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Sulfur Nanoparticles: Synthesis, Characterizations and their Applications

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Abstract

Sulfur Nanoparticles was prepared by different method with different size and shapes, when the sulfur present as nanoparticles they have many practical application in our life. This paper discuses different sulfur nanoparticles synthesis, characterizations and application. Different methods were used for nanosize particle synthesis; among those, chemical precipitation, electrochemical method, micro emulsion technique, composing of oil, surfactant, co-surfactant, aqueous phases with the specific compositions and ultrasonic treatment of sulfur-cystine solution. The sizes and shapes of (S-NPs) were characterized by scanning electron microscope (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. Sulfur nanoparticles are very important application for anticancer, antibacterial, fertilizers, pharmaceuticals, fiber industries, modification of carbon nano tubes and synthesis of nano composites for lithium batteries.

Keywords: Sulfur Nanoparticles (S-NPs), TEM, SEM, XRD.

Introduction

Through a simple literature survey, non-metal sulfur nanoparticle did not take his right in research and study, the number of research in this area are limited compared to metalic nanoparticle material, which was broadly studied, that's why we need to discuss and summarizes the overall sulfur nanoparticle method of syntheis and their application.

The non-metal sulfur (S) in the scales of bulk, micro and nano, has a wide range of applications in different industrial activities such as in fertilizers, sulfuric acid production, plastics, enamels, pulp and paper industries, antimicrobial agents, gun powders and in different other industries [1-29].

For the applications of sulfur in agriculture area, sulfur can be used as fungicide against many plant diseases such as the apple scab disease in the cold conditions, also S used in the culture of grapes, vegetables, straw-berry and many cultivated plants. However; S can be considered as a high efficiency pesticide that used in agriculture where it has good effect against a wide range of powdery mildew diseases as well as black spot [8-14].

Sulfur nanoparticles can be prepared by different successfully methods such as acid hydrolysis of sodium thiosulphate [5–8], oxidation H_2S gas using Fe-chelate [9], ultrasonic treatment of sulfur-cystine solution [10], aqueous surfactant solutions [11], micro emulsion technique [12] and electrochemical method [13]. Microemulsion method is one of the most important methods due to the easily control of the particle size using this method. The disadvantage of this method are the complicated of the method, separation and purification of

the particles from the microemulsion and the needed to oil, huge amount of surfactant, co-surfactant and aqueous phases with the specific compositions.
Despite many exciting applications, there are only a few recent literatures available on synthesis of sulfur nanoparticles by different investigators in both aqueous and microemulsion phase by different routes [9–12]. Deshpande *et al.* synthesized sulfur nanoparticles from H2S gas using biodegradable iron chelate catalyst in reverse micro-emulsion technique [9].

There are various Application of S NPs nowadays such as agrochemical industries [4] fungicides in agriculture fields [14] , modification of carbon nano tubes [15], anti-cancer [16-17], antibacterial [18], pharmaceuticals and synthesis of nano composites for lithium batteries [19-28]. In this paper, preparation methods, characterization techniques and the applications of sulfur nanoparticles are discuss.

1. Preparation methods

Different shapes and size can be synthesized of S-NPs by different methods such as wet chemical precipitation method it used to prepare the S-NPs by dissolving the sodium thiosulpahte in double distilled water and different acid solutions, using different surfactants (TX-100, CTAB, SDBS, and SDS) as the stabilizer effect on the particle size. The anionic surfactant SDBS is higher effective for obtaining a uniform size in both the acid media. The lowest size of particles is (30 nm) were obtained in a certain reactant concentration range using CTAB surfactant [8].

S-NPs were synthesized from hazardous H_2S gas using novel biodegradable iron chelates in water/organic micro emulsion system. Fe^{3+}- malic acid chelate was studied in w/o micro emulsion containing cyclohexane, Triton X-100 and n-hexanol as oil phase, surfactant, co-surfactant, respectively, for catalytic oxidation of H_2S gas at ambient conditions of temperature, pressure, and neutral pH, the morphology of sulfur nanoparticles synthesized is nearly uniform in size (average particle size 10 nm) and narrow particle size distribution (in range of 5–15 nm) as compared to that in aqueous surfactant systems [9].

Monoclinic sulfur nanoparticles have been prepared via the chemical reaction between sodium polysulfide and hydrochloric acid in a reverse micro emulsions system, with theolin, butanol, and a mixture of Span 80 and Tween 80 (weight ratio 8: 1) as the oil phase, co-surfactant and surfactant, respectively. Transparent micro emulsions were obtained by mixing the oil phase; surfactant, co-surfactant, and the aqueous phase in appropriate proportion using an emulsification machine at the room temperature, the sulfur nanoparticles prepared via this method have an average diameter of about 20nm, a narrow size distribution, uniform spherical shape, and high purity [12].

An electrochemical method is used to prepare the sulfur nanoparticles from thiosulfate ion. The particle size of the S-NPs can be adjusted between 35 and 65 nm by by adjusting the operation parameters including the initial sodium thiosulfate. in this case , the used of hot alcohol and cold water as solvent/non-solvent system along with 100 $ml \cdot min^{-1}$ 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 anarrow particle size distribution [13].
Solution processing was developed to prepare conductive sulfur/carbon nanocomposites for electrochemical used as in Figure 1 [27]. Dimethyl sulfoxide (DMSO) was used as the solvent to dissolve sulfur.

2. Characterization of S-NPs

Different shapes and size of Sulfur NPs were obtained depending on the used method and parameters. The Sulfur NPs shapes were found to be spherical nanoparticles, monoclinic, orthorhombic, rombic and nanowires.

Different shapes and size of Sulfur nanoparticles were characterized by using the transmission electron microscopy (TEM), scanning electron microscope (SEM) and X-ray diffraction (XRD) , An electrochemical method is presented for the preparation of sulfur nanoparticles (S-NPs) from thiosulfate ion. The particle size of the S-NPs can be adjusted between 35 and 65 nm by varying parameters such as the initial concentration of thiosulfate [13].

As Orthorhombic (spherical ~10 nm) and monoclinic (cylindrical ~ 50 nm) (SNPs) were synthesized and examined for their effects on the total lipid content and desaturase enzymes of Aspergillus niger [23].

The monoclinic sulfur nanoparticles prepared by water-in-oil micro emulsions technique , the average diameter of sulfur nanoparticles with sodium polysulfide as the reactant is about 20 nm, while the one with ammonium polysulfide as the reactant is about 35 nm [12].

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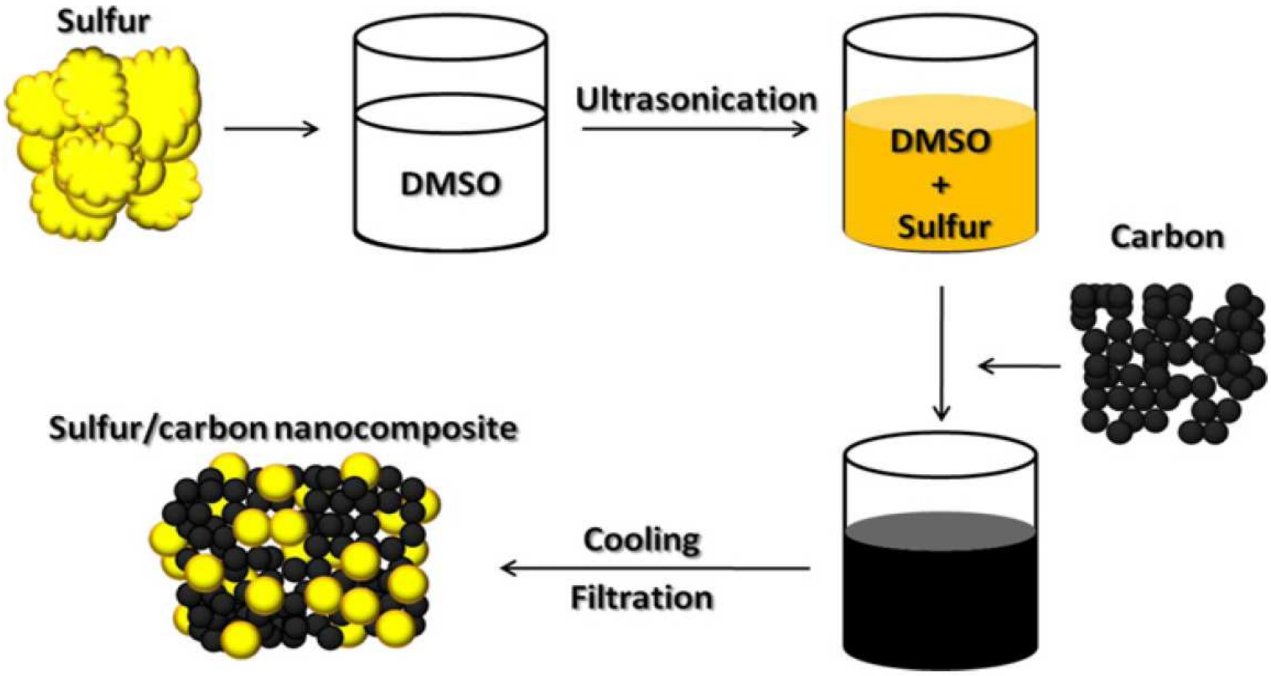

Fig. 1. Schematic of the solution processing for the preparation of sulfur/carbon [27]

Sulfur nano-particles were synthesized from hazardous H_2S gas using novel biodegradable iron chelates in w/o micro emulsion system (Figure 2), the average of particle size is 10 nm and narrow particle size distribution (in range of 5–15 nm) [9]. As Sulfur nanoparticles based method for separation and pre concentration of some heavy metals in marine samples prior to flame atomic absorption spectrometry determination the distribution size of most of the NPs was in the range of 45–55 nm [24]. Sulfur nanoparticles have different particle size with 30-60 nm (Figure 2) was synthesized in different aqueous surfactant solutions [8].

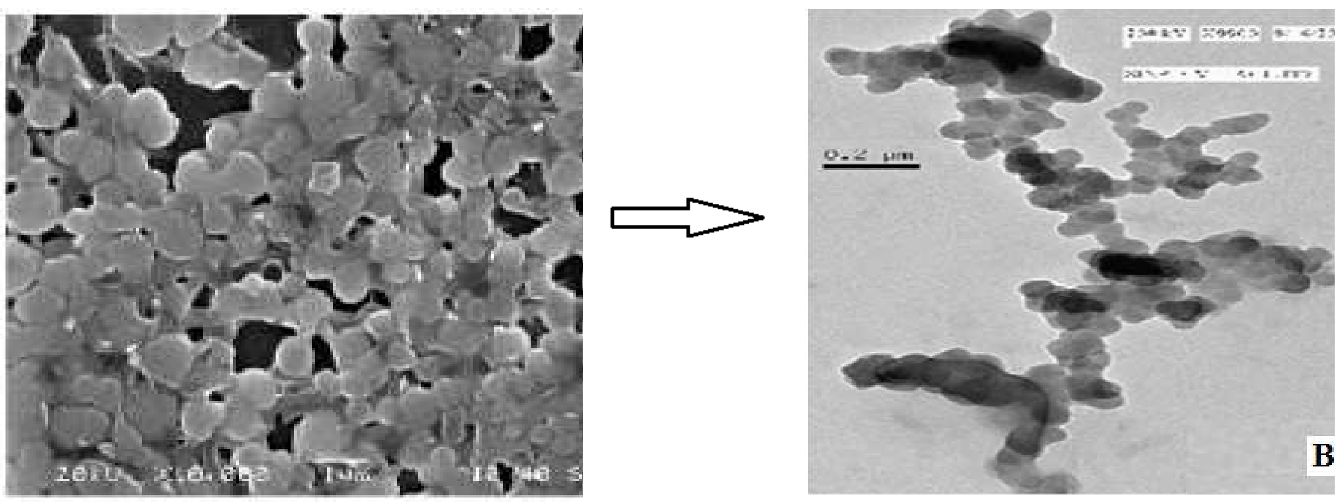

Fig. 2. Obtention of Sulfur Nanoparticles **(B-** TEM image**)** from Sulfur Nanoparticles (**A-** SEM image) [8].

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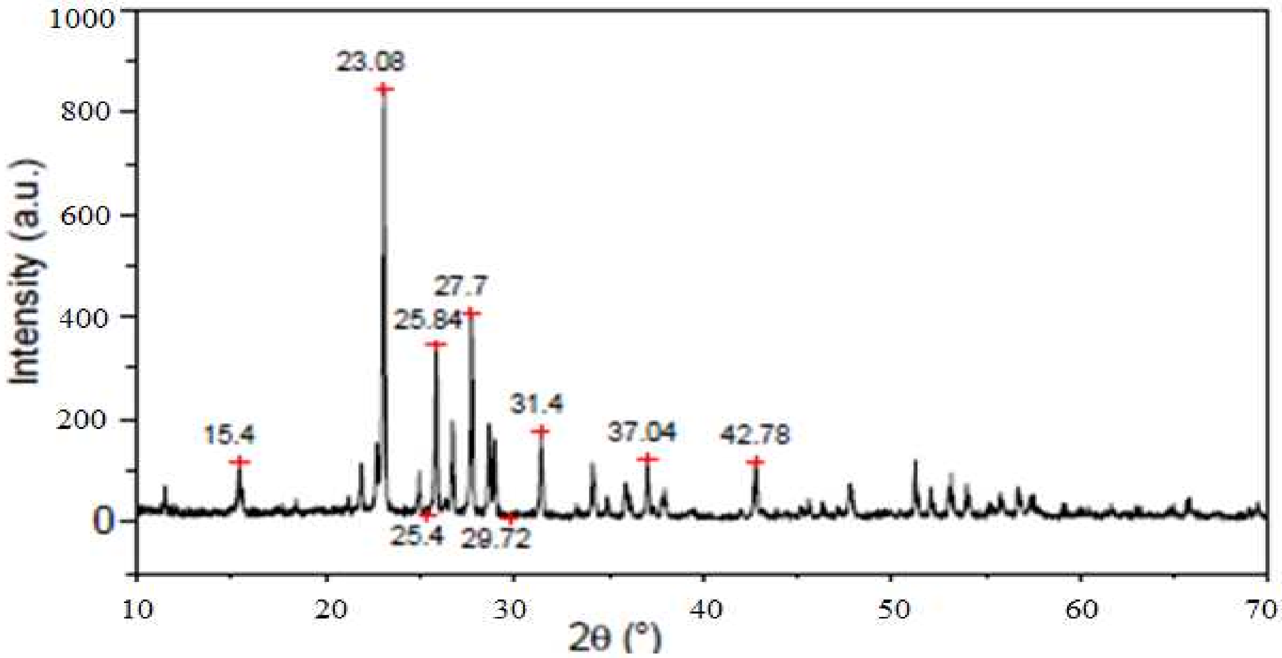

Fig. 3. XRD pattern of the sulfur nanoparticles [12].

3. Application

There are various application of Sulfur nanoparticles in now days, the most important fields of application:

1- In electrochemistry, sulfur nanoparticle was used to enhance the electrochemical activity of lithium batter through a solution-based technique. Lithium sulfur batteries are able to meet the requirements of large-scale applications owing to their high specific capacity, abundance of source materials in nature and the low cost of sulfur. Lithium sulfur batteries operate quite differently and save comparied by lithium ion batteries. Nonaqueous nano S0–PEG sol system has different potential applications such as modification of metal and carbon nano tubes, and synthesis of nano composites for lithium batteries [27]. Sulfur/carbon nano composites demonstrated a high specific capacity and can also be applied to prepare other sulfur containing nano composites such as in carbon nanotubes, graphene and mesoporous carbon matrices [28, 29].

2- As Catalysis for example elemental Sulfur Nanoparticles can dramatically enhance the rate of Cr(VI) reduction [25]. Chromium is one of the most frequently detected soil and groundwater contaminants (In aquatic environments, chromium occurs mainly as species in the oxidation statesof Cr(VI) and Cr(III) . Since Cr(III) species are normally less mobile, the reduction of Cr(VI) to Cr(III) decreases chromium mobility and bioavailability. As a result, Cr(VI) reduction has been used as an effective approach for chromium-contaminated site remediation. Sufur nanoparticles are capable of reducing Cr(VI) in the ambient aquatic environment by directly providing electrons [25].

3- In medical Anticancer of sulfur nanoparticles significantly inhibited C6 glioma cell proliferation and promoted cell apoptosis by inducing the up regulation of Bax and down regulation of Bcl-2 expression [16]. The antibacterial activity of PEGylated S-NPs effect against all tested strains at a concentration between 9.41 and 18.82 mg/L using BMD, the ADM data revealed that S-NPs has uniform MICs (18.82 mg/L) for all tested strains[18]. Orthorhombic (10 nm) and monoclinic (50 nm) sulfur nanoparticles considerably reduced total lipid content of the treated fungal isolates with significant down regulation of the expression of various desaturase enzymes (linoleoyl-CoA desaturase, stearoyl-CoA 9-desaturase and phosphateidylcholine desaturase) [23].

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