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SHORT COMMUNICATION

Phosphine-free synthesis of metal chalcogenide quantum dots by means of in situ-generated hydrogen chalcogenides

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Abstract We proved that various organic solvents react with elemental chalcogens (sulfur and selenium) by liberating hydrogen chalcogenide (H_2X, X = S, Se) during the phosphine-free hot-matrix synthesis of quantum dots. The in situ-produced H_2X reacts further with the metal salt to form the corresponding nanosized metal chalcogenide CdX. The effect of temperature on the rate of H_2X generation was quantitatively studied in various organic solvents. We found that the organic amines reduce the reaction temperature of the phosphine-free quantum dots synthesis, being more effective in situ generators of H_2S than the other tested organics at relatively low temperatures (140–170 °C).

Keywords Nanocrystals · Quantum dots · Hydrogen sulfide · Sulfur · Paraffin · Nanoparticles · CdS · PbS · CdSe · PbSe · Mechanism · Sulfides · Selenides

Introduction

Historically, the first hot-matrix syntheses of CdX nanoparticles (X = S, Se) are phosphine based, because they utilize TOPO (trioctylphosphine oxide) matrix and TOP-X (trioctylphosphine chalcogenides or the respective tributylphosphine derivatives, TBP-X) precursors [1–3]. As phosphine-based syntheses, we will sign these ones, in which the chalcogens are applied as phosphine derivatives. Only recently, Bawendi's group [4] and Alivisatos' group [5] revealed the intimate mechanism of the phosphine-based syntheses of CdX-quantum dots. Not long ago, phosphine-free syntheses have been developed as better environment friendly and cheaper alternative using liquid paraffin [6] or octadecene [7–9] and elemental chalcogens dissolved in suitable organics. As phosphine-free syntheses, we define these procedures that utilize elemental chalcogens as precursors. Regarding the reaction mechanism, it was shown that the elemental selenium reacts with the liquid paraffin at high temperature (~300 °C) with liberating in situ hydrogen selenide (H_2Se) [6]. The H_2Se is passed further through a water solution of Cd salt to form a precipitate identified as CdSe. This fact was used as an indirect proof for the formation of CdSe nanocrystals in the liquid paraffin by a sequence of chemical reactions including the in situ generation of H_2Se. Another drawback of this method is the lack of quantitative measurements on the yield of generated H_2Se. Finally, the general validity of this mechanism for cadmium chalcogenide nanoparticles in a variety of matrixes and ligands was not proven. To recognize the role of hydrogen chalcogenides (H_2X) on the quantum dot synthesis, we carried out three types of experiments:

1. We measured the liberation rate of H_2S and H_2Se in different organic solvents at different temperatures during the reaction between the elemental chalcogens (S and Se) and the organics. It turned out that certain organics as liquid paraffin and hexadecylamine generate appreciable amount of H_2S, which makes them suitable as the matrix for phosphine-free syntheses.

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2. Direct synthesis of nanocrystalline CdX by bubbling of H_2X gas through a heated solution of cadmium carboxylates (free of phosphines) in liquid paraffin. The H_2X gas was generated by the method of point 1. The purpose is to prove the general validity of the reaction mechanism from Ref. [6].
3. Phosphine-free syntheses of nanosized metal sulfides in various organic solvents. Our aim here was to diminish the synthesis temperature using mixtures of liquid paraffin and amines based on the observations from point 1 for more efficient H_2S generation.

Experimental procedures

Quantitative determination of the H_2X (X = S, Se) We proved the liberation of H_2S by bubbling argon gas (carrier) through hot (200–300 °C) solutions of sulfur in various organic solvents (hexadecylamine, liquid paraffin, octadecene, stearic acid, trioctylphosphine oxide, oleic acid, sunflower-seed oil) and then bubbling the resultant gas (argon + H_2S) through water solution of cadmium sulfate. We utilized gravimetric determination of the corresponding precipitate (CdS) to determine the yield of H_2S, as previously described [10]. A mixture of hexadecylamine (3.0 g) and liquid paraffin (15 ml) was reacted with sulfur (25 mg) for determination of the yield of H_2S at different temperatures (Fig. 1a). Reactions between sulfur and liquid paraffin were carried out at different temperatures (Fig. 1b). Similar studies of the reaction between paraffin and selenium were also carried out to generate and measure the amount of H_2Se (Fig. 1c).

Synthesis of nano-CdS from Cd stearate and H_2S gas Two reaction flasks are used. In flask 1, liquid paraffin (LP; 15 ml) is heated at 250 °C, and argon gas flow (50 ml/min) is bubbled through it (Fig. 2). In flask 2, 260 mg of cadmium stearate and 15 ml of LP are mixed and heated to 100 °C. Then, 25 mg of sulfur are added to flask 1 to generate H_2S. The gas stream of argon and H_2S from flask 1 is bubbled through the solution in flask 2 for 2–5 min to obtain CdS nanocrystals. If H_2S is bubbled for longer time, precipitate starts to form. If any other H_2S generators are utilized, it is very important to dilute the H_2S gas with an inert gas carrier to achieve fine control over the dosage of the gas during the reaction.

Phosphine-free synthesis of nanosized metal sulfides in various organic solvents For the preparation of CdS nanocrystals, a mixture of CdO (50 mg) and stearic acid (SA; 0.6 g) was heated under argon at 100 °C to obtain clear solution of cadmium stearate, and then organic solvent (15 g) is added. The reaction mixture was heated up (10 °C/min) to 250 °C. Solution of elemental sulfur in LP (1 ml, 0.128 M) was injected into the hot solution of cadmium stearate. The temperature was kept constant during the nanocrystals' growth (10 min). Syntheses can be performed in various solvents as depicted in Table 1. For the synthesis of PbS and ZnS quantum dots, cadmium oxide was replaced with lead acetate trihydrate (150 mg) and zinc stearate (250 mg), respectively. The synthesis of ZnS nanoparticles usually lead to highly amorphous material. Utilization of sunflower-seed oil resulted in relatively well-defined ZnS nanoparticles.

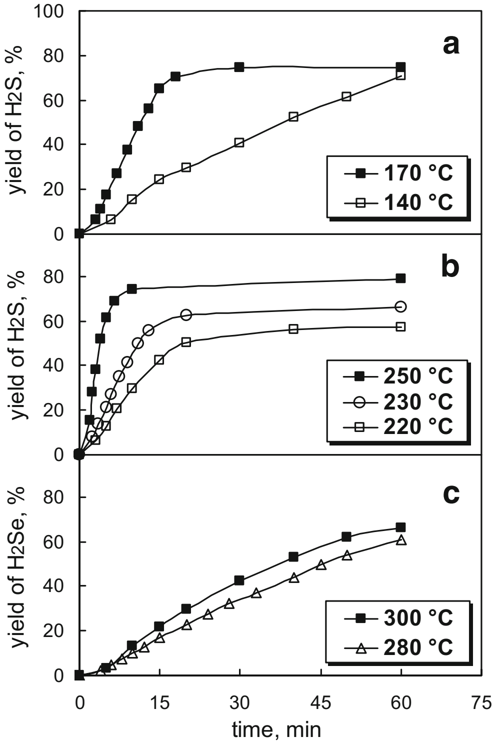

Fig. 1 **a** Yield of H_2S during the reaction between sulfur and paraffin/hexadecylamine mixture (see the "Experimental procedures") at different temperatures. **b** Yield of H_2S during the reaction between sulfur and pure liquid paraffin at different temperatures. **c** Yield of H_2Se during the reaction between selenium and pure liquid paraffin. The initial concentration of chalcogen is 0.05 mmol/g

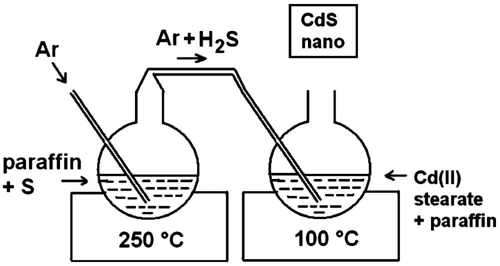

Fig. 2 Schematic representation of CdS nanocrystals synthesis from Cd stearate and H_2S gas

Table 1 Yield of H_2S from reaction between sulfur and various organic solvents at 250 °C

Compound	Yield, %
Liquid paraffin	79
Hexadecylamine	73
Stearic acid	64
Trioctylphosphine oxide	54
Oleic acid	10
Sunflower-seed oil	9
1-Octadecene	6

The initial concentration of sulfur is 0.05 mmol/g, and the reaction time is 1 h.

Phosphine-free synthesis of CdS in paraffin/hexadecylamine For the preparation of CdS nanocrystals in paraffin/hexadecylamine, a mixture of CdO (50 mg), SA (0.6 g), and liquid paraffin (15 ml) was heated under argon at 100 °C to obtain clear solution of cadmium stearate, and then hexadecylamine (3 g) is added. The reaction mixture was heated up (10 °C/min) to 200 °C. If heated above 220 °C, the Cd stearate/amine solution decomposed fast by irreversible precipitation and turned black colored. Solution of elemental sulfur in LP (1 ml, 0.128 M) was injected into the hot solution of cadmium stearate. The temperature was kept constant during the nanocrystals growth (30 min). Nanocrystals can be purified and isolated as previously described [8]. Syntheses were carried out at various temperatures between 140 and 200 °C (Fig. 4). The amine can be replaced with paraffin, but the reaction temperature has to be increased above 200 °C. For the synthesis of PbS quantum dots, cadmium oxide was replaced with lead acetate trihydrate (150 mg). We could not produce CdSe quantum dots from cadmium stearate and elemental selenium in amines at temperatures below 220 °C.

Results and discussion

In the phosphine-free synthesis of quantum dots, the organic solvent (matrix) is a reactant and reacts with the elemental chalcogens (sulfur or selenium) by liberating hydrogen chalcogenide (H_2X, X = S, Se). The liberation of H_2X results from the oxidation (dehydrogenation) of the organic solvent (generally denoted as "RH_2") by the chalcogen (X), following the reaction pathway shown in Eq. 1. Equation 1 should be perceived as a generic expression of different reactions that lead to the formation of H_2X. These processes take place at high temperatures, which is usual for the hot-matrix synthesis. The in situ-produced H_2X can react with the metal salt (MY_2) by forming the corresponding nanosized metal chalcogenide (MX; Eq. 2).

$$X + RH_2 \rightarrow R + H_2X \tag{1}$$

$$H_2X + MY_2 \rightarrow 2HY + MX \tag{2}$$

Here, M = Cd, Pb, Zn and Y = oleate, stearate, alkyl phosphonate as shown in our experiments. Therefore, any high-boiling organic solvent that reacts with elemental chalcogens to produce H_2X has a potential to be utilized in nanocrystals synthesis.

The metal salt serves as both a metal precursor and a surfactant, which limits the crystals' growth to nano-dimensions. The surface-active properties of the metal salt are especially important for the formation of nanocrystals in non-coordinating solvents like ODE [7, 8] and LP [6, 9], where the solvent itself cannot limit the growth of nanocrystals by forming a capping layer. To prove that H_2S could be a precursor for the formation of CdS QDs, a gas mixture of argon (utilized as a gas carrier) and H_2S was bubbled through a solution of cadmium stearate in organic solvent (LP, toluene, etc.). As a result, nanocrystals (3–4 nm) of CdS were formed (Fig. 3). This procedure proves the ability of the stearate salt to limit the crystals growth to nano-dimensions. It is similar to the classic precipitation techniques in microemulsions [11, 12] and Langmuir–Blodget films [13].

Let us consider the reactions between elemental sulfur and organic solvents. It is known that the elemental sulfur oxidizes organics like alkanes [14–18], alkenes [19, 20], and amines at temperatures above 150 °C [21, 22]. The organic solvents generally contain hydrocarbon residues, which react in our experiments with sulfur at temperatures above 150–200 °C and produce H_2S. We observed a brown-colored reaction mixture during the growth of CdS nanocrystals in saturated organic solvents (LP, SA, TOPO). This color was also observed after the addition of sulfur to a pure saturated organic solvent at temperatures above 200 °C. The structure of the brown-colored products is difficult to identify because of the very complex mixture. Probably, various polycyclic aromatic compounds are formed as a result of dehydrogenation reactions between sulfur and organics. For example, we isolated black powder (insoluble in *n*-heptane) after a reaction between sulfur and liquid paraffin (1 h at 250 °C). Elemental analysis showed that it contains (in wt.%) carbon (67.6%), hydrogen (4.8%), and sulfur (24.8%). These products can be separated from the nanocrystals prepared in paraffin by purification with toluene [9].

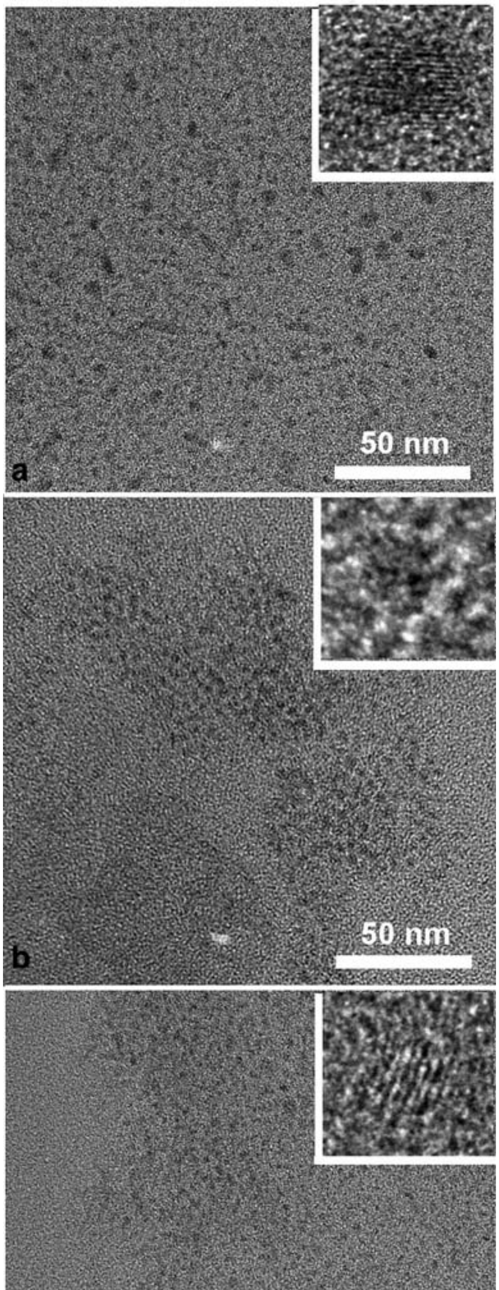

Fig. 3 TEM images of CdS nanoparticles prepared **a** in LP, **b** in sunflower-seed oil, **c** from Cd stearate and H_2S gas. The elemental composition was confirmed by energy dispersive spectroscopy

From the data in Table 1, it is clear that the utilization of organic solvents that contain double C=C bonds (ODE, OA) yields much less amount of H_2S than the saturated organic solvents (LP, SA, TOPO). The reactions of sulfur with olefinic compounds (oleic acid, octadecene, sunflower-seed oil) generally lead to the formation of organic polysulfides and are described in details elsewhere [19, 20].

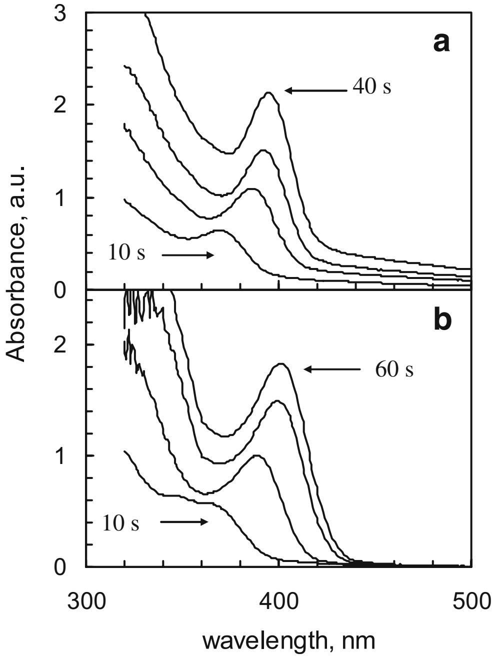

Fig. 4 Temporal evolution of absorbance spectra during growth of **a** CdS at 250 °C in pure liquid paraffin. Aliquot samples were taken at 10, 15, 20, and 40 s. **b** CdS at 170 °C in paraffin/hexadecylamine; aliquot samples were taken at 10, 20, 40, and 60 s

To decrease the reaction temperature, we add hexadecylamine to the liquid paraffin. The most common reaction between sulfur and organic amines is replacement of the active methylene hydrogens with sulfur [21]; however, other reactions that produce H_2S also take place [22]. The reactions of hexadecylamine with sulfur proceed at much lower temperatures than the corresponding reactions with liquid paraffin (Fig. 1). For example, CdS nanocrystals are usually prepared in liquid paraffin (utilizing elemental sulfur) at 250 °C [9, 23]. By using paraffin/hexadecylamine mixtures, the reaction temperature could be reduced to about 140–170 °C (Fig. 4).

Elemental selenium reacts with liquid paraffin at rather high temperatures (above 290 °C), with formation of H_2Se and alkenes. This reaction was previously utilized for the synthesis of CdSe [6]; and, here, we characterized it quantitatively (Fig. 1). It is worth noting that this reaction was discovered as early as 1909 [24]. Unfortunately, it has long been ignored. Elemental tellurium (Te) is not a strong oxidizing agent and cannot produce H_2Te in a reaction with hydrocarbons. That is why phosphine-free hot-matrix synthesis of nanosized metal tellurides by utilizing elemental tellurium is still unknown.

Conclusions

We utilized, here, two versions of the phosphine-free synthesis of metal chalcogenide quantum dots MX (M = Cd, Pb, Zn; X = S, Se) by means of ex situ- and in situ-generated hydrogen chalcogenides H_2X. In the first version, H_2X gas is blown through hot solutions of metal carboxylates in liquid paraffin. In the second version, H_2X gas is generated in situ after the injection of elemental X (S or Se) in the hot organic matrix containing the metal carboxylates. H_2X is then consumed in the growth of MX semiconductor nanoparticles such as CdS, CdSe, PbS, and ZnS. The remarkable decrease of synthesis temperature with amines is because of the corresponding decrease of H_2S-generation temperature. To verify the crucial point (H_2X generation), H_2X has been generated intentionally based on the reaction of elemental X with various organics: liquid paraffin, hexadecylamine, stearic acid, TOPO, oleic acid, sunflower-seed oil, and octadecene, ordered in descending order of gas yield. This implies on the general validity of the H_2X-generation stage in the reaction mechanism of phosphine-free nanoparticle synthesis. A particular case of our research is the results from Ref. [6] on the generation of H_2Se from the reaction of liquid paraffin with elemental Se, as well as the phosphine-free synthesis of CdSe nanoparticles.

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References

1. Murray CB, Norris DJ, Bawendi MG (1993) J Am Chem Soc 115:8706–8715
2. Manna L, Scher EC, Alivisatos AP (2000) J Am Chem Soc 122:12700–12706
3. Peng Z, Peng X (2001) J Am Chem Soc 123:183–184
4. Steckel JS, Yen B, Oertel D, Bawendi MG (2006) J Am Chem Soc 128:13032–13033
5. Liu H, Owen J, Alivisatos AP (2007) J Am Chem Soc 129:305–312
6. Deng Z, Cao L, Tang F, Zou B (2005) J Phys Chem B 109:16671–16675
7. Jasieniak J, Bullen C, van Embden J, Mulvaney P (2005) J Phys Chem B 109:20665–20668
8. Yu WW, Peng XG (2002) Angew Chem Int Ed 41:2368–2371
9. Yordanov G, Dushkin C, Gicheva G, Bochev B, Adachi E (2005) Colloid Polym Sci 284:229–232
10. Coleman HJ, Thompson CJ, Rall HT, Smith HM (1953) Ind Eng Chem 45:2706–2710
11. Pinna N, Weiss K, Urban J, Pileni MP (2001) Adv Mater 13:261
12. Lianos P, Thomas JK (1986) Chem Phys Lett 125:299
13. Moriguchi I, Tanaka I, Teraoka Y, Kagawa S (1991) J Chem Soc Chem Commun 1401–1402.
14. Friedmann W (1916) Ber 49:1344–1352
15. Baker RB, Reid EE (1929) J Am Chem Soc 51:1566–1567
16. Lynn G, Allen M, Beecher BK, Darbyshire RW (1933) Ind Eng Chem 25:916–918
17. Bacon RF, Boe ES (1945) Ind Eng Chem 37(5):469–474
18. Bryce WA, Hinshelwood C (1949) J Chem Soc 3379–3387.
19. Farmer EH, Shipley FW (1947) J Chem Soc 1519–1551.
20. Bateman L, Moore CG, Porter M (1958) J Chem Soc 2866–2888
21. Davis RE, Nakshbendi HF (1962) J Am Chem Soc 84:2085–2090
22. Hodgson WG, Buckler SA, Peters G (1963) J Am Chem Soc 85:543–546
23. Yordanov G, Adachi E, Dushkin C (2006) Colloids Surf A 289:118–125
24. Wuyts H, Stewart A (1909) Bull Soc Chim Belg 23:9