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Phase-transfer assisted synthesis of BiOI nanoplatelets, quantum-confined color and selective modification of surface conditioning

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ABSTRACT

Nanoscale BiOI is prepared via a phase-transfer assisted reaction. To this concern, reaction of $Bi(NO_3)_3 \cdot 5H_2O$ and KI in water/2-propanol leads to the nucleation of BiOI. These nanoparticles are separated by an oleylamine-induced phase transfer to toluene. Colloidal stabilization of BiOI in the non-polar phase can be reversed by hydrazine-initiated removal of oleylamine. With glycine as a colloidal stabilizer the particles are redispersable in a polar phase such as water or alcohol. As-prepared BiOI is platelet-shaped with sizes of $200 \cdot 200 \cdot 18$ nm and a specific surface of 16.0 m^2g^{-1}. Due to one-dimensional size confinement, the color of the BiOI nanoplatelets – in contrast to carmine red bulk-BiOI (E_g: 1.83 eV) – is shifted to yellow (E_g: 2.00 eV). Based on its adaptable dispersibility and its color, BiOI nanoplatelets might be relevant as a color pigment as well as a semiconductor in solar cells.

1. Introduction

Bismuth oxide halides with a composition BiOX (X: Cl, Br, I) received certain attention as light-absorbing semiconductor in solar cells [1], photocatalyst for biomineralization [2–6] as well as a color pigment [7–11]. To the latter concern, especially, BiOCl is widely applied as a less harmful pearlescent pigment in cosmetics [12]. BiOI – exhibiting a bright carmine red color – has been frequently discussed as a red color pigment [7–11]. Here, the material might become relevant as an alternative to the well known cadmium sulfoselenides (CdS_xSe_{1-x}, $0 \leq x \leq 1$). Despite their toxicity these pigments are still used in artist's paint as well as to dye plastics due to their bright and tunable yellow to red color [13]. To replace CdS_xSe_{1-x} by less harmful materials with similar color characteristics is still a challenge. To this concern, bismuth oxide halides can be interesting since the color of BiOX can be tuned too by intermixing of halogens (i.e. $BiOBr_xI_{1-x}$) [10,11] as well as by size-depending band-gap tuning of the semiconductor-type compounds [14].

Nanoscaled BiOI has been yet obtained via solvothermal and stabilizer-mediated precipitation methods in the form of nanolamellas, nanosheets or microspheres [1–6]. Most often the resulting particle size largely exceeds the nanoregime (i.e. with diameter <100 nm) and is restricted to the micronscale (i.e. 0.5–5 μm). Nanoscaled BiOI, 10–25 nm in diameter was first obtained by Kaskel et al. [14]. While decreasing its size, a significant color shift from orange to yellow and even yellowish white has been observed and was ascribed to quantum-confinement effects. Since BiOI was prepared via a microemulsion approach, however, the amount of available material is limited. As-prepared BiOI was furthermore successfully incorporated into polymers. The resulting polymer composites, however, were light sensitive – due to radical starters involved for the polymerization – and immediately turned black upon daylight illumination [15].

In this study, crystalline platelet-like BiOI nanoparticles are realized via a phase-transfer assisted reaction. Based on a precise adjustment of the surface conditioning, the nanoparticles can be dispersed in non-polar (e.g. toluene) as well as polar media (e.g. water, alcohol). Due to the platelet-like morphology and the resulting one-dimensional size confinement, its color is shifted to yellow.

2. Results and discussion

BiOI nanoplatelets were prepared via a phase-transfer assisted reaction. To this concern, a solution of KI, $Na(CH_3COO)$ and oleylamine in deionized water and 2-propanol was provided and topped with toluene. This two-phase system was heated to reflux (~130 °C) and intensively intermixed to guarantee for an intimate contact between the polar and the non-polar phase. Next, a solution

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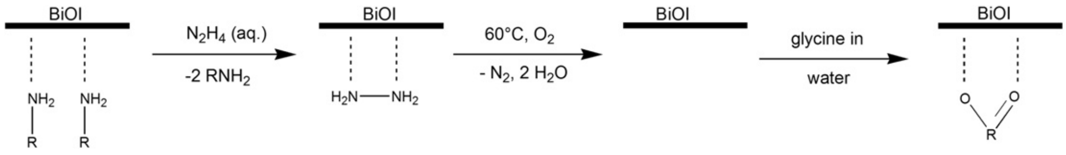

Fig. 1. Scheme illustrating the surface modification of as-prepared BiOI nanoplatelets – removal of oleylamine (NH_2–R) by hydrazine treatment and exchange by glycine.

of $Bi(NO_3)_3 \cdot 5H_2O$ in acetic acid was injected, which – as indicated by its yellow-red color – instantaneously led to the formation of BiOI nanoparticles. To control nucleation and growth, now, the phase-transfer reaction is involved. Accordingly, the surface of the BiOI nanoparticles is coordinated by oleylamine as a surface-active stabilizer right after its formation (Fig. 1). Oleylamine, however, favors the interaction with the non-polar toluene phase and thereby as a next step initiates a phase-transfer of the nanoparticles. This phase-transfer reaction offers certain advantages: 1. Since the nanoparticles were separated from remaining starting materials any further particle growth is excluded; 2. All excess of starting materials and remaining salts are left in the polar phase and thereby well separated from the product; 3. The as-prepared BiOI nanoparticles are well stabilized against agglomeration due to its oleylamine capping. Note that acetate serves as a co-stabilizer of the nanoparticles that furthermore establishes an alkaline pH and a high electrolyte concentration in the polar phase. These aspects favor a clear separation of the liquid phases and facilitate the phase transfer of the nanoparticles even further.

The presence of low quantities of oleylamine and acetate as surface stabilizers on the as-prepared BiOI nanoparticles subsequent to the phase-transfer reation is indicated by FT-IR spectroscopy (Fig. 2). Thus, vibrations at 2924 cm^{-1} and 2853 cm^{-1} (ν(C–H)) as well a 1563 cm^{-1} (ν_{as}(C=O)) and 1413 cm^{-1} (ν_s(C=O)) can be directely related to reference spectra of the pure compounds. Although the present surface conditioning is very beneficial with regard to the phase-transfer reaction, it might not be useful in view of the potential areas of application of the BiOI nanoparticles. As a conceptual study we have therefore addressed a removal of oleylamine and its exchange against another stabilizer, too. Hydrazine has been already reported as a beneficial agent to remove, for instance, oleylamine or oleic acid as a stabilizer from CdSe- or CdTe-based quantum dots [17,18]. With a modified procedure, the oleylamine-stabilized BiOI nanoparticles were here resuspended in hydrazine hydrate containing 2-propanol and heated to 65 °C. When separating the particles by centrifugation, FT-IR spectra indeed confirm oleylamine and acetate now to be absent (Figs. 2 and 3). To monitor a potential redispersion of BiOI in polar media, the aminoacid glycine has been selected. And the glycine-functionalization has been performed in water. FT-IR spectra thereafter show the exchanged stabilizer with its characteristic vibrations (cf. fingerprint of glycine reference) and with weak intensity (Fig. 3).

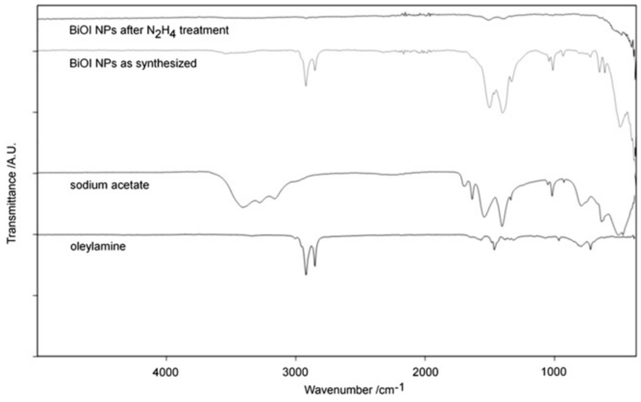

Fig. 2. FT-IR spectra of the as-prepared oleylamine-functionalized BiOI as well as the nanoplatelets subsequent to hydrazine treatment (pure oleylymine and sodium acetate shown as references).

Scanning electron microscopy elucidates size and morphology of the BiOI nanoparticles, which are shown here subsequent to the hydrazine treatment. Accordingly, the platelet-like particles are with diameters of 100–200 nm and a thickness of 15–25 nm (Fig. 4). Thus, an aspect ratio of about 10 is obtained. These results are confirmed by DLS analysis, too (Fig. 5). With the assumption of a spherical morphology, the nanoparticles exhibit a mean hydrodynamic diameter of 180 nm. Taking the platelet-like shape into account, it can be assumed that the Brownian movement is significantly slower perpendicular to the long axis. Consequently, the DLS results correspond well to the SEM images and indicate the

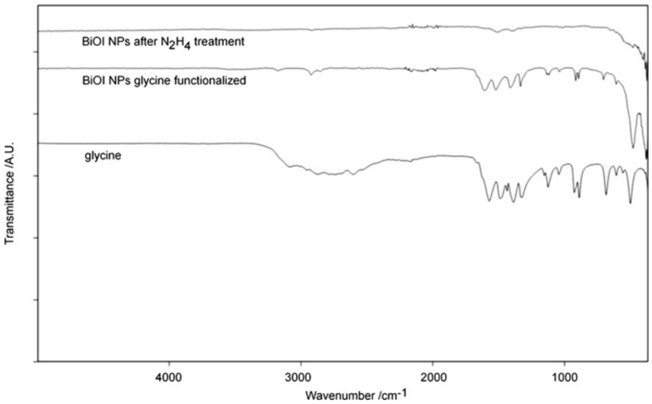

Fig. 3. FT-IR spectra of hydrazine-treated BiOI as well as the nanoplatelets subsequent to glycine-functionalization (pure glycine shown as a reference).

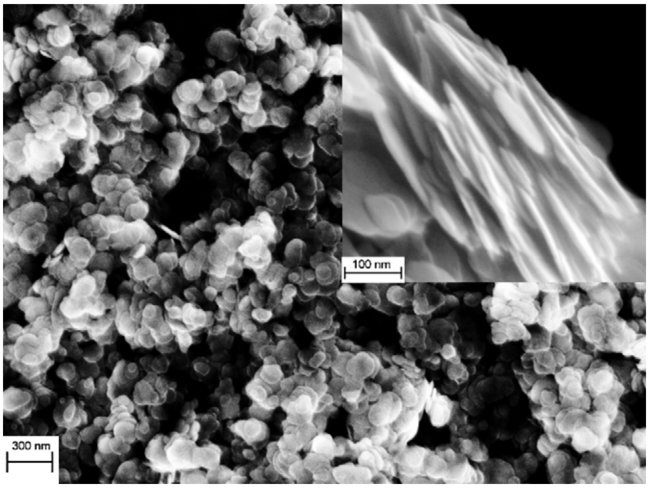

Fig. 4. SEM images of the as-prepared BiOI nanoplatelets.