

Polyol mediated synthesis of nanoscale MS particles (M = Zn, Cd, Hg)

Claus Feldmann* and Christof Metzmacher

PHILIPS Research Laboratories, Weissshausstraße 2, D-52066 Aachen, Germany.
E-mail: claus.feldmann@philips.com

Received 10th April 2001, Accepted 18th June 2001

First published as an Advance Article on the web 21st August 2001

The preparation of nanoscale MS particles (M = Zn, Cd, Hg) with the polyol method is described. Starting with metal acetates and thiourea as precursors, by heating at 180 °C in diethylene glycol, crystalline particles 30–250 nm in size can be yielded. The resulting particle size is examined in DEG–H₂O suspension applying laser diffraction techniques. Moreover, the particle size in the powder state is analysed based on SEM and TEM studies. X-Ray and electron diffraction are applied to investigate the crystallinity of the nanoscale materials.

Introduction

Nanoscale particles of the group IIb sulfides, MS (M = Zn, Cd, Hg), have attracted a growing interest during the recent years, driven by various areas of application. On one hand, particles 10–500 nm in size are of potential importance for photonic crystals, IR windows, or, if doped with additional ions, for luminescent materials.^{1–4} Moreover, quantum-sized sulfides (< 10 nm) are well known as quantum dots. The latter are of potential interest with respect to voltaic solar cells, light emitting diodes or, again, as luminescent materials.^{5–10} For all these applications, highly crystalline particles with almost monodisperse size distribution and regular morphology are required. In fact, many different methods of preparation, liquid-based as well as gas phase-based, are aiming at the fulfilment of these requirements.^{11–16} Nevertheless, there is still a strong interest in the synthesis of monodisperse and crystalline nanoparticles.

A method which proved very attractive with regard to the preparation of nanoscale metal and oxide particles is the so-called polyol method. Based on this process, a metal precursor is heated in a high boiling alcohol (bp > 200 °C). In the case of noble metals, the metal cations are reduced by the alcohol to form particles of the elemental metals.^{17–20} In contrast, while adding a defined amount of water, non-noble metals precipitate to yield nanoscale oxide particles.^{21–25} Owing to the high temperature during the synthesis, normally well crystallised materials are realised. As a further advantage, the polyol medium efficiently complexes the surface of the particles. Consequently, the particle growth is limited. Furthermore, an agglomeration of particles is prevented. All these aspects are, in principle, also interesting in view of sulfide materials.

Till now the polyol method has not been investigated with regard to its suitability for the synthesis of nanoscale sulfides. In fact, the following investigations show that the method is indeed very useful in order to prepare well crystallised and nanoscale metal sulfides such as ZnS, CdS or HgS.

Experimental

Synthesis

Nanoscale metal sulfides MS (M = Zn, Cd, Hg) were prepared by mixing 2.27 mmol Zn(MeCO₂)₂·2H₂O (99.99%, Merck), Cd(MeCO₂)₂ (99.99%, Aldrich) or Hg(MeCO₂)₂ (98%,

Aldrich) and 2.50 mmol thiourea (10 mol% excess, 99%, Merck) in 50 ml diethylene glycol (99%, Merck). These mixtures were heated for 2 h at 180 °C. After cooling to room temperature colloidal stable suspensions were yielded. The solids can be separated from the suspensions *via* centrifugation. The solids were twice re-suspended in ethanol and again centrifuged, in order to remove diethylene glycol completely.

Characterisation

Particle size measurements were performed based on laser diffraction techniques combined with polarisation intensity differential scattering. For this purpose a Coulter LS230 equipped with a laser (750 nm, 5 mW) and a PIDS lamp (tungsten–halogen, 150 lumen at 2900 K) as well as 126 photodiode detectors were used.

A Philips SEM XL30 equipped with a tungsten field emission gun was used for scanning electron microscopy. Samples were sputtered with carbon (300 Å). The investigations were carried out at room temperature applying a voltage of 15–25 kV. The spot size was 20 nm and the free working distance (FWD) 9–12 mm.

X-Ray powder diffraction (XRD) was performed with a Philips vertical goniometer PW1050 with Bragg–Brentano geometry. The diffractometer was equipped with a fixed divergence slit and a proportional counter. Cu-K α radiation was used and monochromatised by a secondary graphite monochromator.

A Philips transmission electron microscope CM12 equipped with a LaB₆ cathode and a scanning unit was used for the TEM investigations ($\lambda L = 36.784$ Å mm). The measurements were performed at 120 kV. Sample preparation was performed by ultrasonically dispersing powder particles and subsequent use of a carbon filmed copper grid as carrier.

Results

Determination of particle size

The preparation of ZnS, CdS or HgS with the polyol method yielded nanoscale particles suspended in diethylene glycol. Acetates of the relevant metals and thiourea were used as the starting materials. The resulting suspensions were colloidal stable for several days. Laser diffraction techniques were

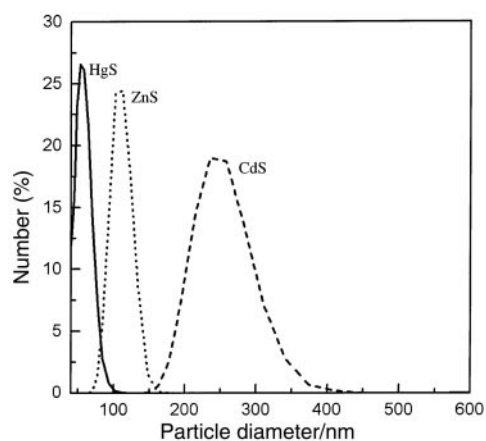


Fig. 1 Size distribution of nanoscale ZnS, CdS and HgS particles in DEG–H₂O-suspension (DEG : H₂O = 1 : 50).

applied to examine the particle diameter and the particle size distribution in suspension. As an example, three different suspensions containing 0.22 wt% ZnS, 0.33 wt% CdS or 0.53 wt% HgS were investigated here. Measurements were performed after dilution with water (DEG : H₂O = 1 : 50). For these suspensions, which are predominately water-based, average diameters (d_{50}) of 106(5) nm for ZnS, 242(8) nm for CdS and 54(3) nm for HgS were detected (Fig. 1). The resulting particle diameter mainly depends on the experimental conditions (concentration of precursors, temperature, time of heating) as well as on the solubility of the metal sulfides. If the solubility is comparably low, then the particles are small as in the case of HgS ($pK_{sp} = 52.7^{26}$). Under similar experimental conditions, in the case of ZnS and CdS with a higher solubility ($pK_{sp} = 24.7$ and $pK_{sp} = 27.0^{26}$), the resulting particles are larger. In general, however, the particle size can be controlled within limits of *ca.* 30–250 nm by adjusting the experimental conditions for all three compounds. This is shown in more detail for ZnS (Table 1). The size distribution is closely related to the average particle diameter: the larger the particle diameter, the broader the particle size distribution (Fig. 1). Based on optimal conditions such as in the case of ZnS, almost monodisperse particles with an average particle diameter of *ca.* 100 nm can be realised.

While stirring the sulfide particles for longer periods of time (*e.g.* 30 min) in water, the average particle diameter remains constant. Obviously, no significant agglomeration occurs. This finding is in contrast to former investigations aimed at the polyol-mediated preparation of nanoscale oxide particles such as CoAl₂O₄ or Nb₂O₅.^{23,24} Here, after mixing of the diethylene glycol suspension with water, a rapid agglomeration of the individual particles was observed. In fact, the agglomeration of oxide particles in water was ascribed to a removal of the diethylene glycol complexing and, by that, stabilising the particle surface. By exchanging DEG against water, hydroxy groups on the oxidic particle surface can dehydrate interparticularly to form agglomerates. Such a situation is not to be expected in the case of sulfides. Therefore, the significantly higher colloidal stability of the sulfide particles in water is not surprising.

After separation and purification, the metal sulfides MS (M = Zn, Cd, Hg) were also studied in the powder state (Fig. 2).

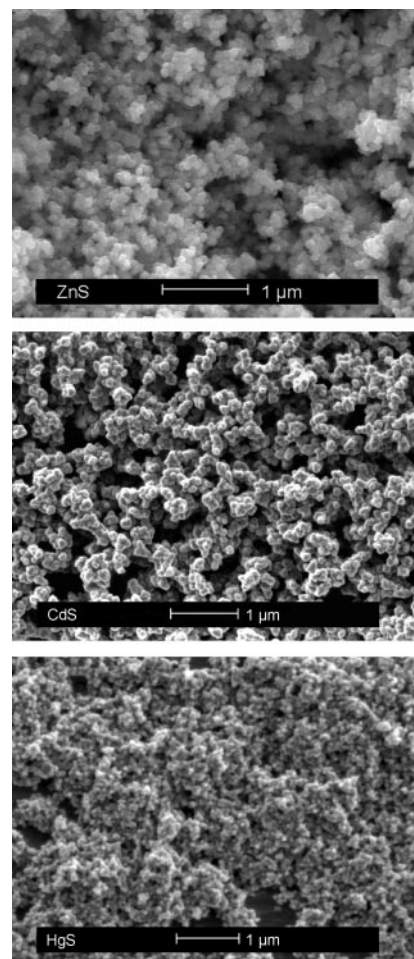


Fig. 2 SEM photographs of nanoscale ZnS, CdS and HgS.

SEM photographs prove the presence of spherical and almost monodisperse nanoscale particles. In addition, the average diameter of primary particles as found by laser diffraction in suspension was confirmed. This finding suggests that individual particles are indeed present in the diethylene glycol as well as in water suspension. This is the more remarkable due to the fact that no further stabilisers were added. Herein, the sulfides behave very similarly to nanoscale oxide particles prepared with the polyol method.^{23–25}

Phase analysis

X-Ray powder diffraction patterns prove that ZnS, CdS and HgS with the sphalerite type of structure are prepared under the conditions of the polyol method (Fig. 3). With 180 °C as the highest temperature during the synthesis all materials were well crystallised. However, the full width at half maximum (FWHM) values of the X-ray reflections indicate that HgS is the best crystallised, although the particles are significantly smaller compared with the ZnS and CdS samples.

The crystallinity of the particles was also verified in the case of HgS by TEM analysis (Fig. 4, top). Again, the spherical shape of the particles and an average diameter of 50–60 nm was observed. The TEM image also indicates that the particles are

Table 1 Experimental conditions for size-selective preparation of ZnS particles

Zn(MeCO ₂) ₂ ·2H ₂ O (per 50 ml DEG)/mmol	(NH ₂) ₂ CS (per 50 ml DEG)/mmol	Temperature/°C	Heating time/h	d_{50} of ZnS particles/nm
1.13	2.50	140	2	41
2.27	2.50	180	2	106
2.27	2.50	180	4	228

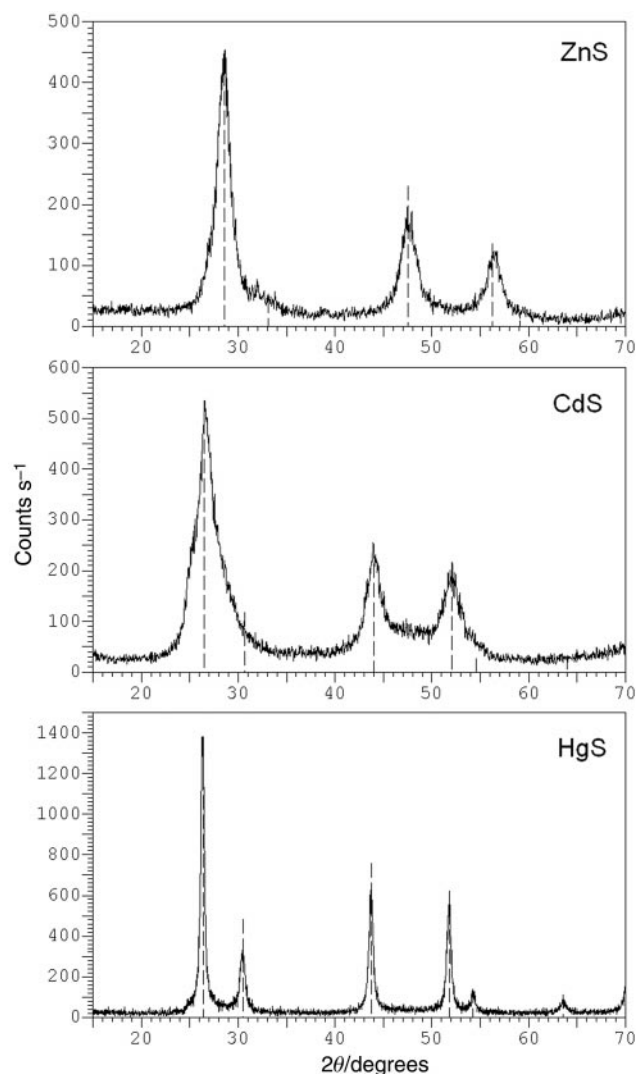


Fig. 3 XRD patterns of nanoscale ZnS (ICDD-Ref. 05-0566), CdS (ICDD-Ref. 42-1411) and HgS (ICDD-Ref. 06-0261).

primary particles and not agglomerates of even smaller grains. Some of the particles show two-dimensional defects. Such defects are well known and can be attributed to local stacking faults of the cubic sphalerite and the hexagonal wurzite type of modification of HgS.²⁷ The crystallinity of the HgS particles was also confirmed by electron diffraction (Fig. 4, bottom). The lattice parameter was calculated to be 5.96(2) Å. Taking into account that the lattice parameters of nanoscale crystals in general are expanded compared with the bulk material, this result is in good agreement with literature data (5.87 Å).²⁸

Conclusions

Nanoscale ZnS, CdS and HgS particles can easily be prepared with the polyol method. The synthesis results in colloiddally stable suspensions of the metal sulfides in diethylene glycol. Herein, the particles are almost non-agglomerated. All sulfide materials crystallise with the sphalerite type of crystal structure. The particles are spherical, with narrow size distribution and show average particle diameters of between 30 and 250 nm. Further investigations will address the preparation of quantum-sized sulfide particles with diameters below 10 nm. To reach this aim, suitable surface stabilisers must be added.

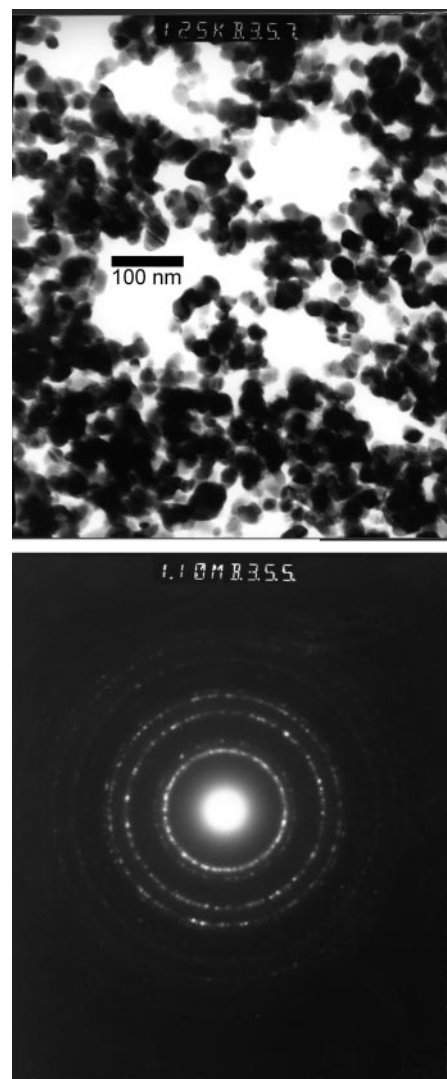


Fig. 4 TEM bright-field image (top) and selected area electron diffraction pattern (bottom) of HgS particles.

Acknowledgements

The authors are grateful to J. Merikhi for performing the SEM analysis.

References

- 1 A. Celikkaya and M. Akinc, *J. Am. Ceram. Soc.*, 1990, **73**, 2360.
- 2 M. Bredol and J. Merikhi, *J. Mater. Sci.*, 1998, **33**, 471.
- 3 M. Ihara, T. Igarashi, T. Kusunoki and K. Ohno, *J. Electrochem. Soc.*, 2000, **147**, 2355.
- 4 Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, 2000, **12**, 693.
- 5 V. L. Colvin, M. C. Schlamp and A. P. Alivisatos, *Nature*, 1994, **370**, 354.
- 6 A. Mews, A. Eychmüller, M. Giersig, D. Schooss and H. Weller, *J. Phys. Chem.*, 1994, **98**, 934.
- 7 A. P. Alivisatos, *Science*, 1996, **271**, 933.
- 8 A. A. Bol and A. Meijerink, *Phys. Rev. B*, 1998, **58**, 15997.
- 9 M. T. Harrison, S. V. Kershaw, A. L. Rogach, A. Kornowski, A. Eychmüller and H. Weller, *Adv. Mater.*, 2000, **12**, 123.
- 10 L. Qi, H. Cölfen and M. Antonietti, *Nano Lett.*, 2001, **1**, 61.
- 11 D. M. Wilhelmy and E. Matijevic, *J. Chem. Soc., Faraday Trans.*, 1984, **80**, 563.
- 12 Q. Yitai, S. Yi, X. Yi, C. Qianwang, C. Zuyao and Y. Li, *Mater. Res. Bull.*, 1995, **30**, 601.
- 13 J. C. Sánchez-López and A. Fernández, *Thin Solid Films*, 1998, **317**, 497.
- 14 S. Gorer and R. M. Penner, *J. Phys. Chem. B*, 1999, **103**, 5750.
- 15 V. Turco Liveri, M. Rossi, G. D'Arrigo, D. Manno and G. Micocci, *Appl. Phys. A*, 1999, **69**, 369.

- 16 J. Zhu, S. Liu, O. Palchik, Y. Koltypin and A. Gedanken, *J. Solid State Chem.*, 2000, **153**, 342.
- 17 F. Fievet, J. P. Lagier and M. Figlarz, *Mater. Res. Bull.*, 1989, 29.
- 18 P. Toneguzzo, G. Viau, O. Acher, F. Fievet-Vincent and F. Fievet, *Adv. Mater.*, 1998, **10**, 1032.
- 19 S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
- 20 P. Toneguzzo, G. Viau, O. Acher, F. Guillet, E. Bruneton, F. Fievet-Vincent and F. Fievet, *J. Mater. Sci.*, 2000, **35**, 3767.
- 21 D. Jezequel, J. Guenot, N. Jouini and F. Fievet, *J. Mater. Res.*, 1995, **10**, 77.
- 22 H.-O. Jungk and C. Feldmann, *J. Mater. Res.*, 2000, **15**, 2244.
- 23 J. Merikhi, H.-O. Jungk and C. Feldmann, *J. Mater. Chem.*, 2000, **10**, 1311.
- 24 C. Feldmann and H.-O. Jungk, *Angew. Chem.*, 2001, **113**, 372; C. Feldmann and H.-O. Jungk, *Angew. Chem., Int. Ed.*, 2001, **40**, 359.
- 25 C. Feldmann, *Scr. Mater.*, 2001, **44**, 2193.
- 26 D. C. Harris, *Quantitative Chemical Analysis*, W. H. Freeman and Company, New York, 3rd edn., 1991, p. 86.
- 27 A. R. West, *Solid State Chemistry*, Wiley, Chichester, 1st edn., 1989, p. AP23.
- 28 K. Aurivillius, *Acta Chem. Scand.*, 1964, **18**, 1552.