The Syntheses of Uniform Metal(2B) Sulfide Particles in Concentrated Systems((2B))

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論　文　内　容　要　旨

Two novel methods on the syntheses of uniform CdS particles in large quanitities had been established. The first method is the preparation of uniform CdS partocles from $Cd(OH)_2$ suspension in a basic medium. The second method is the generation of uniform CdS particles in concentrated homogeneous solutions. Uniform ZnS particles were also obtained employing analogous procedures for generating uniform CdS particles in homogeneous systems.

For the first method, uniform CdS particles having an average diameter of 40 to 100 nm were prepared by aging for 1 hour at 20°C with agitation, 1.0 mol dm^{-3} $Cd(OH)_2$ suspension containing 1.1 mol dm^{-3} thioacetamide, CH_3CSNH_2(TAA), 1.0 mol dm^{-3} NH_4NO_3, and 1wt% gelatin, in the presence of ammonia at different concentrations. The resulting uniform and nearly spherical particles of CdS prepared under the standard conditions were 40nm in mean diameter. The crystal structure of the resulting CdS particles was similar to that of hexagonal greenockite. The CdS particles appeared to consist of randomly oriented much smaller subcrystals (8.60 nm), implying their polycrystalline property. No uniform CdS particles were formed when gelatin was eliminated from the standard conditions, or when pH was adjusted with NaOH, instead of NH_3. The size of the CdS particles can be controlled by varying the concentration of NH_3 in the system. At a high pH with ammonia, the nucleation of CdS was relatively suppressed due to the remarkable improvement of particle growth because of nucleation and growth competitive.

The formation mechanism of the uniform CdS particles basically proceeded through rapid dissolution of $Cd(OH)_2$ particles induced by the reaction of Cd^{2+} ions with S^{2-} ions liberated from TAA in the solution phase. The reaction was finished in ca. 1 minute under the standard conditions. The CdS particeles were formed by a spontaneus mucleation upon the instantaneous addition of TAA. The use of $Cd(OH)_2$ as the solid precursor served as a solute reservoir for the Cd^{2+} ions releasing $Cd(NH_3)_n^{2+}$ complexes by the solvent action of NH_3 added in the system during the growth process. The NH_3-NH_4^+ buffer system served two roles : as a pH buffer and a solvent. As a pH buffer, it maintained a steady supply of Cd^{2+} ions during the growth process. As a solvent for Cd^{2+} ions, the $Cd(NH_3)_n^{2+}$ complexes kept the growth rate of the CdS

particles sufficiently high, maintaining the supersaturation low enough below the critical level for nucleation. The gelatin mainly acts as a block for the $Cd(OH)_2$ inhibiting a direct reaction of the S^{2-} ions onto the dissolving $Cd(OH)_2$ particles. It also prevented coagulation during the formation of the CdS particles.

The polycrystalline structure of the CdS particles implies that their formation was possibly by aggregation of smallr subunits which aggregated in an orderly manner forming larger uniform particles. Investigation was conducted by altering the mode of addition of the TAA. Such tests were conducted basing from the formulated concept with the established standard conditions, which illustrated a spontaneous CdS nucleation upon the instantaneous addition of the TAA. Hence, altering the mode of addition of the TAA, that is, by two-step addition of the required volume of TAA at a specified interval, or a continuous addition of the TAA is to expected to give very small particles as a result of renuceation during the consecutive addition of the TAA. So that if the growth mechanism was by aggregation process, these small particles should aggregates effectively onto the larger particles eventually fotming larger and more uniform particles. However, on the contrary, for the two-step addition process, the particles formed were bimodal in size distribution. For the continuous addition process, the particled formes were polydispersed. Such findings illustrated that the particles generrated under the established standard conditions were not formed by aggergation process. At the outset, they must have grown through deposition of diffusing monomeric species such as CdS molecules formed in the solution phase onto the surface of the growing particles, or a surface reaction of Cd^{2+} ions with S^{2-} ions on the surfaces. In addition, the unform growth of the CdS particles was achieved by the controlled dissolution of the $Cd(OH)_2$ without aggregation of the growing particles CdS after an instantaneous nucleation.

It was also found that S^{2-} ions were furnished through a reaction : $CH_3CSNH_2 \rightleftarrows CH_3CN + 2H^+ + S^{2-}$. The liberation of S^{2-} ions of a very low concentration may immediately react with the Cd^{2+} ions and their ammonia complexes, which must have enhanced the reaction of TAA into $CH_3CN + H_2S$, and the dissolution of $Cd(OH)_2$, to a great extent. This reaction was exceedingly accelerated by the rapid consumption of the S^{2-} ions so that it is thought to be a reversible reaction, though the equilibrium concentration of CH_3CN and H_2S in the absence of Cd^{2+} ions are extremely low. Moreover, the TAA dissociation can easily maintain an equilibrium after the S^{2-} ions were used up by the reaction with the Cd^{2+} ions which were rather concentrated, apparently because the recovery to maintain an equilibrium was quite rapid, so that the supply of S^{2-} ions cannot be the rate-determining step. The overall reaction for the formation of the unform CdS particles from $Cd(OH)_2$ suspension, with TAA as the source of S^{2-} ions can be written as : $CH_3CSNH_2 + Cd(OH)_2 \rightarrow CdS + CH_3CN + 2H_2O$.

For the second method, uniform CdS particles were generated from a reaction mixture containing : 0.24 mol dm^{-3} in $Cd(OH)_2$, 0.24 mol dm^{-3} in TAA, EDTA·2Na (ethylenediaminetetraacetic acid, disodium salt), which is, 1 mol% in excess of the $Cd(OH)_2$ concentration, 1.6 mol dm^{-3} in CH_3COONH_4, 0.048 mol dm^{-3} in NH_3, and 1 wt% gelatin, by aging at 60℃ for 8 hours with agitation. With the above preparation procedures, the $Cd(OH)_2$ particled were totally dissolved giving a clear starting solution. At the outset, the resulting CdS particles having a mean diameter of 0.54 μm showed major XRD line characteristics similar to that of cubic β-CdS. The obtained CdS particles also illustrated a polycrystalline structure, with the subcystal size calculated to be 24.80 nm. With the homogeneous system, the maximum growth of the uniform CdS particles was obtained after 8 hours of aging, compared with the CdS particles obtained from $Cd(OH)_2$ suspension whose growth was almost finished in about 1 minute. This is because the concentrations of free Cd^{2+} ions and $Cd(NH_3)_n^{2+}$ complexes in equilibrrium with $Cd(OH)_2$ were much higher than those in equilibrium with the Cd-EDTA complexes, so that the driving force to release Cd^{2+} ions from the $Cd(OH)_2$ was much greater than that of the Cd-EDTA complexes.

Despite the polycrystalline structure of the CdS particles, the larger uniform particles were not formed by way of aggregation of smaller CdS particles which was confirmed by conducting an investigation which was similar to that employed on the formation of CdS particles from $Cd(OH)_2$ suspension. Further, the subcrystal size of the CdS particles obtained in the concentrated homogeneous solution was much larger than the CdS particles generated from $Cd(OH)_2$ suspension, because the supersaturation for the formation of the surface nuclei as an elementary step of the growth process was much higher in the latter method.

Similar to the first method, when gelatin was eliminated from standard system, no uniform particles were obtained. And when EDTA was eliminated from the established standard conditions, very small spherical particles with a rather higher yield were generated in less than 2 minites aging, while in the absence of the CH_3COONH_4-NH_3 buffer system, polydispersed particles with very low yield were generated after 8 hours of aging period.

The effect of varying the concentration of EDTA·2Na on the formation of the CdS particles were also investigated. With the standard conditions, the concentration of EDTA·2Na was 1mol% in excess of the Cd^{2+} ion concentration. Larger and uniform CdS particles with a yield of 96.0% were obtained after 8 hours of aging. When the concentration of EDTA was 1% lower than the $Cd(OH)_2$ concentration, very small particles were obtained with a yield of 97% were obtained after 6 hours of aging. Further decreasing the concentration of EDTA down to 30% lower than the concentration of the $Cd(OH)_2$ gave very small particles with a yield of almost 100% after 2 hours of aging. These results will show that if EDTA is deficient, tremendous number of nuclei were formed as a result of higher concentration of free Cd^{2+} ions. Such findings also illustrate that the S^{2-} ions do not directly react with the Cd-EDTA complexes.

Ammonia, as a pH buffer and as a solvent was essential on the formation of uniform CdS particles. The effect of other buffer systems were investigated by eliminationg CH_3COONH_4-NH_3 buffer system from the standard condition and employing other buffer mixtures, where, a CH_3COONa-NaOH buffer system and using NaOH only, were investigated separately, In the standard condition where CH_3COONH_4-NH_3 was used as the pH buffer, uniform CdS particles were obtained. On the other hand, polydispersed CdS particles were obtained when CH_3COONa-NaOH, or when only NaOH was adopted. The pH change difference when CH_3COONH_4-NH_3 buffer system after 8 hours of aging was quite small compared with other two buffer system. At the outset, the yield obtained when CH_3COONH_4-NH_3 buffer system was employed, was obviously larger.

In each investigation, wherein CH_3COONH_4-NH_3 buffer system, CH_3COONa-NaOH buffer system, and NaOH were used, the obtained yield were 96.0%, 2.2% and 1.8%, respectively. From the obtained size of the CdS particles, the particle number and growth in each investigation were also calculated. In the presence of NH_3 in the buffer system, the calculated particle number was obviously higher. Such result illustrate that NH_3 accelerated the rate of nuclei formation. At the outset, the calculated growth rate in the presence of NH_3 which was 100-fold higher than the other two buffer systems, clearly illustrates that NH_3 also accelerated the growth of the CdS particles.

Disregarding the pH effect, the effect of NH_3 in the formation was investigated with the pH of the aging sol kept constant along the aging process. In the standard system wherein 2.0 mol dm^{-3} CH_3COONH_4 and 0.6 mol dm^{-3} NH_3 were added, uniform CdS particles with a yield of 69.9% were obtained. When the concentration of NH_3 was decreased, the particles became polydispersed and the yield decreased, even when the pH of the aging sol was kept constant. Such findings clearly illustrate that even at a constant pH, the effect of NH_3 on the formation of the CdS particles is significant.

During the formation of the uniform CdS particles, the supersaturated $Cd(NH_3)_n^{2+}$ complexes and Cd^{2+} ions of high equilibrium concentration, in which the concentration of $Cd(NH_3)_n^{2+}$ complexes was much

greater, and both of which was higher than the critical supersaturation level participated in the nucleation which resulted to a spontaneous formation of the CdS nuclei. After the particle nucleation and rapid growth, the concentration level of the Cd^{2+} ions in the equilibrium dropped down below the critical supersaturation level. Consequently, in the presence of NH_3 a larger number of particles were formed, so that during the growth stage, the consumption rate of the Cd^{2+} ions released from the Cd-EDTA complexes, which mainly served as the reservoir for the Cd^{2+} ions, was sufficiently high, maintaining the concentration of Cd^{2+} ions in equilibrium below the critical supersaturation level, and thus preventing the formation of new nuclei.

Moreover, monodisperse ZnS particles with a mean diameter of 0.77 μm were prepared adopting analogous preparation procedures. The ZnS showed XRD peaks similar to that of sphalerite.

審 査 結 果 の 要 旨

　単分散硫化物微粒子はサイズ，形状，構造が均一であるため高い機能を有する先端素材であるが，従来より凝集防止のため希薄溶液系でのみ合成されており，工業的応用を考慮すると生産性の低さが実用化への高い障碍となっていた。本論文は，濃厚溶液からの単分散金属（２Ｂ）硫化物粒子の新合成方法を開発すること，またその生成機構を解明する目的で行われた研究の成果をまとめたものであり，全６章からなる。

　第１章の序論では，従来の希薄溶液系からの単分散硫化物微粒子の生成機構に関する考察をまとめた上で，新規な合成法として，凝集防止に保護コロイド作用をもつゼラチンを使用し，核生成と成長を分離するため，溶液内の過飽和度を抑制する目的で，金属（２Ｂ）イオンのリザーバーとして水酸化物（不均一系）あるいはEDTA錯体（均一系）を用い，硫化座剤としてチオアセトアミドを用いる反応系を提案した。

　第２章では，水酸化カドミウムをカドミウムイオンのリザーバーとして用い，単分散硫化カドミウム粒子を調製する不均一系合成手法について論じている。その結果，ゼラチン，アンモニアを含む水酸化カドミウム懸濁液にチオアセトアミド溶液を添加し，20℃で経時させることにより，平均粒径40nmの多結晶性の単分散球形硫化カドミウム粒子を得ることに成功した。ゼラチンの保護コロイド効果は出発物質の水酸化カドミウムに及び，オチアセトアミドと直接反応を防止することを明らかにした。

　第３章では，水酸化カドミウムをリザーバーとして用いた不均一系での硫カドミウムカドミウム粒子の生成機構を論じている。溶液内に添加したアンモニアは，水酸化カドミウムから，カドミウムのアンモニア錯体形成を通して，カドミウムを溶出させる重要な役割を演じていることがわかった。チオアセトアミド混合時に平衡量存在するカドミウムイオンとカドミウムのアンモニア錯体のみが核生成に関与し，それは瞬時に終了し，系は臨界過飽和度を下まわり，水酸化カドミウムから放出されるカドミウムの硫化により核は成長し，数分で反応は終了することが明らかとなった。また，オチアセトアミドの硫化物イオンの放出はアセトニトリルを副生成物とする可逆過程の解離反応であることを明らかにした。

　第４章では，EDTA錯体を金属イオンのリザーバーとして用いた均一系の合成手法について論じている。ゼラチン，アンモニア，カドミウムのEDTA錯体存在下，チオアセトミドを作用させ，60℃で８時間程度経時させることにより，平均粒径の0.54μmの多結晶性の単分散球形硫化カドミウム粒子の合成に成功した。また，ゼラチンの凝集防止効果，及び硫化物イオンは直接EDTA錯体と反応を起こさないことを明らかにした。また，同様な手法を他の金属硫化物に適用する試みとして，単分散硫化亜鉛粒子の合成にも成功した。

　第５章では，EDTA錯体を金属イオンのリザーバーとして用いた均一系の硫化物粒子合成反応の機構を論じている。反応は，チオアセトアミド添加時に溶液内に平衡量存在するフリーのカドミウムイオンとカドミウムのアンモニア錯体のみが核生成に関与し，それは１分以内の終了する。以後，８時間までは低い過飽和度の元で成長のみが進行することを明らかにした。また，アンモニアは，核生成と成長の両反応の速度を著しく向上させており，その結果成長中の過飽和度が低く抑えられ，核生成と成長を分離することができたものと考察している。

　第６章は結論である。

　以上要するに本論文は，濃厚溶液系における単分散金属（２Ｂ）硫化物微粒子合成の新手法を提案し，それを実証し，さらに反応機構を解明したもので，資源工学ならびに関連する工業の発展に寄与するところが極めて大である。

　よって，本論文は博士（工学）の学位論文として合格と認める。