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Application of Hydrothermal and Solvothermal Method in Synthesis of MoS_2

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Abstract: *Hydrothermal and solvothermal method were considered as the effective methods for preparation of MoS_2 nanomaterials. The current researches of MoS_2 mainly concerned on electrical properties, the research of reaction system was relatively less. In this paper, synthesis system of MoS_2 was elaborated from precursor, solution, reductant, sulfurizing agent, additive and pH regulator. The application of multifunctional raw materials can greatly simplify reaction system. This provided a reference for the application of hydrothermal and solvothermal method in preparation of MoS_2.*

Keywords*:hydrothermal, solvothermal, MoS_2, graphene-like structure*

1. Introduction

Since the discovery of graphene in 2004 [1], MoS_2 has been widely concerned due to its graphene-like structure [2]. Compared with graphene, MoS_2 is lower cost and considered as an ideal substitute for graphene. MoS_2 is a typical layered material, in the layer is strong covalent bonding of Mo-S, the interaction between layers is Vander Waals forces [3]. As showed in Figure 1, there are three structures for MoS_2 such as 2H(trigonal prismatic), 3R(rhombohedral) and T (trigonal prismatic) [4-6]. For multilayer structure, "Rim-Edge" model is widely accepted [7]. MoS_2 structure with diameter of 3~8nm is nanooctahedra, with diameter of 20~150 nm is polyhedral or nanotubular [8]. Structures with many hundred nanometre is 2H-MoS_2 [9], but 2H-MoS_2 can be converted into 1T- MoS_2 which is driven by the transition metal Mo vacancy [10]. Nowadays, MoS_2 nanomaterials were extensively used in various field such as super dye sensitized solar cell [11], super-capacitor [12,13], hydrogen evolution reaction [14,15], lithium electronic [16,17], sensors [18,19], catalysis [20].

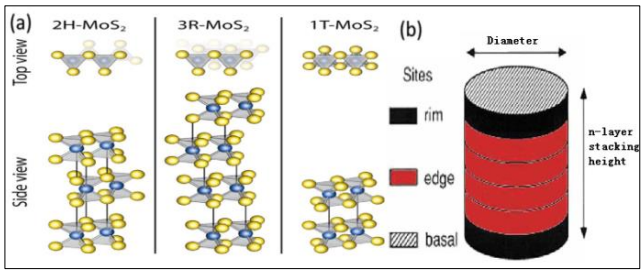

Figure 1. Schematic diagram of MoS_2. a. Layered structure of MoS_2: trigonal prismatic (2H), 3R (rhombohedral and octahedral (1T)), b. "Rim-Edge" model

Many methods were developed to prepare MoS_2, such as solvothermal, hydrothermal, template-assisted [21], chemical vapour deposition [22], liquid exfoliation [23], electrochemical anodization [24], insitu-oxidative polymerization [25] and ultrasonication microwave [26]. MoS_2 nanomaterials with different morphologies were synthesized such as nanosphere, nanoflowers, nanowires, nanofibers, nanoparticles and microspheres. The researches of hydrothermal and solvent thermal method focused on the properties and applications of prepared materials. The route and mechanism of design reaction system of hydrothermal and solvothermal method was rarely discussed. The advantages and applications of MoS_2 nanostructured materials in the area of energy and environment were reported [27,28].

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The properties and performances of two-dimensional layered MoS_2 in electro-chemical application were covered [29]. In this paper, the design route of hydrothermal and solvothermal method for preparation of MoS_2 was studied from six aspects (precursor, solution, reductant, sulfurizing agent, additive and *p*H regulator), which provided a reference for the application of hydrothermal and solvothermal in future.

2. Materials and methods

For hydrothermal and slvothermal method, teflonlined autoclave was used as reactor, deionized water or organic solvent were used as reaction solvent. Solvothermal method developed on the basis of hydrothermal method, in which deionized water was replaced with organic solvent. These methods were extensively applied to chemical reaction, compound prepared and waste treatment [30-32].

Besides precursor, solution, reductant, sulfurizing agent, additive and *p*H regulator, temperature is key manipulated factor for reaction process, which can affect the properties and morphology of MoS_2 [33]. Only amorphous MoS_2 is obtained at 120~150^{o}C [34], with the increasing of reaction temperature, the diameter of products become larger at 230~260^{o}C [35], smaller at 300~375^{o}C [36], monolayer MoS_2 is prepared above 400^{o}C [37]. As the reaction temperature goes up, the crystallinity of MoS_2 increases and the disorder of material decreases [38]. Besides, high initial temperature also promotes nucleation, thus nuclei aggregation and growth [13], which leads to shorter slabs, more defects and higher catalytic activity.

Compared with solvothermalm method, hydrothermal products were poor crystallinity with more defects such as pleats and holes, which were beneficial to electrical and catalytic performance [24,39]. But doping effect of solvothermal method was better. MoS_2/RGO hybrid materials prepared by hydrothermal and solvothermal method were contrasted [40], the results showed that MoS_2 and graphene were well doped under solvothermal condition. When DMF was replaced with H_2O, two separated phases of MoS_2 particles and RGO sheets were obtained. Hydrothermal and solvothermal method carried out at low concentrations, morphologies and properties of MoS_2 were easy to fabricate. For low yield, the products were rarely used in industrial catalysis, only applied to the study of catalytic mechanism. So, the preparation of MoS_2 at high concentration and its application in the field of industrial catalysis may be a hot issue in future.

3. Results and discussions

3.1. Precursor

MoO_3, Na_2MoO_4 [41], H_2MoO_4, $(NH_4)_6Mo_7O_{24}$, $(NH_4)_2MoS_4$, $Mo(CO)_6$ and organic precursor were used in the synthesis of MoS_2 commonly. Precursors play an important role in the reaction process, different precursors obtain difference composition and morphology. The concentration of precursor affected the morphology of MoS_2 crystallites [35]. With the increasing of concentration, the diffusion rate of ions increases, which can decrease the interfacial reaction rate. High concentration impedes the formation of crystal nucleus leading to larger particle size.

Compared with other precursors, $(NH_4)_2MoS_4$ is special which contains S and Mo element [36, 39, 40, 50, 61, 65]. It can decompose into MoS_3 at 573K, and then MoS_3 can converted into MoS_2 [43,44] at 633K. MoS_2 microspheres with uniform morphology were prepared with $(NH_4)_2MoS_4$ as precursors [50]. Among those precursors, MoO_3 was used as bridge to connect other precursors. MoO_3 can be easily convert to other precursors such as Na_2MoO_4, $(NH_4)_6Mo_7O_{24}$), meanwhile other precursors can become MoO_3 by high temperature oxidation. MoS_2 was prepared by hydrothermal and solventhermal method with MoO_3 as precursor, NaSCN as S resource and reducing agent, HCl as *p*H regulator (Figure 2 a, b). The reaction mechanism was interpreted [43,45] as showed (1,2). Pan [47] prepared MoS_2 by solvothermal method with MoO_3 as precursor and ethylene glycol as solvent. Among those precursors, MoO_4^{2-}, $Mo_7O_{24}^{2-}$ can transform into each other easily in different environments. 3D flower-like MoS_2 microspheres (Figure 2 c, d) was synthesized by hydrothermal method with Na_2MoO_4 as precursor [46] which was comprised by bent sheets with 600nm diameters. Porous MoS_2 microspheres were prepared with $(NH_4)_6Mo_7O_{24}$) [48,49]. Compared with inorganic precursor, the reaction temperature of organic

precursor was lower. Hierarchical MoS_2 /Polyaniline Nanowires were prepared by hydrothermal with organic precursor ($Mo_3O_{10}(C_6H_8N)_2.H_2O$) [51]. Mesostructured lamellar MoS_2 was synthesized mesostructured lamellar MoS_2 with $Mo(CO)_6$ at 140℃ [42]. New precursor was synthesised through aging, then prepared poor crystalline MoS_2 was obtained by hydrothermal stages, the products displayed excellent hydro-desulphurisation performance [91]. In a word, the species and concentration of precursor have large effects on MoS_2 crystallity, composition and morphology. Nowadays, it's easy to convert from precursors to MoS_2 but harder to reverse, which limits cyclic utilization of Mo resource. To achieve this process, MoO_3 precursor maybe an appropriate choice.

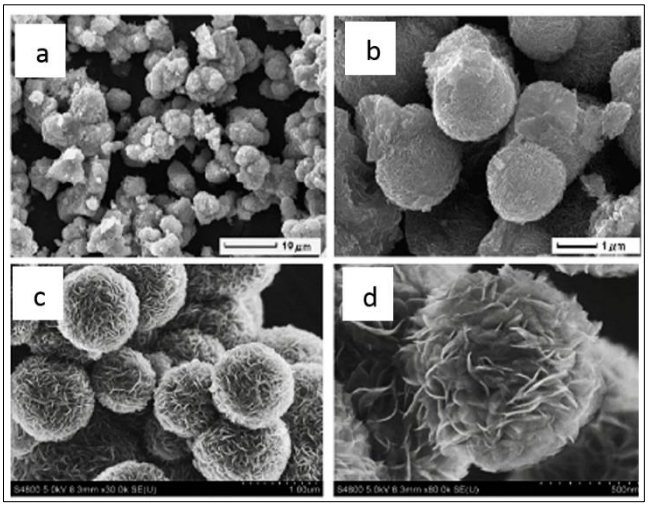

Figure 2. a. MoS_2 by hydrothermal with MoO_3 precursor, b. MoS_2 by solvothermal with MoO_3 precursor, c, d. MoS_2 synthesised by hydrothermal with Na_2MoO_4 as precursor

$$NaSCN+2H_2O+HCl \rightarrow NH_3\uparrow+H_2S\uparrow+CO_2\uparrow+NaCl \quad (1)$$

$$4MoO_3+9NaSCN+10H_2O+7HCl \rightarrow 4MoS_2+Na_2SO_4+7NaCl+9NH_3\uparrow+9CO_2\uparrow \quad (2)$$

3.2. Solvent

Deionized water, ethanol, pyrrolidone, N,N-Dimethylformamide (DMF) [40], alkane, N- methyl -2 pyrrolidone (NMP), ethylene glycol [52], n-dodecylamine [53], pyridine [54] and other organic solvents were used as solvent. During the reaction process, the solvent can act as reaction medium and exfoliation agent. The exfoliation effects of nine organic substances were investigated on MoS_2 [55]. The results showed that exfoliation of NMP and cyclohexane was the best and the prepared MoS_2 was 2~5 layers, effects of other solutions were not obvious regularity. Besides, the exfoliation of methanol, ethanol, propyl alcohol and butanol on MoS_2 was studied [57], the rank of denudation ability was methanol < ethanol < propyl alcohol < butanol. Although some solutions no exfoliation ability, their mixed-solvent have certain exfoliation ability. The exfoliation of different concentration of ethanol was investigated [56]. The concentrations of ethanol was 45%, the exfoliation of MoS_2 was the best, which can be explained by Hansen solubility parameters. The results of the experiment were well in agreement with Hansen solubility parameters [94] (Figure 3a,b). Mixed-solvent molecular size has an important role in the exfoliation attributing to the larger steric repulsion and this phenomenon is elaborated by Leonard-Jones.

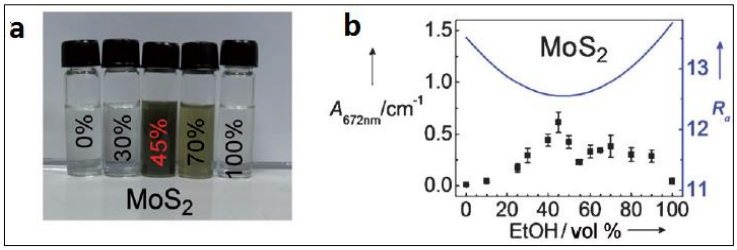

Figure 3a. MoS_2 dispersions in various ethanol/water mixtures; b. The absorbance of the MoS_2 suspensions in ethanol/water mixtures with different composition are shown as dots, and the calculated Ra values as solid lines

NMP and pyrrolidone can induce 1T-MoS_2 to transform into 2H-MoS_2 [58-60]. Unique column-like MoS_2 superstructure composed of edge-terminated MoS_2 nanosheets (CLET MoS_2, Figure 4a, b was synthesised with NMP as solvent and reductant [41]. These structures exhibited excellent electro-chemical performance in both lithium ion storage and hydrogen evolution reaction, because CLET MoS_2 exposed more active edges and sites. Pyrrolidone group degraded to produce CO, which improved the purity of MoS_2 for high reducibility of CO [61]. Compared with the hydrothermal method, MoS_2 prepared by solvothermal method was smaller and uniform. Mesostructured lamellar MoS_2 was obtained with n-dodecylamine as the medium [42]. MoS_2 nanoflowers decorated reduced graphene oxide paper were prepared with DMF as solvent [62].

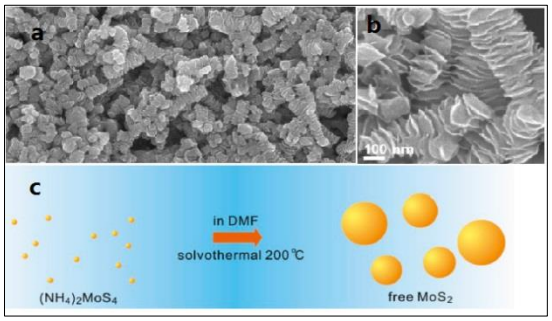

Figure 4. a, b SEM of CLET MoS2; c. Route of solvothermal (DMF as solvent)

There are two theories were applied to select solution such as Young's equation (3) and Hansen solubility parameters [63]. Young's equation involves solid-liquid, solid-gas, liquid-gas surface tension, this method reflects the influence of solution through angle of interfacial tension. Young's equation can be applied to forecast the optimal co-solvent concentration of exfoliation [57]. Hansen solubility parameters combined the effects of dispersion forces, dipole-permanent dipole and hydrogen bonding forces. Hasan solubility parameter can be used in solvent prediction [64, 65], the results were coincident with the experimental results. Hansen solubility parameters was suitable for pure solvent and mixed solvent (5). Hansen solubility parameters was applied to predict the exfoliation of layered compounds in different concentration of ethanol [56]. Besides, steric effect, boiling point and molecular weight should be taken into account when select the reaction solution. So, liquid paraffin, diphenyl ether, oleamine, oleic acid, other high molecular weight and high boiling point alkane solvents also are good potential solution.

$$\gamma_{sl} = \gamma_{sg} - \gamma_{lg}\cos\theta_c \tag{3}$$

$$R_a = \left[4\left(\delta_{D,solv} - \delta_{D,solu}\right)^2 + \left(\delta_{P,solv} - \delta_{P,solu}\right)^2 + \left(\delta_{H,solv} - \delta_{H,solu}\right)^2\right]^{-0.5} \tag{4}$$

$$\delta_{blend} = \sum \phi_{n.comp} \delta_{n.comp} \quad (5)$$

γ_{sl}, γ_{sg}, γ_{lg}, θ_c, which are the solid–liquid, solid-gas, liquid-gas interfacial energy, and equilibrium contact angle. R_a, δ_D, δ_P, δ_H, Φ, which are HSP distance, dispersive, polar, and hydrogen-bonding solubility parameters, volume fraction for each composition.

3.3. Reductant

The reductant can reduce $Mo^{6+}$to Mo^{4+}, so the addition of reductant can improve the crystallinity of MoS_2. The application of reductant reduce the reaction temperature. Generally, water soluble reductants were used in the hydrothermal method, the oil soluble reductants were applied in solvothermal method.

Generally, reductant contains reductive functional groups such as –OH, -C=O, -C=C-, -NH_2. $N_2H_4 \cdot H_2O$, $NH_2OH \cdot HCl$ [34,66], ethylene glycol and $NH_2OH.H_2SO_4$ [67] were widely used. Among these reductant $NH_2OH \cdot HCl$ is special and oxidation product is N_2, which does not coat the active site. MoS_2 was synthesized with $N_2H_4 \cdot H_2O$ as reductant at different temperatures, the mechanism of reaction was illustrated (6,7) [68,69]. Flower-like MoS_2 was prepared with $NH_2OH \cdot HCl$ as reducing agent at assistance of ionic solution (Figure 5), the mechanism of which was stated (8) [50].

The species of reductant have differen influence on the chemical composition of products. Chemical composition of prepared MoS_2 was studied with various reductant [53]. When the reductants were N_2H_4, NH_2OH, N_2H_4-NR_4Cl, NH_2OH-NR_4Cl, the products were $MoS_{2.4}$, $MoS_{3.05}$, $MoS_{2.1}C_{1.58}$, $MoS_{2.19}C_{1.62}$. Small molecule reductants were widely used, the applications of macro-molecular reductants were relatively less. Compared with small molecule reductant, there are two advantages for macromolecular reductant. On the one hand, the reducibility of macromolecule reductants is more stable, on the other hand, macromolecule reductants play a role of coating which can affect the morphology of reaction products. Reductants for hydrothermal and solvothermal method are relatively less, reducing agents for other transition metal materials deserve to study and advocate. For example, H_2 [70], lithium borohydride [71], 1-octadecene [72], 1,2-dodecanediol [73], ascorbic acid [74].

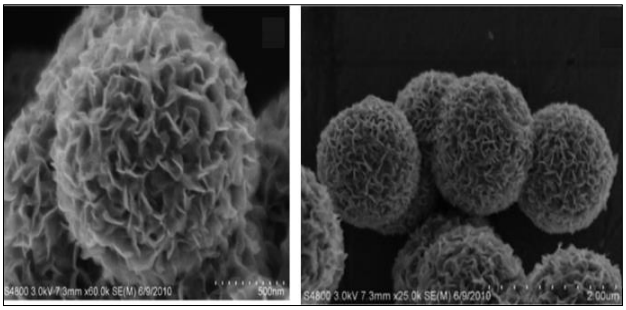

Figure 5. SEM of microspheres

$$Mo^{6+} + 2NH_2\text{-}NH_2 + 2OH^- \longrightarrow Mo^{4+} + 2H_2O + 2N_2 \uparrow \quad (6)$$

$$MoS_4^{2-} + 2NH_2\text{-}NH_2 \longrightarrow MoS_2 + S^{2-} + 2N_2 \uparrow \quad (7)$$

$$MoS_4^{2-} + 2HONH_3Cl^- \longrightarrow MoS_2 + 2H_2S + N_2 \uparrow + 2H_2O + 2Cl^- \quad (8)$$

3.4. Additive

Macromolecular surfactant and inorganic salt were used as additives. Surfactants served as template and anchor, which controlled the morphology of the products. Additives improved the dispersion of precursor in solution by creating microenvironment, which increased the dispersion of products [75]. Additives affected interfacial reactions by adjusting interfacial tension. PEG, PVP, P123, SDS, CTAC, AOT, CTAB [65], ionic liquid, $C_{16}H_{36}BrN$, TOP and compounds with large molecules and high boiling points were widely used. The effects of PEG, P123, SDS, AOT and CTAB on product morphology were

investigated by hydrothermal method [69] (Figure 6a~f), the results showed that various surfactants led to different morphologies. MoS_2 microspheres were synthesized with $C_{16}H_{36}BrN$ as additive, the mechanism was elucidated (Figure 7a) [45]. After adding $C_{16}H_{36}BrN$, the surface of microspheres became smoother. The application of additives was favourable to fixation and nucleation, MoS_2/Fe_3S_4, $CoMoS/Fe_3S_4$, $NiMoS/Fe_3S_4$ and $MoS_2/SiO_2/Fe_3O_4$ with CTAB and SDS were synthesized as additives [76,77]. The application of additive make the morphology of products become more homogeneous. uniform $C@MoS_2$ was prepared PVP as additive and carbon source [78]. Flower-like MoS_2 was prepared with TOP as additive and MoS_2NFs composed of crumpled MoS_2NSs with more active edges [62]. Ionic liquid also played a crucial role in the formation of MoS_2 micro-spheres.

With adding ionic liquid, ion-covered vesicles can be formed, which provide nucleation domains for the hydrothermal reaction. MoS_2 nanosheets grew larger, stacked together and curled on the vesicle surfaces during hydrothermal process, resulting in the formation of MoS_2 microspheres. The mechanism of the MoS_2 microspheres with ionic liquid was illustrated (Figure 7b). Without ionic liquid the structure of products changed obviously [50,79] (the peak of (002) became weaker). Inorganic salts affected the structures and properties of product through synergistic effect and shielding effect. The effects of CH_3COONa and NH_4Cl on the synthesis of MoS_2 was investigated [35]. CH_3COONa and NH_4Cl can inhibit the formation of MoS_2 crystal nucleus at interface, which increase the particle size of product. Wu [80] deemed that the introduction of NH^{4+} can improve the ability in the electrical conductivity. Nowadays, the application of additives mainly concentrated on macromolecular surfactants, the research on inorganic salts was rare. The effects of inorganic salt on the products need to be investigated further.

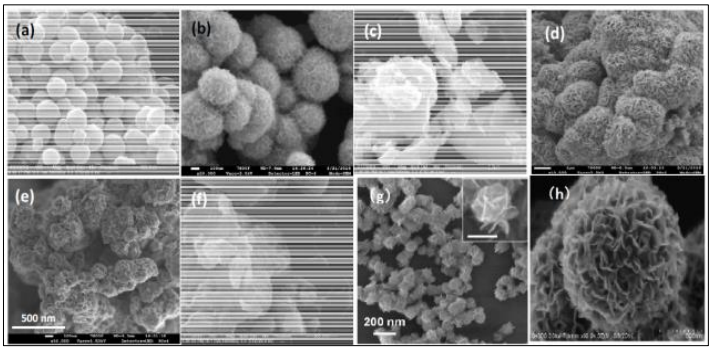

Figure 6. SEM images of MoS_2 samples synthesized with different surfactants. a. MoS_2-PEG; b. MoS_2-PVP; c. MoS_2-AOT; d. MoS_2-P123; e. MoS_2-SDS; f. MoS_2-CTAB; g. MoS_2-TOP; h. MoS_2-[BMIM][BF_4]

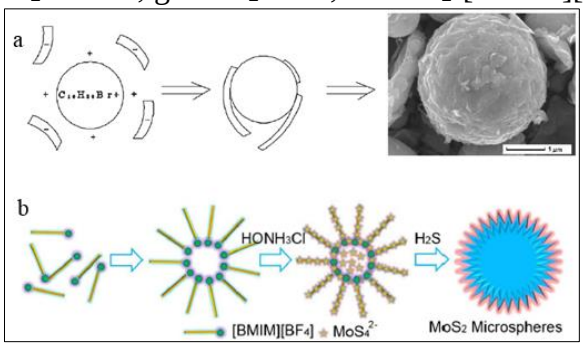

Figure 7. Formation mechanism of the MoS_2 microspheres with additive. a. $C_{16}H_{36}BrN$; b. [BMIM][BF_4]

3.5. Sulfurizing agent

In the preparation process, the sulfurizing agent acts as a sulfur source, some sulfurizing agent acts as a reductant agent. Thiourea, cysteine, elemental sulfur [42,54], sodium sulfide [34], NaSCN, $(NH_4)_2S$, CS_2 [81], H_2S, DMDS(Methyl disulfide) [81], thioglycolic acid [93], thioacetamide [69,78,79] were used. Functionally, sulfurizing agents can be divided into two types, one is directly providEs S^{2-}, such

as Na_2S, $(NH_4)_2S$, the other is the decomposition to produce H_2S, such as thiourea, cysteine, thioacetamide. When the former is used as sulfurizing agents, the reaction temperature is higher. Only H_2S and S elemental were used as sulfurizing agents, the products were MoS_2 [39]. High activity MoS_2 nanocatalyst was prepared with Na_2S as sulfurizing agent [33]. Besides, sulfurizing agents also affected the morphology of product. Spherical MoS_2 nanoparticles can be obtained with L-cysteine, MoS_2 nanosheets were formed with thiourea [82]. Mo/S can influence the chemical compositions of product. The effects of Mo/S were studied [54] under solvothermal condition. When Mo/S was 0, 1:1, 1:2, 1:3, the reaction products were MoO_2, MoO_2 and MoS_2, MoS_2, MoS_2 respectively. Polysulfide compounds on poor crystallinity MoS_2 surfaces was observed [83]. Excessive thiourea adhered to the surface of the crystal and affected further growth of crystal [84] (Figure 8). The mechanism was expounded [68] (9~10), and different mechanisms were proposed [85]. Nowadays, the applications of macromolecule sulfurizing agent were less. Compared with small molecule sulfurizing agent, macromolecule sulfurizing agents play a certain role in coating. Smaller particles and uniform product can be synthesized with macromolecule sulfurizing agent. Nanocrystals with a diameter of 10nm was prepared with bis (trimethylsilyl) sulfide (TMS) [72] as sulfurizing agent.

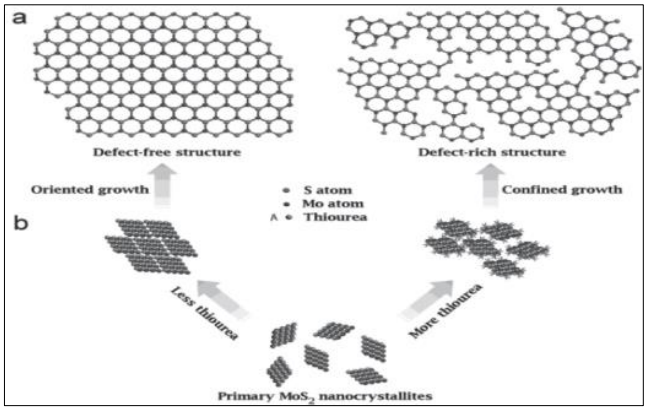

Figure 8. Route of thiourea function

$$CH_4N_2S+OH^- \longrightarrow SH^- + H_2O + CH_4N_2 \quad (9)$$

$$SH^- + OH^- \longrightarrow S^{2-} + H_2O \quad (10)$$

$$CH_4N_2S + 2H_2O \longrightarrow NH_3 + H_2S + CO_2 \quad (11)$$

$$CH_3CSNH_2 + 2H_2O \longrightarrow H_2S + CH_3COOH + NH_3 \quad (12)$$

$$HSCH_2CHNH_2COOH + H_2O \rightarrow CH_3COCOOH + NH_3 + H_2S \quad (13)$$

3.6. *p*H regulator

The acidic environment plays an important role in preparation of MoS_2 [86], which can accelerate rate crystallization [87] through adjusting the consumption of H^+ [88, 92]. Park believed that H^+ catalyzed hydrothermal reaction process [82]. The concentration of H^+ also affects the existence state of precursors [89, 92]. *p*H varies from 0 to14, Mo precursor changes largely (14). Besides, *p*H affected the bonds between additives and nanoparticles during MoS_2 crystallinity process.

$$\underset{}{\overset{PH>6}{[MoO_4]^{2-}}} \rightarrow \underset{}{\overset{PH=1.5\text{-}2.9}{[Mo_2O_{24}]^{6-}}} \rightarrow \underset{}{\overset{PH<1}{[Mo_8O_{26}]^{4-}}} \rightarrow MoO_3 \bullet H_2O \quad (14)$$

The common used *p*H regulators were HCl [85], H_2SO_4, $NH_3.H_2O$ [56] and NaOH. The effects of *p*H on products were investigated [34]. *p*H below 6.0, the products consisted of a little MoO_2 and MoS_2, *p*H above 7.5, the products were little MoO_2 as well as MoS_2 and much MoO_3, pure MoS_2 powder was obtained only when *p*H between 6.0 and 7.5. Mo conversion increased as the *p*H increased [77]. Ultrathin MoS_2 films with exposed layered structure were grown on fluorine-doped tin oxide (FTO) at *p*H=10[68]. Flower-like MoS_2 was synthesized with high purity via hydrothermal at *p*H=6 [66]. Ammoniated MoS_2 was prepared with ammonia as the reaction medium [80]. MoS_2 nanorods were successfully prepared with sillicontungstic acid [90], the products were nanoparticle without sillicontungstic acid (hydrochloric acid or nitric acid). once sillicontungstic acid was added, the products were nanorods with uniform morphology. Nowadays, the application of *p*H regulators was limited to inorganic acids, organic acids were less. Compared with inorganic acids, the molecule of organic acids is larger and contains more functional groups. The application of organic acids affect the morphology of products and lead to the formation of metal dopants. Taking citric acid for example, which were applied to the synthesis of nanomaterial [52].it not only can adjust pH, but also can play a role in reduction process.

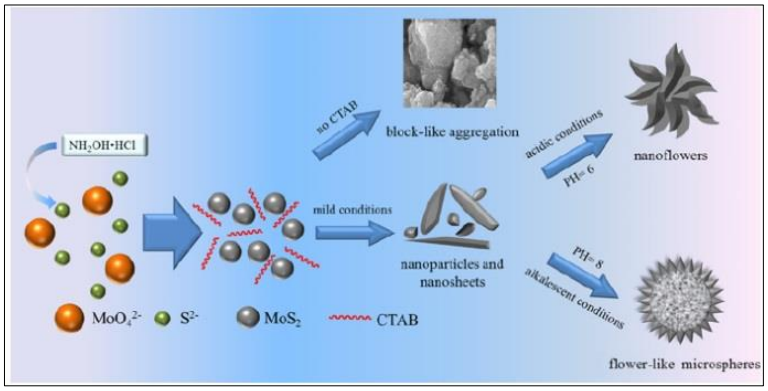

Figure 9. Schematic illustration of different MoS_2 nanostructures [65]

4. Conclusions

The current researches of MoS_2 mainly concerned on electrical properties, the research of reaction system was relatively less. In this paper, the hydrothermal and solvothermal reaction system was divided into 6 parts, but not every part needed. The application of multifunctional raw materials can greatly simplify reaction system. Besides, low cost, stable and recyclable MoS_2 catalysts are also a direction for future research.

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