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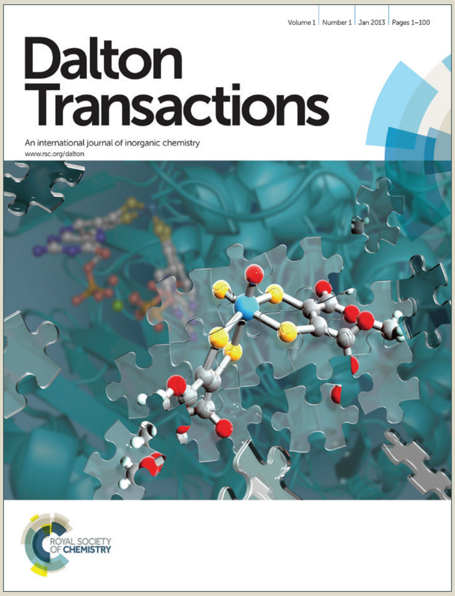

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# Epitaxial growth of silver chloride crystals on bismuth oxychloride

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In this work, studies of morphological and structural characteristics of BiOCl/AgX heterostructures (X=Cl, I) synthesized using ion-exchange reactions have been conducted. It was found that silver chloride AgCl crystals precipitating on the surface of bismuth oxychloride crystals show orientation ordering with the (001)BiOCl||(100)AgCl crystallographic relationship. Using two synthesis routes differing in the sequence of ion-exchange reactions, BiOCl/AgI heterostructures have been synthesized for the first time. It was shown that, in contrast to the BiOCl/AgCl system, silver iodide crystals precipitate on the basal planes of bismuth oxychloride without any preferred orientation. The synthesis strategy of bismuth oxychloride-based heterostructures proposed in this work can be used to synthesize bismuth oxyhalide-silver halide $BiOX_1/AgX_2$ ($X_1$, $X_2$= Cl, Br, I) heterostructures of different compositions.

## 1. INTRODUCTION

In recent years, the development of composite heterostructures promising for practical applications has received much attention. Among heterostructures with attractive technological properties are binary heterostructures based on bismuth oxyhalides $BiOX_1/BiOX_2$ and bismuth oxyhalides and silver halides $BiOX_1/AgX_2$ ($X_1$, $X_2$ = Cl, Br, I). In a detailed review of the properties and applications of materials based on bismuth-containing compounds, Cheng et al.[1] point out that bismuth oxyhalides, which are Bi-based semiconductors, are of immense importance due to their outstanding optical and electrical properties and promising performance as pharmaceuticals,[2] pigments,[3] catalysts,[4] and gas sensors.[5] Pure bismuth oxychloride and bismuth oxychloride-based materials show photocatalytic activity and can be used to remove contamination of organic nature from aqueous solutions.[6, 7] It was also shown that combinations of two bismuth oxyhalides $BiOX_1/BiOX_2$ and bismuth oxyhalide/silver halide BiOX/AgX show higher photocatalytic activity than the individual compounds contained in these heterostructures.[8-12] A strong ability of the AgCl/BiOCl heterostructures to catalyze degradation of rhodamine B (RhB) dye under visible light irradiation has been demonstrated in ref.[13]

Most commonly, the synthesis of these heterostructures is carried out by two simple methods, which are based on co-precipitation and ion-exchange reactions. For instance, the BiOCl/BiOI heterostructure was synthesized by precipitation of BiOI microcrystals followed by precipitation of BiOCl.[8]

AgCl/BiOCl and AgBr/BiOBr heterostructures were obtained by co-precipitation from a solution containing silver and bismuth nitrates upon addition of potassium chloride or cetyltrimethyl ammonium bromide (CTAB).[13,14] These methodological approaches to the synthesis of different bismuth oxyhalide-based heterostructures were discussed in refs.[15-19]

Depending on the synthesis method — co-precipitation or ion-exchange reactions, different mutual orientations of the components can develop in the AgX/BiOX heterostructures and, in particular, in AgCl/BiOCl[17] with separate non-contacting particles of the components as the limiting case of the structural configuration. The character of the interface in a heterostructure will inevitably affect the photocatalytic activity of the composite particles.[17]

It should be noted that in heterostructures, the structure of the interface plays an extremely important role and determines the physical and chemical properties of the material. . At present, no reliable data exist on the mutual orientation of the BiOX and AgX phases forming heterostructures. In order to enable their target functionality, the $BiOX_1/BiOX_2$ ($X_1 \neq X_2$=Cl, Br, I) and BiOX/AgX crystals are usually synthesized in the form of nanoparticles. The difficulty of determining the orientation relationships in very fine composite crystals is a possible reason for a lack of information on the mutual orientation of the phases in these systems. There are only two refs. available,[20,21] in which the authors, drawing their conclusions from the powder diffraction data, suggested that AgBr crystals grew epitaxially along the {102} crystal surface of BiOBr. However, the powder diffraction was obviously insufficient to conclude on the presence of epitaxial growth and correctly describe the orientation relationship between the phases. The mutual orientation of the phases in the BiOX/AgX heterostructures — the presence or absence of epitaxial growth — can have a crucial influence on the catalytic properties of the composite particles.

The importance of orientation relationships for the properties of heterostructures was a stimulus for the present work. We have studied the morphological, phase, and structural characteristics of the BiOCl/AgCl heterostructures synthesized by an ion-exchange reaction. Special attention was directed to determining the mutual orientation of the BiOCl and AgCl crystals. We have also studied the evolution of the morphological characteristics of the BiOCl/AgCl heterostructures with increasing amount of silver chloride precipitating on the surface of the BiOCl crystals. A synthesis strategy has been proposed for a new heterostructure — BiOCl/AgI, which was synthesized via two routes differing in the sequence of ion-exchange reactions.

## 2. EXPERIMENTAL

### 2.1. Characterization.

TEM investigations of BiOCl were carried out using a JEM-2000FXII microscope at an accelerating voltage of 200 kV. TEM samples were prepared by directly placing the BiOCl crystals on a Cu TEM grid previously covered with a holey carbon film. SEM investigations of BiOX/AgX heterostructures were carried out using a Hitachi electron microscope at an accelerating voltage of 30 kV. Powder X-ray diffraction patterns (XRD) were recorded by means of a D8 ADVANCE powder diffractometer (Bruker AXS) equipped with a one-dimensional Lynx-Eye detector using Cu Kα radiation ($\lambda$=1,541 Å).

### 2.2. Materials.

All materials were of analytical grade, purchased from ALDRICH and used without additional purification.

### 2.3. Synthesis of platelet-shaped BiOCl crystals.

Bismuth oxychloride crystals are usually synthesized in acidic solutions by an ion-exchange reaction between a soluble bismuth-containing compound and a source of chloride ions. The bismuth chloride is hydrolyzed at a rate that depends on the concentrations of the reactants, pH, and solution temperature. For synthesizing BiOCl, bismuth nitrate is usually used, although other soluble bismuth compounds can be selected. In order to reduce the degree of hydrolysis and prevent the precipitation of insoluble bismuth compounds, acidic solutions are used. In this work, the synthesis of bismuth oxychloride was carried out according to the procedure described in patent.[22]

166 ml of concentrated hydrochloric acid HCl was added to deionized water until pH ~ 1 was reached. Upon continuous mixing, 420 ml of bismuth nitrate solution containing 0.2 g/ml of bismuth was added to the prepared HCl solution heated up to 70 °C at a rate of 2.5 ml/min. Simultaneously, sodium hydroxide solution (6N) was added at the same rate. Bismuth oxychloride crystals of platelet shape were separated by sedimentation and decantation followed by filtering. The synthesized crystals were washed with deionized water and dried at 60 $^{o}$C.

### 2.4. Synthesis of BiOCl/AgCl heterostructures.

The BiOCl/AgCl heterostructure was synthesized using the method described in refs.,[13,19] which is based on the following ion-exchange reaction:

$$\mathrm{BiOCl} + \mathrm{Ag}^{+} \rightarrow \mathrm{AgCl}\downarrow + \mathrm{BiO}^{+}.$$

As the crystals of bismuth oxychloride are treated by silver nitrate, silver chloride crystals precipitate, while bismuth oxynitrate remains in the solution in the selected conditions of synthesis.

The platelet-shaped BiOCl crystals obtained by the above described procedure were used to produce BiOCl/AgCl heterostructures with different substitution degrees of the silver ion for the bismuthyl ion. 1 g of BiOCl microcrystals was placed in 100 ml of deionized water. Then 50 ml of $AgNO_3$ solution was added to the water suspension of BiOCl microcrystals at 40$^{o}$C. The $AgNO_3$ solution contained calculated amounts of silver nitrate to enable different substitution degrees of the silver ion for the bismuthyl ion.

The mixture was agitated for 1 h. After that the suspension was filtered, and the crystals were washed with deionized water and dried at room temperature. In order to prevent photodegradation of the synthesized AgCl crystals, all procedures were conducted under red light illumination.

## 3. RESULTS AND DISCUSSION

Electron Microscopy studies have shown that the synthesized bismuth oxychloride crystals are of platelet shape with a thickness of 300-500 nm and a width of up to 10 µm (Figure 1a, b). The selected-area electron diffraction (SAED) patterns obtained from the individual microcrystals placed normal to the direction of the electron beam can be indexed as corresponding to tetragonal BiOCl with the [001] zone axis (Figure 1 c). This analysis allowed us to conclude that the well-developed surface of the BiOCl crystals is made by the {001} facets. The XRD measurements performed on the BiOCl crystals support this conclusion. The XRD pattern of the synthesized platelet-shaped crystals (Figure 1d) was indexed as a tetragonal structure (JCPDS: 06-0249). A characteristic feature of the pattern is increased intensities of the (00l) Bragg reflections, which also indicate the presence of the well-developed {001} facets of the BiOCl crystals. Worth mentioning are the results of ref.[11], in which BiOCl crystals with the same crystallographic indices of the facets were synthesized: the {001} and {110} facets were identified, the latter forming the lateral surface of the crystals.

SEM images in Figure 2a and 2b show a general and a more detailed views of the BiOCl crystals treated by silver nitrate solution (the transformation degree of BiOCl into AgCl is 20 wt.%), respectively. It can be seen that multiple AgCl crystals separated from each other precipitated on the (001) surface and lateral facets of the BiOCl crystals (Figure 2a). It is likely that the formation of AgCl crystals as a result of the ion-exchange reaction occurs at the more reactive sites, which are defects of different types, such as dislocations or growth steps on the surface of the BiOCl crystals. Moreover, it was found that all AgCl crystals have a cubic habit and the same orientation (Figure 2a, b). In the XRD patterns of the synthesized BiOCl/AgCl heterostructures (Figure 2c), reflections corresponding to the cubic silver halide (JCPDS: 31-1238) are present along with the reflections of BiOCl. As the substitution degree of the silver ion for the bismuthyl ion increased, the intensity of the AgCl reflections increased accordingly. Such an arrangement of crystals unambiguously indicates the epitaxial growth of the cubic AgCl crystals on the (001) surface of the BiOCl crystals. It can be assumed that the cubic habit of the AgCl crystals is made up by the {100} facets. Consequently, the $(001)_{\mathrm{BiOCl}}\|(100)_{\mathrm{AgCl}}$ orientation relationship is observed as AgCl crystals precipitate on the (001) plane of platelet-shaped BiOCl crystals as a result of an ion-exchange reaction. As the concentration of silver nitrate in solution was increased to obtain 30 wt.% of AgCl in the heterostructure, larger AgCl crystals formed. When the transformation degree of BiOCl into AgCl reached 50 wt.%, the AgCl crystals coalesced forming an ordered cellular structure (Figure 2d). Similar morphological characteristics of the products of ion-exchange reactions were observed in refs.[23, 24] for sulfidation of BiOCl by thioacetamide solution. Superstructures were observed to form by the preferential growth of [001]-oriented $Bi_2S_3$ nanorods on the top facets of (001)-oriented BiOCl discs along the two perpendicular [100] and [010] directions of BiOCl. It is known that bismuth oxyhalides possess a layered tetragonal structure (space group P4/nmm, lattice parameters a=b=3.89 Å, c=7.34 Å). Silver chloride crystalizes in the cubic system (space group Fm-3m, lattice parameter a=5.549 Å). Despite a substantial difference between the crystalline structures of BiOCl and AgCl, they contain identical elements. Comparison of the projections of the $(001)_{\mathrm{BiOCl}}$ (Figure 3a) and $(100)_{\mathrm{AgCl}}$ (Figure 3b) planes shows that the position symmetry and the distance between the chloride ions along the [100] and [010] directions in the structure of silver chloride (5.549 Å) coincide with the position symmetry and the distance between the chloride ions along the [110] and [1-10] directions in the structure of bismuth oxychloride (5.49 Å).

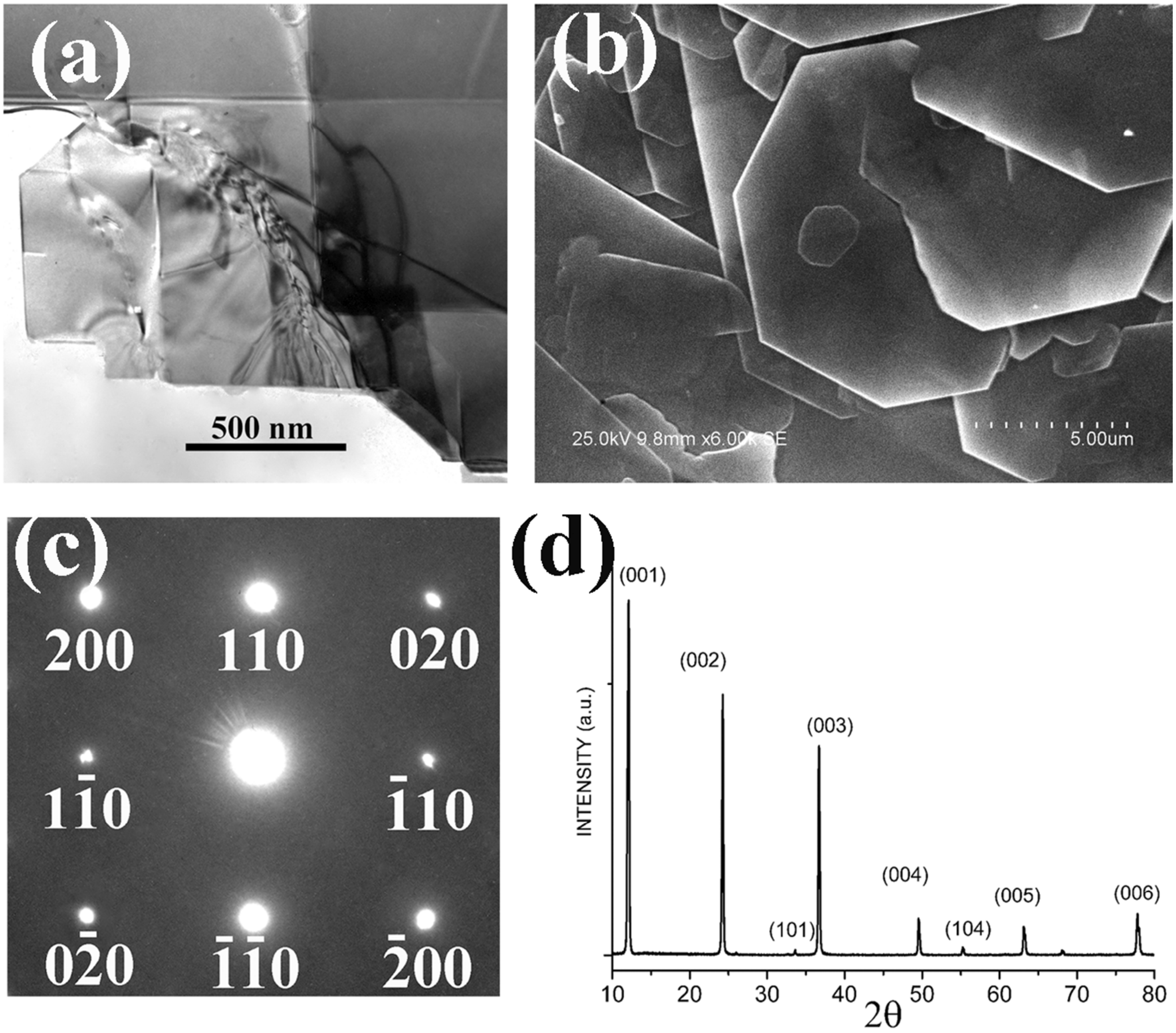

**Fig. 1** (a) TEM image, (b) SEM image, (c) SAED pattern, and (d) x-ray diffraction pattern of the BiOCl crystals.

Therefore, along with the orientation relationship $(001)_{BiOCl}||(100)_{AgCl}$, another relationship - $[110]_{BiOCl}||[100]_{AgCl}$ — should be observed between the phases of bismuth oxyhalide and silver halide. The latter was confirmed by scanning electron microscopy, which provided evidence of the epitaxial intergrowth: the facets of cubic AgCl crystals were parallel to the facets of the platelet-shaped crystals of BiOCl or made an angle of 45° with them. In these orientations, the $[110]_{BiOCl}||[100]_{AgCl}$ relationship is observed, as, according to the literature data,[11] the facets of platelet-shaped BiOCl crystals are parallel to the [110] and [100] directions, which make an angle of 45° between each other. It should be noted that orientation relationships observed in this work for the BiOCl/AgCl heterostructures are different from those reported in ref. [23, 24] for the BiOCl/$Bi_2S_3$ heterostructures because of the differences in the crystalline structures of bismuth sulfide and silver chloride.

While characterizing the heterostructres by electron microscopy, we noticed that when the BiOCl/AgCl crystals are exposed to the electron beam, silver chloride microcrystals degrade gradually. The products of degradation become visible in the images of the samples after several minutes of exposure (Supplementary Video and Figure S1).

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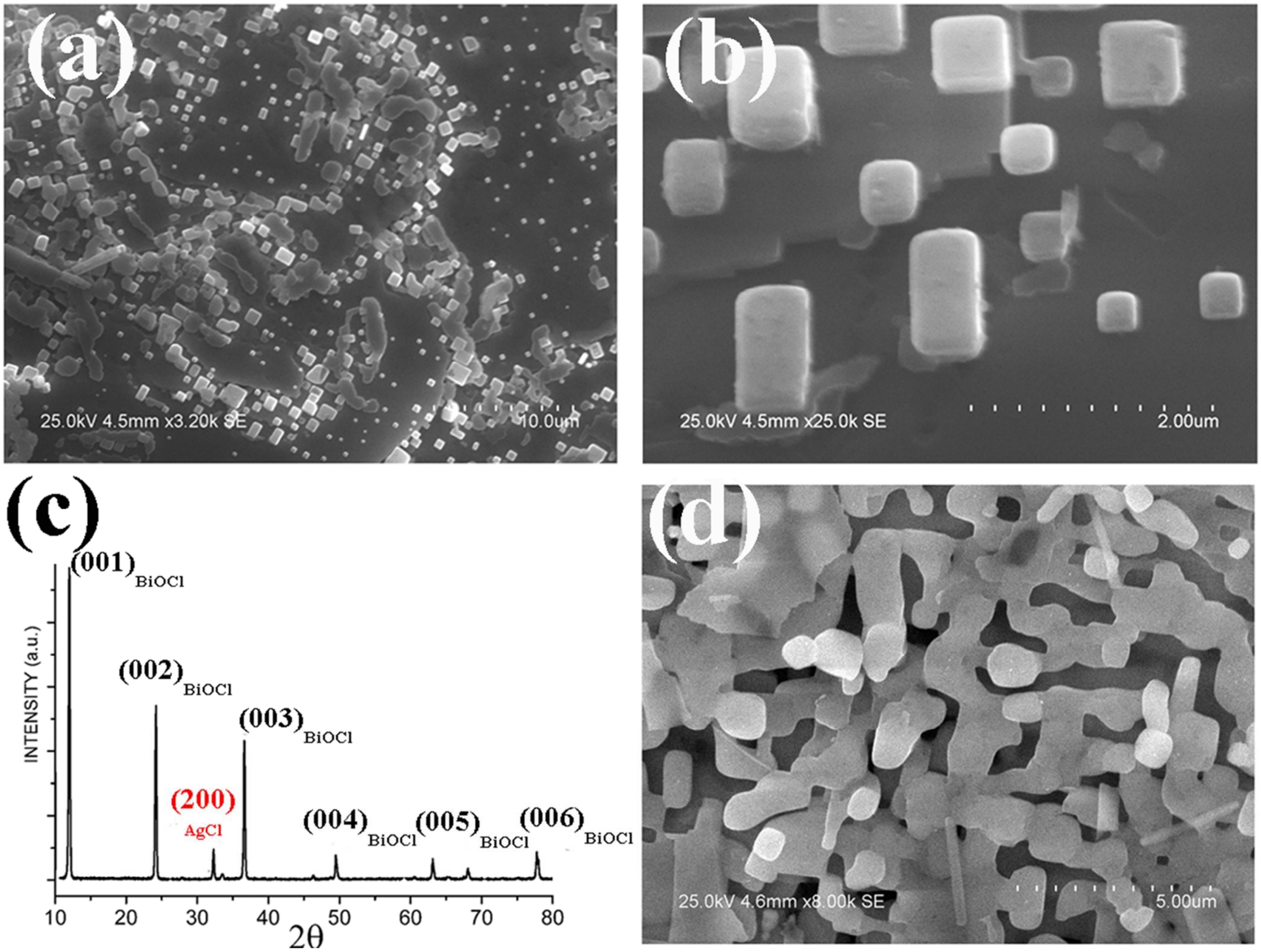

**Fig. 2** (a, b) SEM images and (c) x-ray diffraction pattern of the AgCl crystals precipitated on the basal {001} facets of the BiOCl crystals (the transformation degree of BiOCl into AgCl in the heterostructures is 20 wt %). (d) SEM images, of the BiOCl/AgCl heterostructures (the transformation degree of BiOCl into AgCl 50 wt %).

On the facets, and vertices of the silver chloride microcrystals, nanoparticles of metallic silver gradually crystallized. Similar effects caused by decomposition of AgCl crystals were observed during ex situ experiments, when the BiOCl/AgCl crystals were exposed to the UV light. The result of the UV exposure of the BiOCl/AgCl heterostructures was complete decomposition of silver chloride microcrystals (Figure 4). These observations are in agreement with a well-known photographic sensitivity of silver halide crystals. The observed phase changes in the BiOCl/AgCl heterostructure point to a possibility of its transformation into the BiOCl/AgCl/Ag heterostructure, or even into BiOCl/Ag upon a prolonged UV exposure.

Despite a large number of publications on the synthesis and properties of bismuth oxyhalide-based materials, little information, if any, is available on the possibilities of preparation of BiOX$_1$/AgX$_2$ crystals, in which X$_1$ and X$_2$ are different halide ions. In order to fill this gap, we synthesized such a heterostructure via two routes differing in the application order of halide-ion containing solutions during the treatment of BiOCl crystals. The schemes of the proposed synthesis routes are shown in Figure 5.

In the first route, the BiOCl/AgI crystals are synthesized using the BiOCl/AgCl crystals, whose synthesis, morphology, and crystalline structure have been described above, as precursors. When BiOCl/AgCl crystals are treated with sodium iodide solution, BiOCl/AgI heterostructures form according to the following reaction scheme: BiOCl/AgCl + NaI → BiOCl/AgI. The second synthesis route includes two stages. At the first stage, the platelet-shaped BiOCl are treated with sodium iodide solution so that the reaction

BiOCl+NaI→BiOCl/BiOI could take place. We have experimentally confirmed that this ion-exchange reaction is possible. The XRD patterns of the reaction products show reflections of the BiOI phase along with those of the BiOCl phase (Figure S2). The EDS of the BiOCl crystals treated by NaI solution reveals iodide lines (Figure S3). At the second stage, the synthesized BiOCl/BiOI crystals are treated by silver nitrate solution to carry out the reaction BiOCl/BiOI+AgNO$_3$→ BiOCl/AgI.Our studies have shown that the structural, phase, and morphological characteristics of the BiOCl/AgI crystals produced by these two routes are similar to each other. Independent of the synthesis route, the XRD patterns of the BiOCl/AgI crystals (Figure 6a), along with reflections of the BiOCl phase, contained those of γ-AgI. The precipitation of beta, gamma, and hexagonal phases of AgI on the surface of bismuth oxyiodide microcrystals was observed in refs.[15, 17, 25, 26] It should be noted that the XRD patterns of the BiOCl/AgI crystals do not contain any reflections of silver chloride or bismuth oxyiodide. This fact shows that when BiOCl/AgCl crystals are treated by NaI solution or BiOCl/BiOI crystals are treated by AgNO$_3$ solution, the formation of silver iodide crystals is preferred, as the solubility of AgI is lower than that of BiOI or AgCl.

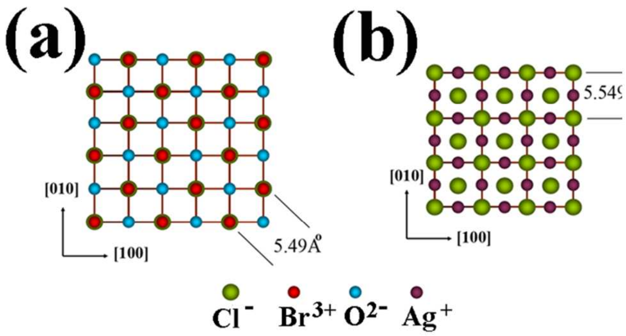

**Fig. 3** (a) The projections of BiOCl crystal structure on the (001) plane. (b) the projections of AgCl crystal structure on the (100) plane.

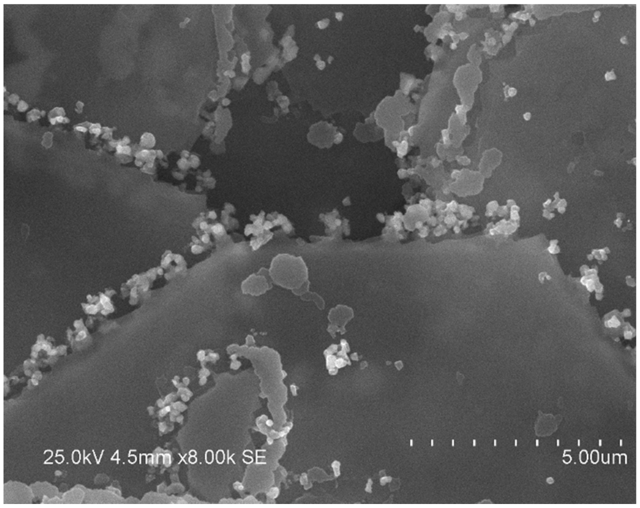

**Fig. 4** SEM images of the BiOCl/AgCl heterostructures after UV irradiation.

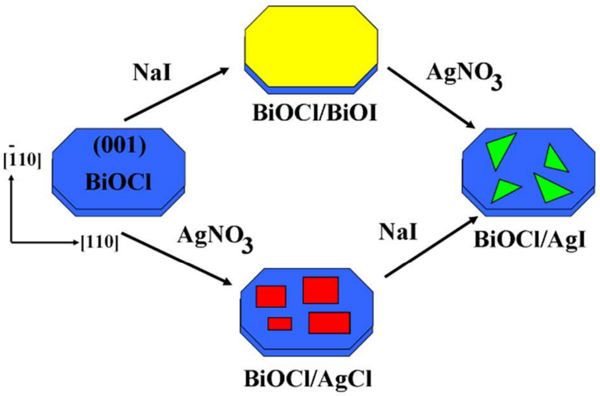

**Figure 5.** The schematic illustration of the proposed synthesis routes of BiOCl/AgI heterostructure.

Electron microscopy studies have shown that the silver iodide microcrystals synthesized by these two routes have similar morphological features. The AgI crystals formed as a result of ion-exchange reactions possess a triangular habit and do not show any preferred orientation relative to the surface of the platelet-shaped crystals of bismuth oxychloride (Figure 6b). Oriented growth of AgCl in BiOCl/AgCl and the absence of preferred orientation of AgI crystals relative to BiOCl in the BiOCl/AgI heterostructure can be explained by substantial differences between the lattice parameter of γ-AgI with a cubic structure (JCPDS: 9-399, space group F-43m, lattice parameter a= 6.495 Å) and that of silver chloride. The AgI crystals contained in the BiOCl/AgI heterostructure were stable and did not experience degradation upon electron beam exposure, in contrast to AgCl in BiOCl/AgCl

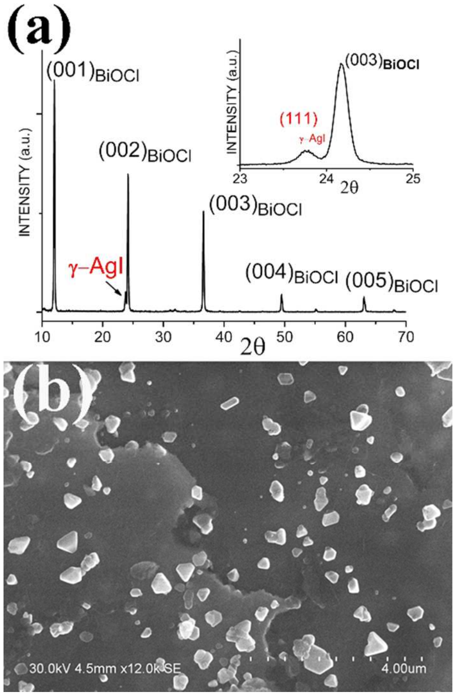

**Fig. 6.** (a) X-ray diffraction pattern, and (b) SEM image of the BiOCl/AgI heterostructures.

## Conclusion

In conclusion, our investigations of the morphological and structural features of the BiOCl/AgX (X=Cl, I) heterostructures synthesized using ion-exchange reactions have revealed orientation ordering of silver chloride crystals precipitating on the surface of bismuth oxychloride crystals. The synthesis strategy proposed in this work can be used to obtain other bismuth oxyhalide-silver halide heterostructures. We believe that heterostructures obtainable by the proposed strategy can become interesting and promising objects for studying their photocatalytic activity as a function of composition. The synthesis routes described above are suitable for synthesizing BiOCl/AgBr, BiOBr/AgBr, and BiOBr/AgI heterostructures. Taking into account close values of lattice parameters of AgCl and AgBr, epitaxial intergrowth can be expected in BiOCl/AgBr and BiOBr/AgBr heterostructures.

Owing to the epitaxial relationship and well-defined interfaces between the phases, the BiOCl/AgCl heterostructure produced by an ion-exchange reaction offers advantages over heterostructures formed by co-precipitation or by simple mixing of the components with regard to the catalytic properties. These advantages will be related to a lower energy barrier that an electron has to overcome when crossing an interface between the phases grown epitaxially compared to an incoherent interface or a spatial gap between the particles of the components.

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## Notes and references

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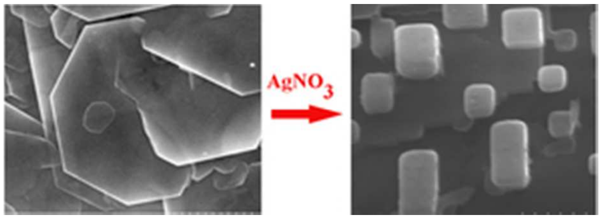

AgCl crystals precipitating on the surface of bismuth oxychloride crystals show orientation ordering with the (001)BiOCl∥(100)AgCl
25x8mm (300 x 300 DPI)