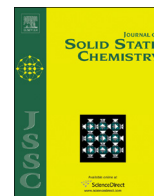




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Non-aqueous metathesis as a general approach to prepare nanodispersed materials: Case study of scheelites



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ABSTRACT

A general approach to the preparation of inorganic nanoparticles is proposed, using metathesis of precursor salts in non-aqueous liquids. Nanoparticles of scheelites AMO_4 ($A = \text{Ba, Sr, Ca}$; $M = \text{Mo, W}$), were obtained with a quantitative yield. Precipitations in formamide, *N*-methylformamide, propylene carbonate, DMSO and polyols often provide narrow particle size distributions. Advantageous morphology was explained by strong ionic association in non-aqueous solvents, leading to slow nucleation and negligible Ostwald ripening. Mean particle size below 10 nm and high specific surface areas were obtained for several $\text{Ca}(\text{Sr})\text{Mo}(\text{W})\text{O}_4$ materials, making them promising for applications as adsorbents or catalysts. Zeta-potential of scheelites in aqueous suspensions showed negative values in a wide range of pH. Systematic study of optical properties demonstrated variation of optical gap in the sequences $\text{W} > \text{Mo}$ and $\text{Ba} > \text{Sr} > \text{Ca}$. The observed trends were reproduced by DFT calculations. No quantum confinement effect was observed for small particles, though the surface states induce low-energy features in the optical spectra.

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1. Introduction

Controlled synthesis of nanoparticles is important both for academic and practical reasons in different fields, from biomaterials and drugs to plasmonics and quantum dots. Arguably the most powerful approach to the preparation of nanoparticles is chemical precipitation in liquid homogeneous solutions [1]. The fundamentals for the precipitation by nucleation and growth in solutions are being studied for long time and now are reasonably well understood [2–4]. A large number of narrow size distributed dispersions of different compositions and shapes can be obtained by homogeneous precipitations [5]. Despite a great number of available procedures, researchers still strive to develop novel preparation methods evermore simple and robust, environmentally friendly and cheap, extending the scope of available compositions, sizes and shapes. To this aim versatile methods were applied, including sol-gel [6,7] hydrothermal [8], microemulsions [9,10], use of dendrimers [11], natural products [12], etc.

In the synthetic triad “precursor–solvent–additive”, the solvent represents an important dimension to explore. Reactions in non-aqueous solvents are intensively studied in materials chemistry. Ionic liquids [13], molten salts [14] and polyols [15] have been applied to prepare inorganic nanoparticles. However, to our

knowledge there are no works where an extended series of different solvents would be applied to prepare inorganic nanoparticles. Meanwhile, such an approach could be useful from both fundamental and applied sides.

An important family of inorganic materials is sparingly soluble salts of polyvalent oxo-anions, including phosphates, carbonates, sulfates, molybdates, etc. Scheelite-structured alkaline earth molybdates and tungstates AMO_4 ($A = \text{Ca, Sr, Ba}$; $M = \text{Mo, W}$) have been employed as solid state phosphors, scintillation detectors or photocatalysts [16]. These solids were prepared by aqueous precipitation [17], solid-state reaction [18], solvothermal [19], sol-gel [20,21], hydrothermal [22], electrospinning [23], spray pyrolysis [24], electrochemical [25] and molten salt [26,27] routes. Recently developed low temperature solution precipitations use microwave radiation [28], surfactants and complexing agents [29].

Ethylene glycol was first used as medium to prepare scheelites at 180 °C [30]. Then room-temperature synthesis has been reported by Thongtem et al. [31]. Recently we applied a simplified version of this method to prepare scheelites [32]. In our catalysis-focused studies, variable particle sizes were needed of few tens nm and smaller. Being inspired by simplicity of the ethylene glycol preparation, we strived to extend this technique on versatile solvents and materials.

Here we report on the preparation of inorganic nanoparticles in the series of organic solvents, focused on sparingly soluble molybdates and tungstates. Practical usefulness of the technique

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is demonstrated by measurements of specific surface areas and optical properties of obtained materials.

2. Experimental

2.1. Preparation of solids

All reactants and solvents were high purity grade purchased from Aldrich. Unless otherwise stated, equimolar mixture containing 0.025 mol of each salt was loaded in a flask and then 25 ml of a non-aqueous solvent was added. Then the mixture was kept under 300 min⁻¹ stirring for a variable time, from several hours to two months. Unless otherwise stated the reaction time was 12 h (stirring overnight). The obtained solids were separated by centrifugation at 3500 min⁻¹, washed with the reaction solvent (twice), then with ethanol and acetone and then dried at room temperature. Such complex washing procedure was applied to remove inorganic products of metathesis and eventual impurities of non-reacted precursors, without perturbing the samples morphology. Indeed, washing with water, particularly of the samples with very small particles (5–10 nm), could produce recrystallization. Otherwise, if unreacted precursors remain in the mixture, they would instantly react upon aqueous washing, producing a solid product with undesired morphology. Unless otherwise stated we used in our preparations Ca(NO₃)₂·4H₂O, Sr(NO₃)₂, Ba(NO₃)₂, Na₂MoO₄·2H₂O and Na₂WO₄·2H₂O precursors. In some experiments BaCl₂, SrCl₂, CaCl₂, CaBr₂ and K₂MoO₄ were applied. For brevity, we often designate the samples by the names of a solid compound and an abbreviated solvent. Thus, SrMoO₄-FA designates SrMoO₄ prepared in formamide.

2.2. Characterizations

X-ray diffraction (XRD) patterns were obtained on a Bruker diffractometer with Ni-filtered Cu K α radiation, in the range of 2 θ between 3° and 80°. Crystalline phases were identified with standard ICDD files. Particles size was calculated using the Scherrer formula. The morphology and composition were examined by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) on a JEOL 2010 microscope with an accelerating voltage of 200 kV. For TEM and HRTEM analysis, the nanoparticles were dispersed in ethanol by ultrasound. Then, a drop of suspension was transferred to a holey carbon film supported on a copper grid and evaporated naturally. Size distribution histograms were built using Digital Micrograph software by Gatan.

Hydrodynamic size distribution was measured using Dynamic Light Scattering (DLS) on a Wyatt Nanostar device. Prior to measurement the powders were ultrasonically dispersed for 2 h in absolute alcohol containing 0.1 wt% cetyltrimethylammonium bromide, in order to break soft agglomerates and liberate primary particles. Suspensions containing about 0.5 g/l of solids were applied for the DLS measurements. Size distribution was obtained from averaging the series of 100 single measurements 2 s each. Autocorrelation function was cut below 1.5 and above 1000 nm. Surface areas and pore radii distributions were measured by low temperature nitrogen adsorption and calculated using BET equation for specific surface area, BJH for mesopores and Horvath-Kawazoe equation for micropores distribution.

Zeta-potential (ZP) was determined from electrophoretic mobility in aqueous suspensions on a CAD Zetacompact device. Weighted amounts of about 100 mg of were ultrasonically dispersed in 200 ml of 10⁻² M KCl solution. The pH values were adjusted with either HClO₄ or KOH 0.1 M solutions. Electrophoretic

migration rate was converted to zeta potential by the Helmholtz-Smoluchowski equation. Low values of ZP are highly uncertain since the mobility is influenced by current-induced flow, making the apparent ZP strongly dependent on the laser position. To decrease uncertainty, at each pH we determined ZP in several points outside the stationary position and built the curves of ZP vs. focal position. Then we compared the corresponding curves for different pH (Fig. S1 of the Supplementary material).

Reflectance UV-visible spectra were collected and converted to Kubelka Munk function using a Perkin-Elmer Lambda 9 scanning spectrometer equipped with an integrating sphere over the spectral range 200–2500 nm (6.2–0.5 eV). The band gap energies were determined by Shapiro [33] and Tauc [34] methods using Kubelka Munk function as absorbance intensity (Fig. S2).

The band structures of the solids were calculated using plane wave CASTEP code, implemented in Cerius² environment. The calculations were performed using the generalized gradient approach (GGA). The kinetic energy cutoff for the plane waves was 300 eV.

3. Results and discussion

3.1. Survey of the solvents

Blending of precursor salts in non-aqueous polar solvents appears to be a powerful strategy for nanoparticles preparation. It combines extreme simplicity and versatility, yielding particles from several nm to microns size. About twenty polar solvents have been tried, and many of them appeared suitable for syntheses. Ethylene glycol (EG) was extensively studied as reaction medium by Thongtem et al. [31,35]. Recently EG was applied to prepare doped CaMoO₄ at 130 °C [36]. We reproduced the sizes of particles from Refs. [31,35] with a good agreement (Table 1). Remarkably, lesser amounts of EG were sufficient and no complete solubilisation of precursors was necessary for successful preparations. A natural extension of the technique was on other polyols. Indeed, propylene glycol and diethylene glycol were suitable to prepare

Table 1
Summary of performed syntheses and XRD particle sizes.

Metals couple solvent	BaMo	BaW	SrMo	SrW	CaMo	CaW
EG	45 20 ^b	55 26 ^b	18 55 ^c 12 ^b	21 41 ^d	21 16 ^b	11
DiEG	17	40	–	–	–	–
TriEG	10	16	–	–	–	–
PRG	12	300	18 27 ^c	19	20	30
DiPrG	10 ^f	15 ^f	–	–	9 ^f	–
Glycer	16 ^d	20 ^d	–	–	–	–
PRC	120	60 ^f	26 ^f 23 ^b	NR	30 ^f	22 ^f
DMSO	65 ^e	NR	30 ^f	–	–	–
Sulfol	NR ^a	NR	NR	–	30 ^f	25 ^f
DMF	22	NR	18	NR	23	–
NMF	25	40	16 ^b 18	–	11	11
FA	25	35	9 12 ^c	6	30 6 ^b	5
Ethanol amine	37	40	11	–	14	11
Ethylene diamine	13	15	7	15	12	10

^a No reaction

^b K₂MoO₄ precursor (default Na₂MoO₄).

^c SrCl₂ precursor (default Sr(NO₃)₂).

^d No reaction at RT but precipitate formed after heating to 100 °C.

^e Reaction time 2 months.

^f Reaction time 72 h, otherwise reaction time is 12 h.

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