



Surfactant-free synthesis of sub-stoichiometry tungsten oxide nanoparticles and their use as anode buffer layers in organic solar cells



Lennart Brüttsch^a, Jens Czolk^b, Radian Popescu^c, Dagmar Gerthsen^c,
Alexander Colsmann^b, Claus Feldmann^{a,*}

^a Karlsruhe Institute of Technology (KIT), Institute of Inorganic Chemistry, Engesserstraße 15, D-76131 Karlsruhe, Germany

^b Karlsruhe Institute of Technology (KIT), Light Technology Institute, Engesserstraße 13, D-76131 Karlsruhe, Germany

^c Karlsruhe Institute of Technology (KIT), Laboratory for Electron Microscopy, Engesserstraße 7, D-76131 Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 10 April 2017

Received in revised form

19 May 2017

Accepted 22 May 2017

Available online 25 May 2017

Keywords:

Nanoparticles
Tungsten oxide
Surfactant free
Organic solar cell

ABSTRACT

A surfactant-free synthesis of small-sized tungsten trioxide is presented. Nanoparticles with an average size of 4.6 ± 1.5 nm are prepared via hot-injection techniques in ethanol. Due to the reducing properties of ethanol, a sub-stoichiometry composition WO_{3-x} ($x \approx 0.4$) is obtained. The partial reduction of W^{+VI} to W^{+V} becomes visible in the bluish color of suspensions and powder samples and in optical spectroscopy (UV-Vis). The nanoparticles are further characterized by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDXS) and infrared spectroscopy (FT-IR). Due to their small size, their high colloidal stability and the absence of surfactants, layers from the as-prepared WO_{3-x} nanoparticles are ideally suited to form anode buffer layers in organic solar cells. Exemplary solar cells show good power conversion efficiency of 6.3%.

© 2017 Elsevier Masson SAS. All rights reserved.

1. Introduction

Tungsten trioxide (WO_3) exhibits versatile material properties that enable various optoelectronic and sensor applications [1–7]. For example, the redox transition from W^{+VI} to W^{+V} requires little energy and is accompanied with a significant color change from pale yellow to deep blue [8], which is ideal for electrochromic devices and smart glasses [5,9–11]. Bulk WO_3 can yield high work functions between 5.7 and 6.7 eV [12,13], a band gap between 2.6 and 3.4 eV [11,13–16] and a broad range of conductivities [16] depending on its morphology and stoichiometry. For nanoparticulate WO_3 – depending on particle size and synthesis – band gaps up to 4.2 eV [11] and work functions up to 5.0 eV [2,17] have been reported. Although the conductivity of nanoparticulate WO_3 thin-films is somewhat lower [12,18], they are of specific interest as anode buffer layers in organic solar cells [2,18–21], for photoelectrochemical water splitting [22,23] and for semiconductor-type gas sensing [24–26].

In organic solar cells, WO_3 can be used to replace the omnipresent poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

(PEDOT:PSS), which is acidic and therefore partly dissolves the indium tin oxide (ITO) electrode underneath. When incorporated into organic solar cells, WO_3 must form homogenous and haze-free thin-films, preferably with thicknesses <20 nm. WO_3 layers that were produced from precursors in principle comply with these requirements, but particle size, agglomeration, stoichiometry and crystallinity are difficult to control. To control stoichiometry and crystallinity, layers can be deposited from nanoparticle suspensions. The homogeneity of such nanoparticulate thin-films is nevertheless strongly related to the size and size distribution of the nanoparticles. Hence, smaller WO_3 nanoparticles often yield better transparency, less scattering and improved surface roughness.

Based on liquid-phase synthesis strategies, WO_3 nanoparticles have been obtained via solvothermal routes [27–29]. These approaches typically require strong-binding stabilizing agents such as oleylamine to control particle nucleation and particle growth, and thus, to adjust the particle size and size distribution. However, such strong-binding surfactants containing long-chained alkyl groups are difficult to remove after the synthesis and very much hamper the electrical contact between the nanoparticles. As a consequence, the conductivity of thin-films is low if the surfactants remain on the particle surfaces. Alternative synthesis routes result in agglomerated WO_3 nanoparticles or anisotropic shapes (e.g. rods or plates), which can be highly desired, for instance, for obtaining porous

* Corresponding author.

E-mail address: claus.feldmann@kit.edu (C. Feldmann).

layers used for gas-sensing applications [24–26,29]. Aiming at transparent, low-scattering thin-films, however, small-sized and non-agglomerated spherical nanoparticles are sought for – most preferentially in absence of any long-chained, strong-binding surfactants. So far, only few reports have addressed surfactant-free WO₃ nanoparticles with average particle diameters <10 nm and their incorporation into organic solar cells [2,18], all of which were synthesized by spray pyrolysis resulting in certain particle agglomeration.

Here, we present a surfactant-free, hot-injection synthesis of sub-stoichiometry tungsten oxide (WO_{3-x}) nanoparticles with an average size of 4.6 ± 1.5 nm. Besides synthesis and material characterization, we employ the as-prepared nanoparticles to form anode buffer layers in organic solar cells.

2. Results and discussion

2.1. Synthesis via surfactant-free hot-injection

To form homogenous thin-films suitable for optoelectronic devices, the tungsten oxide nanoparticles have to be smaller than the intended layer thickness (typically <20 nm) [2,19]. To accomplish this challenging task, we implement a reaction of tungsten (VI) chloride (WCl₆) and acetic acid in ethanol as the liquid phase. Hot-injection was used for the addition of the reactants, which is a well-known technique to efficiently control particle nucleation and particle growth [30,31].

WCl₆ was dissolved in ethanol to yield a yellow solution that was heated to reflux. Thereafter, diluted acetic acid was injected. The immediate color change from a yellow solution to a bluish suspension indicates the formation of nanoparticles. The injection of aqueous acetic acid into refluxing ethanol initiates rapid hydrolysis of WCl₆ and guarantees an efficient control of the particle nucleation according to the model given by LaMer and Dinegar [32]. The acidic conditions established by acetic acid and released HCl, furthermore, support a proceeding dehydration to WO₃. Moreover, HCl can be easily removed after the synthesis via evaporation. Due to the reducing features of ethanol at elevated temperatures, sub-stoichiometry tungsten oxide was formed as indicated by the blue color that originates from partial reduction of W^{+VI} to W^{+V}. We note that the blue color retained under inert conditions (Ar, N₂), whereas it vanished over a period of several weeks if the suspensions were exposed to air.

Ethanol as a highly polar solvent (ϵ_r : 24.5 F m⁻¹ [33]), moreover, turned out to be sufficient for effective stabilization of the polar tungsten oxide surface resulting in an excellent colloidal stability of the as-obtained WO_{3-x} nanoparticle suspensions (Fig. 1f). Thus, additional stabilizing agents are not required. Subsequent to synthesis and washing, the as-prepared nanoparticles can be redispersed in water, ethanol or isopropanol. For colloidally stable suspensions and optimal wetting on arbitrary substrates, isopropanol is used in the following. Thus, suspensions of the as-prepared WO_{3-x} nanoparticles in isopropanol were prepared with a solid content of 1.75 wt-% without any additional surfactant.

2.2. Material characterization

To determine size and morphology of the as-prepared nanoparticles, transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed (Fig. 1a and b). Accordingly, spherical nanoparticles with rather uniform size and shape are observed. A statistical evaluation of more than 600 nanoparticles on numerous high-resolution (HR)TEM and HAADF-STEM images yields an average diameter of 4.6 ± 1.5 nm (Fig. 1e). Moreover, the

as-prepared nanoparticles turned out as crystalline as demonstrated by HRTEM images (Fig. 1c). The crystal structure of the nanoparticles is consistent with the monoclinic structure commonly observed in WO₃. This is demonstrated by the agreement between the diffractogram and the calculated diffraction pattern of bulk-WO₃ (Fig. 1d) [34] for representative nanoparticles.

The SAED pattern of a nanoparticle ensemble confirms the HRTEM results (Fig. 2a). All observed Debye-Scherrer rings are in accordance with the sole presence of the monoclinic WO₃. The SAED pattern shows only few reflections on Debye-Scherrer rings at large reciprocal lattice distances. The loss of this valuable diffraction information can be prevented by azimuthally averaging the SAED intensity, which is plotted as a function of spatial frequency k together with the corresponding whole-pattern fit and the difference plot (Fig. 2b). From the Bragg peak positions, lattice parameters $a = 7.35 \pm 0.02$, $b = 7.53 \pm 0.02$, $c = 7.73 \pm 0.03$ Å and $\beta = 91.7 \pm 0.3^\circ$ were determined which are in good agreement with the corresponding reference data [34] and the HRTEM results.

The average chemical composition of nanoparticles was determined from EDX spectra measured by scanning a square region containing a single nanoparticle (dashed frame in Fig. 3a). The EDX spectrum reveals the characteristic X-ray lines of O-K _{α 1}, the W-L and W-M series, besides the lines of the Cu-K and Cu-L series from the grid and the C-K _{α 1} line from the amorphous carbon substrate (Fig. 3b). The quantification of the W and O content on the basis the W-L series and the O-K _{α 1} line results in 29 ± 4 at-% W and 71 ± 4 at-% O. Thus, an average chemical composition of W_{28±5}O_{72±4} was obtained from EDXS area scans of 10 different nanoparticles, indicating the formation of sub-stoichiometric tungsten oxide WO_{2.6}. This finding is in accordance with the characteristic blue color of suspensions and powder samples.

To further study the chemical composition and especially the surface conditioning of the nanoparticles, we have performed FT-IR spectroscopy (Fig. 4). Here, sharp vibrations at 3690 cm⁻¹ (ν (O–H)), 2950–2850 cm⁻¹ (ν (C–H)) and 1020 cm⁻¹ (ν (C–O)) indicate the presence of surface-adsorbed ethanol and are well in agreement with the literature [35]. Moreover, vibrations at 670 and 470 cm⁻¹ relate to γ (O–W–O) and δ (O–W–O) [36]; a broad vibration at 3600–3000 cm⁻¹ (ν (O–H)) indicates the presence of water. Altogether, we conclude the presence of ethanol on the particle surfaces and the absence of any other surfactant. This is a remarkable difference to earlier reports in the literature and a major advantage for the layer processing in optoelectronic applications.

UV-Vis spectra of the WO_{3-x} nanoparticles show a strong absorption in the UV (<350 nm) as well as in the yellow to red spectral regime (>600 nm) (Fig. 5). A minimum of absorbance is observed at 350–450 nm, which is in accordance with the strong blue color of suspensions and powder samples. This absorption originates from the W^{+VI}-W^{+V} metal-to-metal-charge-transfer (MMCT) transition and, again, confirms the presence of sub-stoichiometry tungsten oxide. The band gap of 3.5 eV was calculated from the absorption onset at 350 nm. Compared to the band gap of bulk-WO₃ (2.6–3.4 eV) [13–15], the band gap of nanosized WO_{3-x} is known to be slightly larger [11]. Taking into account the small particle size of 4.6 nm, such shift may originate from quantum-confinement effects as they were already described for surfactant-stabilized, nanosized tungsten oxide before [11,37].

The high work function of tungsten oxide is optimal for hole extraction from organic bulk-heterojunctions [2,17,20,21,31]. Layers deposited from the nanoparticles synthesized herein exhibit a work function of $\Phi_a = 5.3$ eV according to photoelectron yield spectroscopy measurements in air (PESA). With their small size (4.6 ± 1.5 nm), the sub-stoichiometry, the absence of strong-binding surfactants and the increased band gap (3.5 eV), the as-prepared WO_{3-x} nanoparticles exhibit ideal properties for thin-

Download English Version:

<https://daneshyari.com/en/article/5443890>

Download Persian Version:

<https://daneshyari.com/article/5443890>

[Daneshyari.com](https://daneshyari.com)