Polyol-mediated low-temperature synthesis of crystalline tungstate nanoparticles MWO_4 (M = Mn, Fe, Co, Ni, Cu, Zn)

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ABSTRACT

A polyol-mediated synthesis is presented as a general access to nanoscaled transition-metal tungstates MWO_4 (M = Mn, Fe, Co, Ni, Cu, Zn). Using simple inorganic salts as starting materials, uniform and readily crystalline nanoparticles are prepared under mild conditions ($T < 220\,^\circ$C). The nanoparticles are of high quality in terms of small diameter (<20 nm), high surface area (up to 200 $m^2\,g^{-1}$), phase purity and yield ($>85\%$). Size, morphology and composition can be adjusted by precise variation of the reaction parameters, including type of starting material, duration and temperature of reaction. The transition-metal tungstate nanoparticles are fully functional, exhibiting typical properties of this class of materials, for instance, superparamagnetism ($CoWO_4$), luminescence ($ZnWO_4$) and photocatalytic activity ($CuWO_4$).

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1. Introduction

Pseudo-ternary tungstates represent a most versatile class of inorganic functional materials. Of particular interest are divalent metal tungstates with a composition M(II)WO$_4$. Depending on the size of the cation M^{2+}, two structure types are most common for the solid metal tungstates. Comparably large cations with $r(M^{2+}) > 0.99$ Å are found in the scheelite-type, whereas the wolframite-type is typical for small cations ($r(M^{2+}) < 0.77$ Å) [1]. The scheelite-type comprises fairly regular $[WO_4]^{2-}$ tetrahedra with M^{2+} being eightfold coordinated, whereas distorted $[MO_6]$ and $[WO_6]$ octahedra make up the wolframite-type structure.

In wolframite-type tungstates, the M–O-bonds exhibit a predominantly covalent character. The resulting mixing between the M s-orbitals and O $2p$-orbitals is highly relevant for the material properties, and, for instance, influences the optoelectronic properties of the considered metal tungstate. Thus, a careful selection of the cation M^{2+} allows band-gap engineering, while choosing a mixture of several cations $M'_{1-x}M''_xWO_4$ ($0 < x < 1$) even allows fine tuning. For that reason, wolframite-type tungstates of transition metals (M^{2+} = Mn, Fe, Co, Ni, Cu, Zn) are most attractive for a multitude of applications. These include luminescent materials [2],

optical fibers and scintillators (being considered to be the most favorite scintillating materials for medical imaging based on X-ray computed tomography) [3], as well as photocatalysts [1,4–6], conventional oxidation catalysts [7,8], magnetic materials [6], multiferroics [6,9] or sensors [10,11]. Accordingly, there are already hundreds of publications on wolframite-type tungstates. Surprisingly, a general synthesis, applicable to the full series of transition-metal wolframite-type tungstates, offering readily crystalline nanoparticulate products with adjustable properties is missing.

The synthesis of ternary metal tungstates is challenging. Existing wet-chemical approaches to wolframite-type tungstates are most often precipitation reactions, starting from solutions of M^{2+} and $[WO_4]^{2-}$. In general, such quick precipitation reactions are limited to amorphous products. Therefore, most of the established strategies to prepare tungstates are two-step reactions: the precipitation of an amorphous intermediate is followed by a thermal post-treatment for crystallization. This thermal treatment is either done at comparably mild temperature ($<200\,^\circ$C) but with long reaction times (around 10 h) [1,6,12,13], or at elevated temperature (500–1000 °C) with short reaction times (around 2 h) [14–16]. Predominantly, this includes for instance, hydrothermal reactions and/or subsequent calcination steps. Hydrothermal reactions quite often lead to hierarchically organized structures and are difficult to control, whereas calcination strongly boosts particle aggregation and growth. Therefore, a general access to wolframite-type tungstates that allows preparing readily crystalline nanoparticles with

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small size and high specific surface via a one-pot, liquid-phase synthesis could be highly advantageous in view of a range of different material properties. Here, we report on a polyol-mediated synthesis of crystalline nanoparticles of the full series of transition-metal tungstates (M = Mn, Fe, Co, Ni, Cu, Zn) with small diameters (<20 nm) and high surface area (up to 200 m^2 g^{-1}). The compounds are phase pure and available in reasonable yields (>85%).

2. Results and discussion

2.1. Polyol-mediated synthesis of nanoscale transition metal tungstates

Polyol-mediated syntheses are based on high-boiling multidentate alcohols such as ethylene glycol, diethylene glycol or glycerol [17]. Due to their high polarity, these polyols can be considered as water-equivalent solvents with comparable solubility of simple metal salts (e.g., metal chlorides) that can be used as low-cost starting materials. In contrast to water, the high viscosity and the chelating properties are ideal for controlling nucleation and growth of nanoparticles as well as for stabilizing the particle surface and avoiding agglomeration [17]. As high-boiling solvents (boiling points of 250–350 °C), furthermore, the polyols as solvents often allow preparing readily crystalline nanomaterials without the need of high pressure and autoclaves [17b,18]. Highly crystalline nanomaterials, in general, are prerequisite in view of various material properties, including magnetism, fluorescence, catalytic activity or conductivity [17,18]. In contrast, non-crystalline nanomaterials do not exhibit a high quality in terms of the above material properties due to the huge number of defects. The widely applied post-sintering of powder samples as a second step subsequent to the initial precipitation, however, is accompanied by severe particle agglomeration. Therefore, such measure is not useful for high-quality nanomaterials. The polyol-mediated synthesis, finally, is easy to perform and has been already up-scaled on an industrial scale [19].

Polyol-mediated syntheses have been already proven to be very suitable for the preparation of a variety of high-quality nanomaterials [17,18,20]. As the polyols become reductive at elevated temperatures, synthesis is not only limited to metal oxides or metal sulfides but allows preparing metal nanoparticles as well [17a]. In fact, the polyol-mediated synthesis was first described for obtaining metal nanoparticles such as Co, Ni, Pd, Pt, Ag, Cd, Au, Sn, Pb [21]. As the reduction potential of the polyol increases with the temperature, even less noble metals such as In or Sn can be obtained at > 200 °C [22]. Notably, the synthesis of metal oxides and metal sulfides can be eventually restricted by the reducing properties of the polyol and the formation of elemental metals. To this concern, diethylene glycol has turned out as most advantageous for preparing metal oxide nanoparticles [17b,20], whereas the stronger reducing glycerol is often preferred for obtaining elemental metals [17a,21,22].

Aiming at metal molybdates and tungstates, a general access to a wide range of compounds MWO$_4$ (M = Mn, Fe, Co, Ni, Cu, Zn) is lacking. Moreover, liquid-phase syntheses–including polyol-mediated syntheses–only led to non-crystalline nanomaterials, so that a post-sintering of powder samples has been yet required to obtain crystalline materials [14]. In fact, it is definitely a challenge to develop a polyol-mediated synthesis to phase-pure transition-metal tungstates MWO$_4$. On the one hand, phase segregation and formation of binary oxides M$_x$O$_y$ and WO$_{3-z}$ have to be avoided. This is the more difficult the more the conditions of precipitation of the two respective metal oxides differentiate. On the other hand, any reduction of the metal cation M^{2+} and formation of the respective elemental metal M$^{\pm 0}$ have to be avoided. The latter is the

more difficult the nobler the respective metal is. In order to succeed, a precise selection of the available parameters is required, including the type of starting materials, temperature and duration of the reaction as well as the acidity of the solution.

The difficulty of the synthesis and the importance of choosing suitable conditions are best illustrated with CuWO$_4$. Here, conventional polyol-mediated synthesis in diethylene glycol with, for instance, copper halides as a typical starting materials yields elemental copper even at low temperature (∼100 °C) due to the high electrochemical potential of copper ($E_0(Cu^{2+}/Cu^0) = 0.34$ V) (Fig. 1a). When taking Cu(NO$_3$)$_2$ × 5H$_2$O as the starting material, i.e., using the oxidative effect of the nitrate anion, the formation of elemental copper can be impeded, though. In doing so, however, either the dehydrate CuWO$_4$ × 2H$_2$O is obtained (<200 °C) (Fig. 1b) or binary oxide side products are formed such as Cu$_2$O and CuO (>200 °C) (Fig. 1c). These side products can be avoided as well when conducting the reaction in a slightly acidic milieu. Notably, the formation of WO$_{3-x}$ × H$_2$O is favored at too low pH. All these types of side products can be successfully prevented by applying an acetate buffer providing a compromising pH of 5.5. Complying the reaction conditions discussed above, phase-pure and highly crystalline CuWO$_4$ nanoparticles can be obtained directly as-prepared without any thermal post-treatment (Fig. 1d). The additional transition-metal tungstates MWO$_4$ (M = Mn, Fe, Co, Ni, Zn) were prepared as readily crystalline nanoparticles via the polyol-mediated synthesis similar to the strategy for CuWO$_4$ described above.

2.2. Size and crystallinity of the as-prepared nanoscale transition metal tungstates

Following the synthetic strategy described above, the full series of wolframite-type transition-metal tungstates MWO$_4$ (M = Mn, Fe, Co, Ni, Cu, Zn) can be obtained via the polyol-mediated synthesis. According to scanning electron microscopy, the nanoparticles are uniform with a sphere-like to lens-type shape at narrow size distribution (Fig. 2). The mean particle diameters were deduced via statistical evaluation of at least 100 particles for each compound and range between 3 and 12 nm (Table 1). The specific surface area of the powder samples was determined by volumetric gas sorption with N$_2$ as the sorbent via the Brunauer–Emmett–Teller (BET) formalism. Accordingly, specific surface areas of 15 m^2 g^{-1} to 212 m^2 g^{-1} were obtained (Table 1). Notably, the specific surface area does not only relate to the particle size but also to the material density and the microstructure of the powder samples. The color of the powder materials coincides with the respective bulk compounds (Fig. 2). Owing to the small particle size, however, the reflectivity is increased and results in a seemingly lower absorption. As the color originates from transitions between atomic and molecular energy levels (including $d \rightarrow d$ transitions due to ligand-field splitting of Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} as well as the charge-transfer absorption on [WO$_4$]$^{2-}$), quantum-confinement effects are not to be expected.

In order to evidence the chemical composition and purity of the as-prepared nanomaterials, X-ray powder diffraction (XRD) analysis (Fig. 3, Table 1) and energy-dispersive X-ray analysis (EDX) were performed (Table 2). XRD evidences all nanoparticles to be both crystalline and phase-pure (Fig. 3). The obtained powder-diffraction patterns are well in accordance with the relevant reference data throughout. The observation of Bragg peaks showing broad peak widths correlates with the small crystallite size of the nanoparticles. Based on the Scherrer equation, the crystallite sizes were determined to 3–28 nm (Table 1). These data also correlate with the particle diameter as determined from SEM as well as with the specific surface area. Due to absorption of the used CuK$_{\alpha 1}$