Size Selective Synthesis of Tetraoctylammonium Bromide Stabilized/Nonstabilized Sulfur Nanoparticles

تحضير حبيبات نانومترية من الكبريت المثبت والغير مثبت بواسطة TOAB

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Abstract

Sulfur nanoparticles (S NPs) were prepared by a quick precipitation method in the absence and presence of tetraoctylammonium bromide (TOAB) that was used as a stabilizer to control the nanoparticles size. Scanning electron microscope (SEM), transmission electron microscope (TEM) and X-Ray Diffraction (XRD) were used to characterize the obtained S NPs. The average size of S NPs was in the range 2.4 – 8.9 nm, with spherical like shape. The NPs size was controlled by changing the preparation parameters: temperatures, different acid concentrations, different acid types and the presence of TOAB stabilizer.

Keywords: Nanoparticles, XRD, TEM, Size selective synthesis, Stabilizer, Sulfur.

ملخص

تم في هذه الدراسة تحضير حبيبات الكبريت بحجم الناومتر وبشكل كروي وبعدة احجام مختلفة وذلك عن طريق تفاعل ترسيب الكبريت على درجات حرارة مختلفة واستخدام تراكيز

وانواع من احماض مختلقة تم ذلك بوجود وعدم وجود TOAB. المثبت السطحي تم تشخيص تشخيص العينات المحضرة باستخدام الاجهزة التالية: SEM, XRD, TEM . اظهرت النتائج ان حجم حبيبات الكبريت المحضرة يتراوح ما بين8.9-2.4 nm .

الكلمات المفتاحية: حبيبات نانومترية، اشعة سينية، مجهر الكتروني، تحضير حجمي انتقائي، مثبت سطحي، الكبريت.

1. Introduction

The sulfur, as gores-grain (bulk), micro and to much less extent as nano, is widely used in different industrial applications activities such as production of sulfuric acid, nitrogenous fertilizers, antimicrobial agents, plastics, petroleum refining, pulp and paper industries(Kutney 2007).

Sulfur nanoparticles (S NPs) have many applications now a days such as; modification of metal and carbon nanotubes, and synthesis of nanocomposites for lithium batteries (Wang *et al.* 2014), anti-cancer agent (An *et al.* 2011, Porras 2011), antibacterial agent (Choudhury *et al.* 2012), agrochemical industries (Kutney 2007) fungicides in agriculture fields (Ellis *et al.* 1998), synthesis of sulfur nanowires with carbon to form hybrid materials with useful properties for gas sensor and catalytic applications (Santiago *et al.* 2006) and as adsorbent for the extraction of metal ions (Ghanemi *et al.* 2011).

Different methods were used to prepare S NPs (Suleiman *et al.* 2013). One of the common methods used is wet chemical precipitation method. In which the sodium thiosulfate was dissolved in double distilled water in different acidic solutions, using different surfactants (TX-100, CTAB, SDBS, and SDS) as stabilizer to control the particle size. The anionic stabilizer SDBS was found to be more effective to obtaining a uniform sizes NPs. While, the smallest S NPs (30 nm) were obtained by using CTAB as stabilizer (Chaudhuri & Paria 2010).

Monoclinic S NPs have been prepared via the chemical reaction between sodium polysulfide and hydrochloric acid in a reverse microemulsions system, with theoline, butanol and a mixture of Span 80 and Tween 80 (weight ratio 8:1) as the oil phase, surfactant and co-surfactant, respectively. Transparent microemulsions were obtained by

mixing the oil phase; a surfactant, co-surfactant, and the aqueous phase in appropriate proportion using an emulsification machine at room temperature. The S NPs prepared via this method were found to have an average diameter of around 20 nm, with a narrow size distribution, uniform spherical shape, and high purity (Guo *et al.* 2006).

S NPs were synthesized from hazardous H_2S gas using novel biodegradable iron chelates in water/organic microemulsion system (Suleiman *et al.* 2009). Ferric malic acid chelate was studied in water/organic microemulsion containing cyclohexane, n-hexanol and Triton X-100 as oil phase, a surfactant, co-surfactant, respectively, for the catalytic oxidation of H_2S gas at ambient conditions of temperature, pressure, and neutral pH. The S NPs were nearly uniform in size (average particle size 10 nm) with narrow particle size distribution (in range of 5–15 nm) as compared to that in aqueous surfactant systems (Deshpande *et al.* 2008).

M. Shamsipur et al used an electrochemical method to prepare the sulfur nanoparticles from thiosulfate ion. The size of S NPs obtained were in the range of 35 and 65 nm by adjusting the operation parameters including; the initial concentration of sodium thiosulfate. It was found that, the use of hot alcohol and cold water as solvent/non-solvent system along with100 mL .min^{-1} flow rate for co-mixing of non-solvent resulted in the formation of S NPs in a typical size of 250 nm that are fairly homogeneous in shape and have a narrow particle size distribution (Shamsipur *et al.* 2011).

M. Alexandrovichm et al. prepared S NPs at room temperature by mixing sodium polysulfide aqueous solution with various inorganic and organic acids, the average size of the obtained NPs was (22-25 nm) (Alexandrovich *et al.* 2012).

In this study, orthorhombic or α sulfur with S_8 structure have been synthesized by quick precipitation method in the absence and in the presence of tetraoctylammonium bromide (TOAB) that was used as a stabilizer to control the nanoparticles size. In this work we were able to

synthesis the smallest S NPs ever reported up to now, to the best of our knowledge.

2. Material and methods

2.1 Material

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) were purchased from Frutarom Co., Hydrochloric acid (HCl) 32% conc. were purchased from Merck Co., Tetraoctylammonium bromide (TOAB) 98% conc. were purchased from Sigma Co.

2.2 Preparation of sulfur nanoparticles

A mixture of Sodium thiosulfate and TOAB was prepared by combining 50.0 mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0 mL of 0.02M TOAB aqueous solutions. The mixture was stirred mechanically at 120 rpm and heated in constant temperature bath at 30, 40, 50 and 60 °C, respectively. Then 40.0 mL of different acid solutions (HCl, HNO_3, H_2SO_4, and H_3PO_4) were added to the mixture under continuous stirring. A yellow precipitate was observed immediately, the reaction was stopped after 40 min. The produced yellow precipitate was collected, washed with distilled water and dried.

3. Characterization of sulfur nanoparticles

The shape and the morphology of the prepared S NPs were characterized by Scanning electron microscope (SEM) using (Inspect F50, Jordan).

The size and the shape of particles were observed under a transmission electron microscope (TEM) using (ZEISS EM10CR, Jordan).

X-ray diffraction technique was used to determine the structure and the size of the S-NPs using (Rigaku Dmax 2500, India) with Cu source (Cu-Kα1 line, λ=1.5045 Å) employing a scanning rate of 5°/min in the 2hr range from 10° to 40°.

4. Results and Discussion

In this work optimization of the preparation parameter of SNPs was studied. Where the effect of different preparation parameters on the size and the morphology on the obtained S NPs was investigated.

The size of the S NPs was determined from TEM and XRD. Estimation of the N Ps size from XRD was preformed utilizing the full width at half the maximum (FWHM) of the diffraction peaks which is inversely proportional to the size of the NPs according to Scherrer formula.

4.1 The Temperature effect

To study the effect of preparation temperature on the size of the SNPs, the preparation was performed at 30°C, 40°C, 50°C and 60°C. All runs were performed by using mixture of Sodium thiosulfate and TOAB. The mixture was prepared by combining 50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0 mL of 0.02M TOAB aqueous solutions. Then the mixture was stirred mechanically at 120 rpm and heated in constant temperature bath at 30°C, 40°C, 50°C and 60 C, respectively. Then 40.0 mL of different acid solutions 2.0M HCl were added to the mixture under continuous stirring. The reaction was stopped after 40 min. The produced yellow precipitate was collected, washed with distilled water and dried.

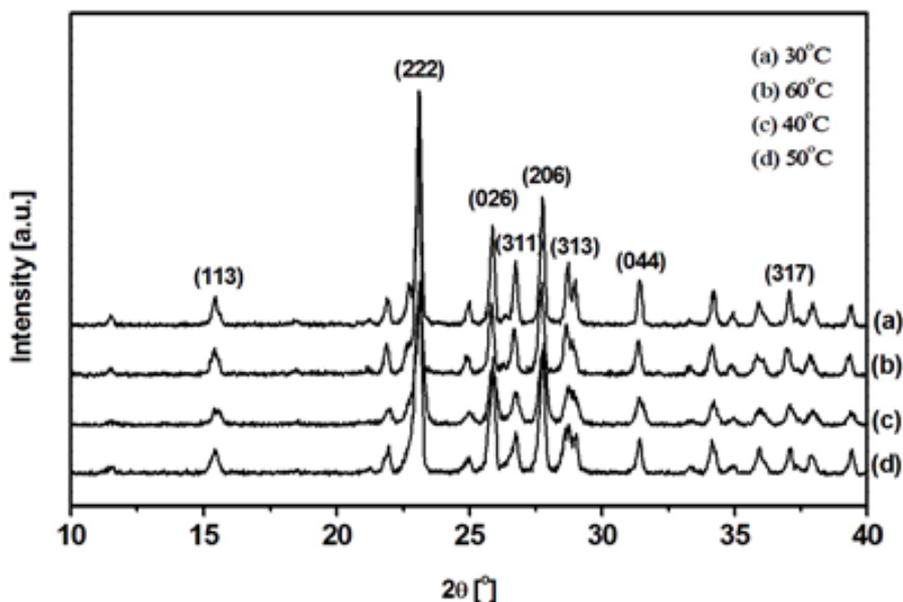The XRD of the as prepared S NPs are shown in Figure 4.1

Fig (4.1): XRD pattern of the as-prepared S NPs prepared at different temperatures by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of 2.0M HCl: (a) 30°C, (b) 60°C (c) 40°C and (d) 50°C.

The diffraction peaks were clearly observed from the XRD of the S NPs located near to (15.4, 23.0, 25.8, 26.6, 27.7, 28.8, 31.4 & 37.1) of 2θ positions, that are well attributed to the (S-(113), S-(222), S-(026), S-(311), S-(206), S-(313), S-(044) & S-(317)) miller planes, respectively.

X-ray structural analysis of the obtained S NPs samples show that all the samples are have orthorhombic phase with S_8 structure with traces of monoclinic structure. Our structural results are in accordance with the results which were obtained by X. Xie et al. (Xie *et al.* 2012) according to JCPDS file No. 83-2285.

By applying Scherrer equation on the XRD pattern, the particle size have been be calculated:

$$D = K\lambda / (B\cos\theta)$$

Where D is the mean size of crystallites (nm), K is crystallite shape factor to a good approximation is 0.9, λ is the X-ray wavelength, *B* is the full width at half the maximum (FWHM) in radians of the X-ray diffraction peak and θ is the Braggs' angle (deg.) (Holzwarth & Gibson 2011).

Based on four different XRD peaks analysis, the average size was founded to be 9.2, 10.1, 11.6 and 13.4 nm for TOAB stabilized S NPs which were prepared at 30, 40, 50 and 60 °C, respectively. These results show that increasing the preparation temperature lead to an increase in nanoparticles size. These results are summarized in Table 4.1.

Table (4.1): Compression of the estimated size using XRD and TEM of as-prepared S NPs prepared at different temperatures obtained by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of 2.0M HCl.

Temperature (ºC)	Size of TOAB stabilized S NPs (nm)	
	XRD	**TEM**
30	9.2 (±0.21)	6.9
40	10.1 (±0.18)	7.3
50	11.6 (±0.15)	7.6
60	13.4 (±0.11)	8.2

TEM analysis show also that the size of the S NPs increases with increasing the temperature, these results are shown in Figure 4.2 and summarized in Table 4.1.
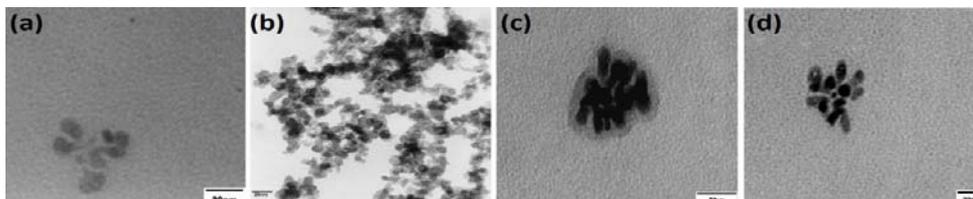
Figure (4.2): TEM images of the as-prepared S NPs prepared at different temperatures by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of 2.0M HCl: (a) 30°C, (b) 40°C (c) 50°C and (d) 60°C.

The difference in the S NPs size estimated from the XRD and TEM is due to the estimation methods limitation. Its known the TEM is more accurate in obtaining the size especially for nano-meter-sized samples (Suleiman *et al.* 2009).

These results show that increasing the preparation temperature increases the obtained S NPs size. This is due mainly to the endothermic nature of the acid (HCl), which will increase the reactivity and the diffusivity of the sulfur atoms with increasing the temperature (Chaudhuri & Paria 2011). It is known that the diffusion rate increases with increasing the temperature, as a result the overall diffusion of sulfur atoms from bulk phase to solid-liquid interphase increases. This leads to an increase in the obtained NPs size with increasing the temperature. This explain our results shown in Table 4.1.

4.2 Stabilizer effect

The effect of the stabilizer on the size and morphology of the S NPs was studied, four runs were performed at different HCl concentrations with and without using TOAB stabilizer at 40°C.

The four TOAB stabilized S NPs samples were prepared, where in each run a mixture of (50.0 mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0 mL of 0.02M TOAB aqueous solutions) was stirred mechanically at 120 rpm and heated in constant temperature bath at 40°C. Then 40.0 mL of

different acid solutions of (0.5M, 1.0M, 2.0M and 3.0M) HCl were added to the mixture under continuous stirring. The reaction was stopped after 40 min. The produced yellow precipitate was collected, washed with distilled water and dried. Another four samples of non-stabilized S NPs were prepared using the same preparation conditions and steps of the four TOAB stabilized S NPs samples.

The XRD of the as-prepared TOAB stabilized and non-stabilized S NPs are shown in Figure 4.3 and Figure 4.4 respectively.

The size of the as-prepared TOAB stabilized and non-stabilized S NPs was estimated from XRD. These results are summarized in Table 4.2. It's clearly seen that the non-stabilized samples have larger sizes than the TOAB stabilized S NPs samples prepared at same conditions. In this work the four non-stabilized samples were found to have the sizes 9.8nm, 10.7nm, 11.5nm and 8.3nm, respectively. On the other hand, the sizes of TOAB stabilized S NPs were: 3.4nm, 8.2nm, 10.1nm and 7.6nm, respectively. This indicates the important role of the stabilizer in preventing the agglomeration of the NPs and hence resulting in smaller sizes at same preparation conditions.
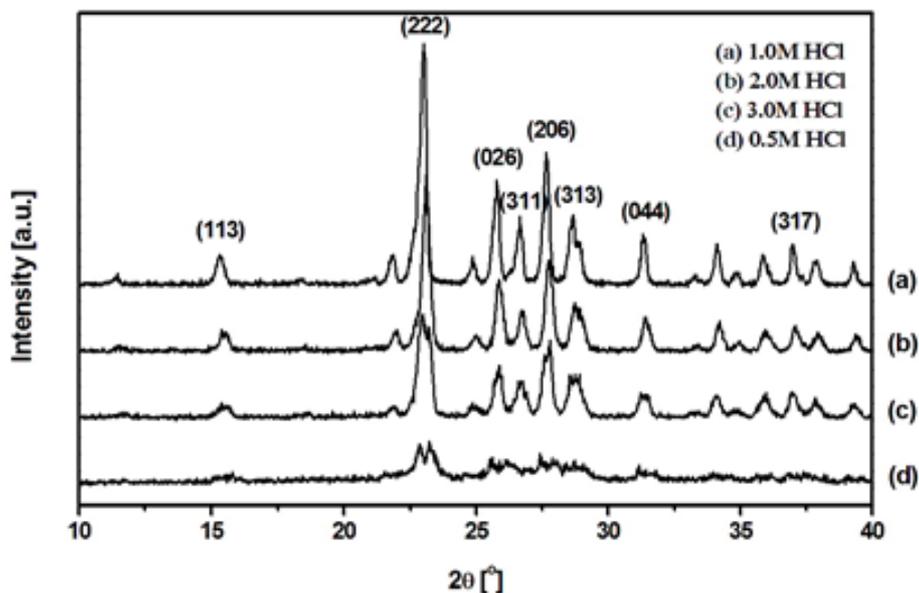
Fig (4.3): XRD pattern of the as-prepared TOAB stabilized S NPs prepared by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of: (a) 1.0M HCl, (b) 2.0M HCl, (c) 3.0M HCl and (d) 0.5M HCl. at 40°C.

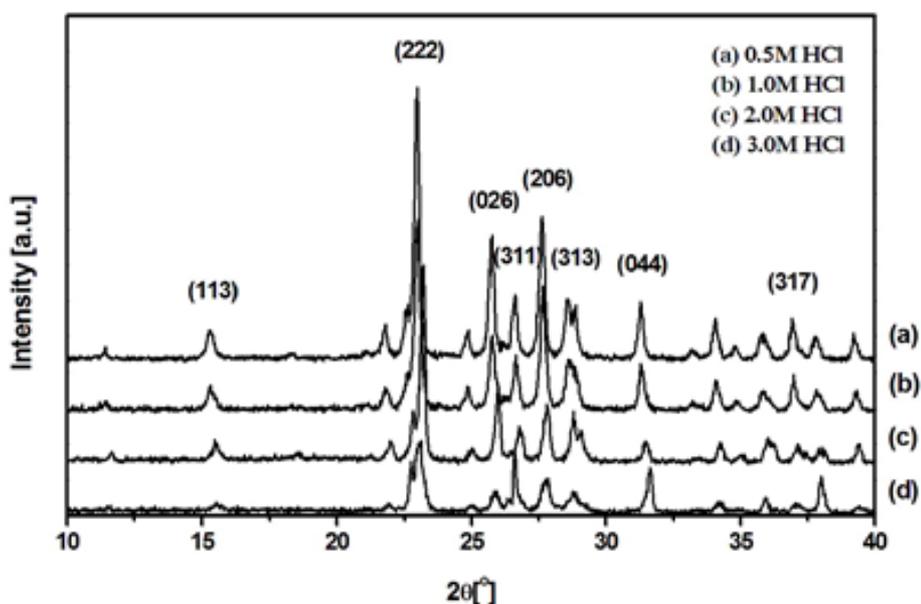**Fig 4.4:** XRD pattern of the as-prepared non-stabilized S NPs prepared by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$) with 40.0mL of: (a) 1.0M HCl, (b) 2.0M HCl, (c) 3.0M HCl and (d) 0.5M HCl at 40°C.

The sizes of the TOAB stabilized samples and non-stabilized samples were also investigated by TEM, Figure 4.3 and 4.4. The size analysis using TEM confirms the results obtained by XRD analysis, see Table 4.2.

Table (4.2): Compression of the estimated size using XRD and TEM of as-prepared TOAB stabilized and non-stabilized S NPs prepared by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with/without 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of: (0.5M, 1.0M, 2.0M and 3.0M) HCl at 40°C.

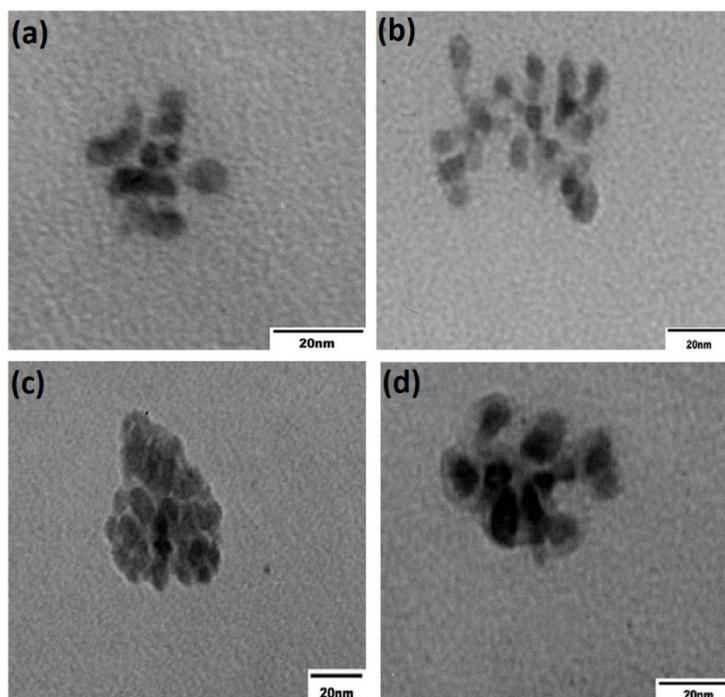| [HCl]	Size of non-satbilized S NPs (nm)		Size of TOAB stabilized S NPs (nm)	
	XRD	**TEM**	**XRD**	**TEM**
0.5M	9.8 (±0.12)	6.1	3.4 (±0.68)	3.1
1.0M	10.7 (±0.14)	6.3	8.2 (±0.16)	5.7
2.0M	11.5 (±0.15)	8.4	10.1 (±0.18)	7.3
3.0M	8.3 (±0.14)	7.1	7.6 (±0.17)	6.1

Figure (4.5): TEM Images of as-prepared non- stabilized S NPs prepared by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$) with 40.0mL of: (a) 0.5M HCl, (b) 1.0M HCl, (c) 2.0M HCl and (d) 3.0M HCl at 40°C.
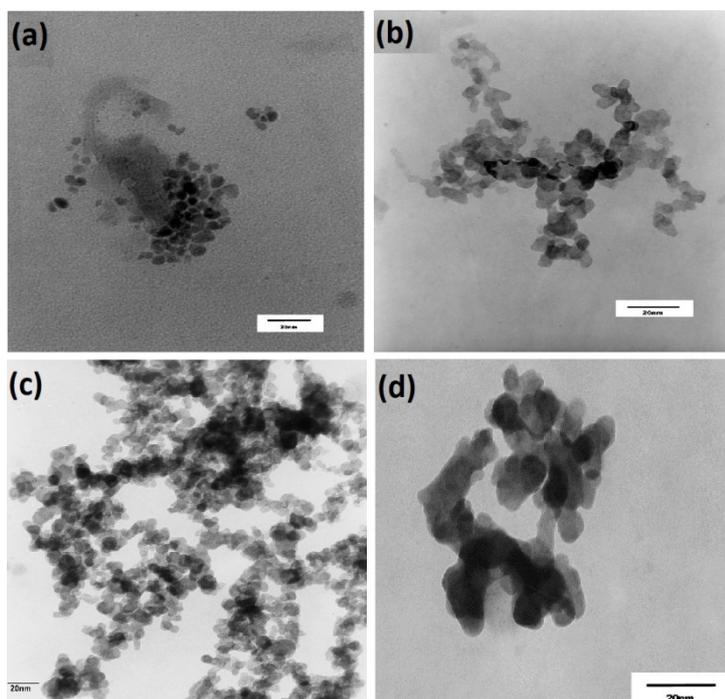
Figure (4.6): TEM Images of as-prepared TOAB stabilized prepared by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of: (a) 0.5M HCl, (b) 1.0M HCl, (c) 2.0M HCl and (d) 3.0M HCl at 40°C.

The importance of the stabilizer was also confirmed using SEM. In this work, spherical shape S NPs was obtained for all samples that were prepared at different temperatures; 30, 40, 50 and 60 ℃, different concentration of HCl (0.5M, 1.0M, 2.0M and 3.0M) and different acids (HCl, HNO_3, H_2SO_4 and H_3PO_4). More regular spherical shape was obtained for TOAB stabilized S NPs Figure 4.7(b) in compression to the non-stabilized ones Figure 4.7(a). The most regular spherical shape was obtained for TOAB stabilized S NPs at 40 ℃ using 0.5M HCl, see Figure 4.7.
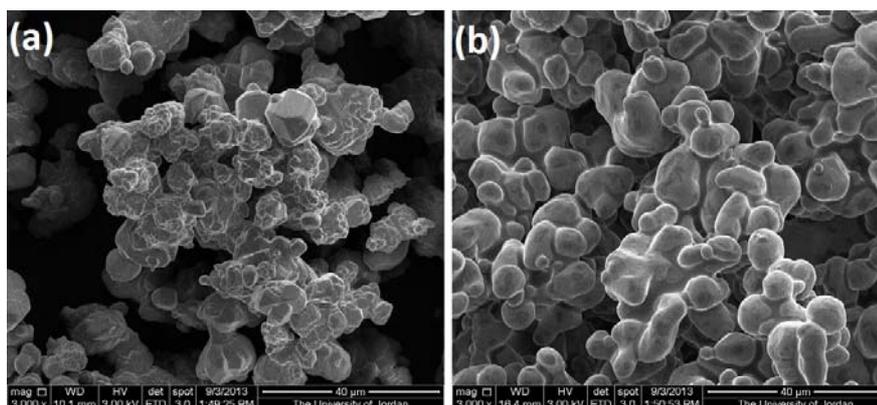
Figure (4.7): SEM Images of as-prepared non-stabilized S NPs prepared by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$) with 40.0mL of0.5M HCl at 40°C (a) and SEM Images of as-prepared TOAB stabilized S NPs prepared by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of 0.5M HCl at 40°C.

4.3 Acid type effect

The effect of the acid type was also studied in this work. Four runs were performed by mixing a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL 2.0M of (H_3PO_4 ,H_2SO_4 ,HNO_3 and HCl), respectively. The XRD diffraction pattern of as-prepared S NPs are shown in Figure 4.8, and confirms orthorhombic structure. XRD size estimation shows that the size of SNPs are:10.1nm, 3.9nm, 5.8nm and 6.3 nm which were prepared at 40°C using different acid solutions (HCl, HNO_3, H_2SO_4 and H_3PO_4), respectively. These result were confirmed using TEM; Figure4.9 and Table 4.3.

The increasing orders of particle size in the presence of different acids are: $HNO_3 < H_2SO_4 < H_3PO_4 < HCl$. The most dependent factor in acid types to the size of the formed S NPs is the ionization constant of the acid, the stronger acid (large ionization constant) has higher reaction rate.

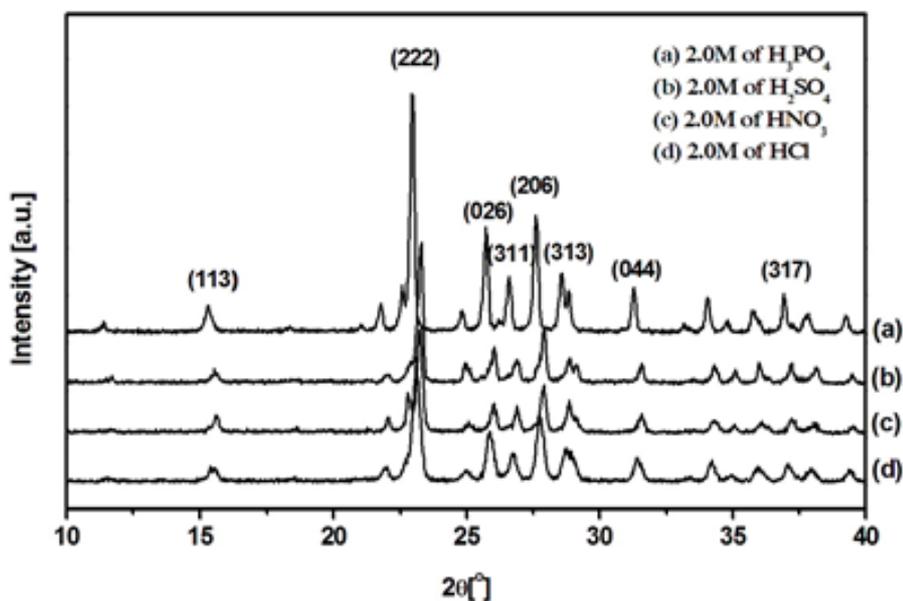Therefore, the denser nuclei are formed and the formed S NPs are with larger size(Chaudhuri & Paria 2010).

Fig (4.8): XRD pattern of the as-prepared S NPs prepared at 40°C by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of 2.0M: (a) H_3PO_4(b) H_2SO_4 (c) HNO_3 and (d) HCl.

Based on this role, H_3PO_4 is expected to form the less sized particles in comparison to the other used acids, but a contrast behavior was observed, where larger sized nanoparticles were formed. Unlikely, we have not a clear explanation for this behavior. Similar effect was also observed in literature (Chaudhuri & Paria 2010, 2011) in the work of R. Ghaudhuri et al. were they have used oxalic acid.

The sizes results of TOAB stabilized S NPs prepared at 40°C using 2.0M solution of different acids are summarized in Table 4.3
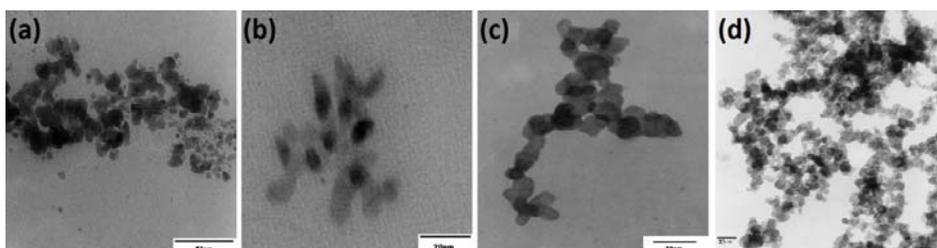
Fig (4.9): TEM images of the as-prepared S NPs prepared at 40°C by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of 2.0M: (a) H_3PO_4(b) H_2SO_4 (c) HNO_3 and (d) HCl.

Table 4.3: Compression of the estimated size using XRD and TEM of as-prepared TOAB stabilized S NPs prepared at 40°C by combining a mixture of (50.0mL of 0.80M $Na_2S_2O_3.5H_2O$ with 20.0mL of 0.02M TOAB aqueous solutions) with 40.0mL of 2.0Mof different acids (H_3PO_4, H_2SO_4, HNO_3 and HCl).

Conc. of acid solution	Size of TOAB stabilized S NPs (nm)	
	XRD	**TEM**
2.0M of HCl	10.1 (±0.18)	7.3
2.0M of HNO_3	3.9 (±0.15)	2.4
2.0M of H_2SO_4	5.8 (±0.47)	3.3
2.0M of H_3PO_4	6.3 (±0.36)	5.9

With comparing the S NPs that was prepared in this work by quick precipitation method with that prepared by other workers (Alexandrovich *et al.* 2012, Chaudhuri & Paria 2010, Guo *et al.* 2006, Shamsipur *et al.* 2011), one can see that in this work S NPs in the range 2.4 to 9 nm can be prepared selectively with relatively narrow size distribution and regular spherical shape. To best of our knowledge these are the smallest S NPs obtained up to now.

Conclusions

In this work S NPs with very low dimensional nano-meter-sized less than 10 nm were selectively prepared by varying the preparation parameters: temperature, acid type, acid concentration and the presence of TOAB stabilizer. The smallest S NPs size obtained in this work was 2.4nm and to the best of our knowledge it's the smallest S NPs ever prepared.

X-Ray analysis showed that all obtained sulfur NPs have mainly orthorhombic structure S_8 with traces of monoclinic structure. Spherical shape for all prepared S NPs was observed, but more regular spherical shape was obtained in the presence of the TOAB stabilizer.

Acknowledgements

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