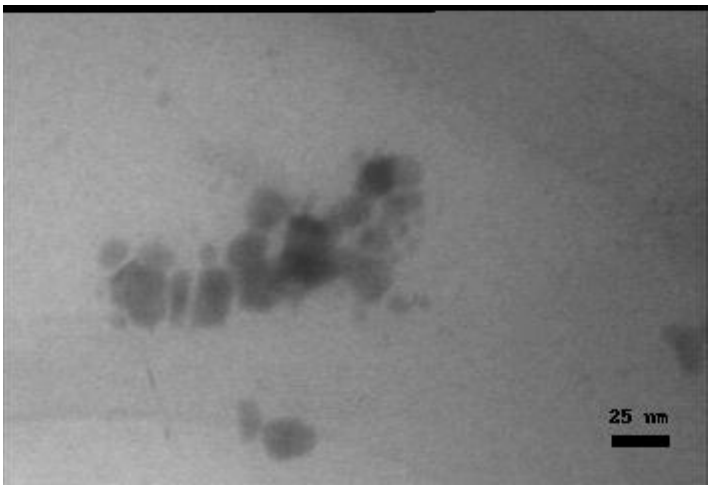

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
40	2	20	120K
41	2	20	120K
42	2	20	200K

Figure 40-Sample 6

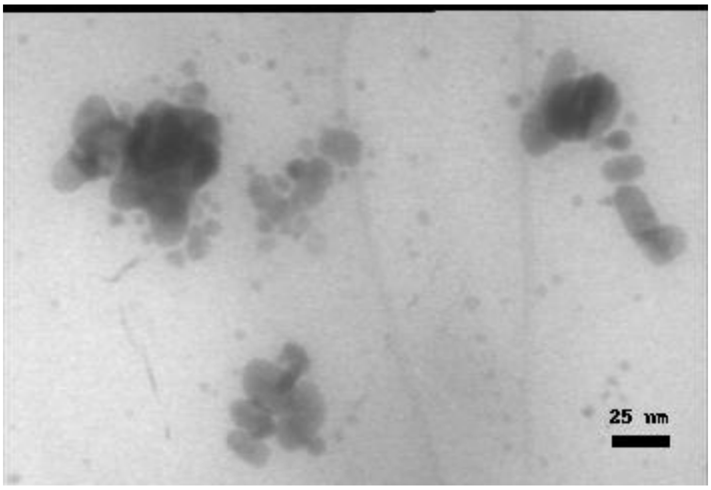

Figure 41-Sample 6

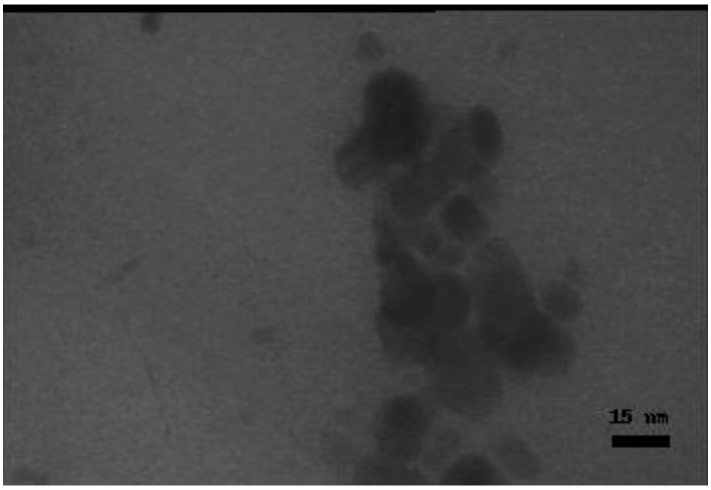

Figure 42-Sample 6

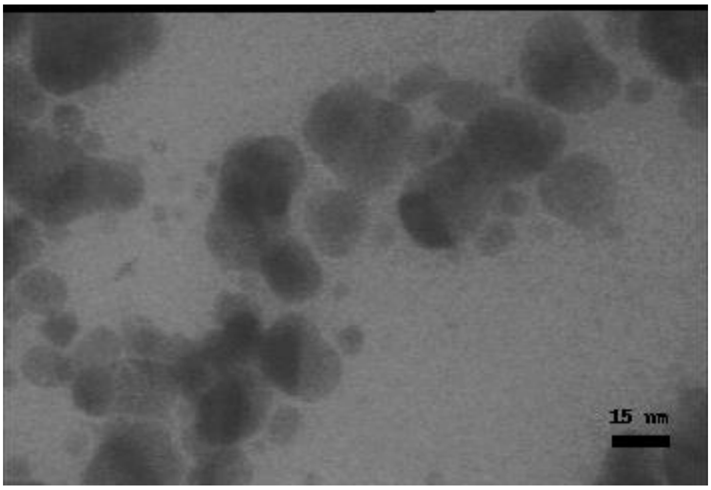

Figure	Wt% Ag	Water/Surfactant molar ratio	Zoom in
43	2	20	200K
44	2	20	200K
45	2	20	200K

Figure 43-Sample 6

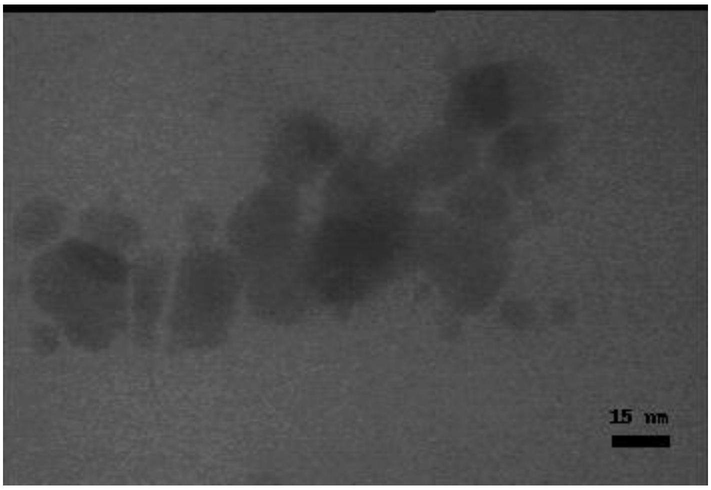

Figure 44-Sample 6

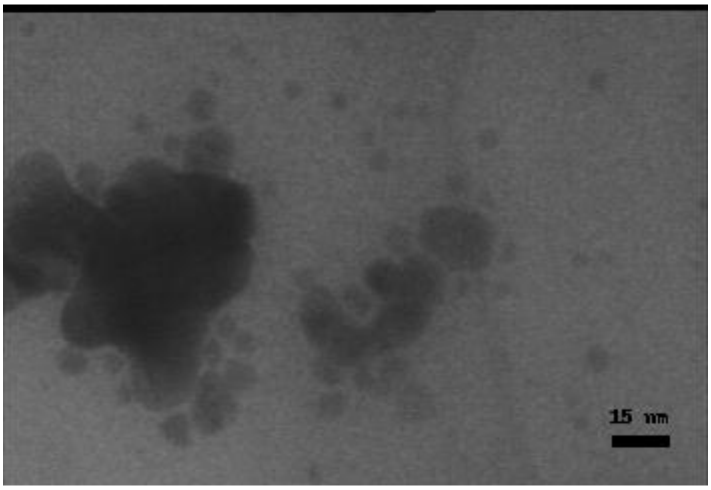

Figure 45-Sample 6