Transient FTIR Measurements at Nanoseconds Resolution:
Correlating between Faceting and Photocatalytic Activity in BiOCl

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Recent years have shown a growing interest in the photocatalytic properties of bismuth oxyhalides [BiOX, where X = F, Cl, Br, I or a mixture of them]. 1,2 In part, this growing interest is closely related to the internal polarization in these materials due to the layered structure, comprised of Bi2O3 layers located between two layers of halogen atoms, 3 which assists charge separation. All layers are stacked together by van der Waals interactions, leaving some space between the layers and facilitating easy cleavage along the (001) plane. Accordingly, the growth of BiOX crystals is characterized by an anisotropic growth along this plane. The valence band orbital is composed of O2p and X-np (n = 2, 3, 4, and 5 × = F, Cl, Br and I respectively), while the conduction band is formed by Bi6p orbitals. Consequently, the higher the Z number of the halogen is, the narrower is the bandgap.

Bismuth oxy-chloride is probably the most studied photocatalyst within this group. It is used as a pigment in the cosmetic industry, as a photocatalyst for degradation of pollutants, and as a good candidate for optoelectronic and in photovoltaic devices such as light-emitting diodes, lasers and solar cells. A lot of effort has been made to tune its activity into the visible range of the spectrum, for example by adding metal ions or by forming heterojunctions with other photocatalysts such as Fe3O4 or BiVO4. 5,6

Another way to improve the photocatalytic activity of BiOCl was to control its facets, since many photocatalytic reactions, such as the degradation of rhodamine B, 7–9 were found to be promoted in BiOCl particles exposing large [001] facets. This effect was explained by the presence of high density of oxygen atoms at the surface, which contribute to the formation of oxygen vacancies in the bulk, having shallow traps below the conduction band. 10 or, in the case of photosensitization, to the accommodation of electrons injected from the photosensitized dye. 11

Transient Infra-red spectroscopy can be one of the most valuable techniques for studying transient phenomena in photocatalysts, as it may provide information on specific, localized, species involved in the photocatalytic processes by monitoring changes that they induce in the spectra of the photocatalytic materials. This has to do with the fact that trapped electrons and holes are expected to cause local-field distortion leading to induced spectral shifts and intensity variations. 12 In other cases, they may provide indications for intra-band transient processes, affecting the whole baseline. 13

Transient changes in the IR spectra of compounds can be monitored by using FTIR in a “Step-Scan” mode. 14,15 In this mode of operation, the moving mirror of the FTIR interferometer is fixed at a specific position, and the detector measures a time-dependent signal, triggered by a short excitation pulse. Then, the moving mirror is relocated at a next fixed position and the whole process of excitation and measuring is repeated. At the end, a two dimensional array of data (intensity versus location and time) is obtained. The data belonging to a specific time, amassed from all mirror positions, is then Fourier-Transformed to provide a spectrum, representing a point in time relative to the laser shot.

The feasibility of utilizing the “step-scan” approach for measuring transient evolution in the IR spectra of photocatalytic materials following their excitation was demonstrated by us recently. 16 We have shown that it was possible to measure IR spectral changes at the nanoseconds timescale on samples of bismuth vanadate, where a transient split in the IR peaks associated with localized VO4 stretch modes was observed in monoclinic BiVO4. These changes in the spectra were in line with DFT calculations published independently by a different group, predicting a distortion (hence a breakage of symmetry) in the VO4 group, due to formation of polarons upon excitation. 17 In a different system, recently studied by us, we have used the same technique to explain the effect of the pyrolysis temperature during the preparation of graphitic carbon nitride on the photocatalytic efficiency of this compound. 18

In what follows we report on nanoseconds-scale transient changes in the FTIR signatures of various types of BiOCl particles, having different facet ratios. The interplay between transient FTIR phenomena, faceting and photocatalytic activity is then discussed.

Experimental

Preparation of faceted BiOCl particles by hydrothermal method.—In a typical hydrothermal synthesis process, 0.513 g of Bi(NO3)3 × 5H2O, 0.057 g NH4Cl and a varied amount (0.00 g, 0.047, 0.10 g and 0.20 g) of Sodium Dodecyl Benzene Sulfonate (SDBS) were separately dissolved, each of them in 10 ml of nitric acid solution. For most cases the HNO3 concentration was 2M, however for one type of sample (denoted as B5) the nitric acid concentration was 0.5M (see Table I). Then, the three solutions were mixed under vigorous stirring. 30 ml of de-ionized (DI) water were also added into the prepared solution. The final 60 ml solution was transferred into a 100 ml Teflon-lined autoclave and maintained at 170°C for 24 h, after which it was naturally cooled to room temperature. A white non-soluble product was collected and washed several times with DI water to remove ions.

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Table I. The various types of prepared BiOCl samples and the SDBS/Bi molar ratio in these samples.

| BiOCl sample | Added SDBS (mg) | pH during preparation | SDBS/Bi molar ratio |
|--------------|-----------------|-----------------------|---------------------|
| B1           | 0               | 0                     | 0.000               |
| B2           | 47              | 0                     | 0.128               |
| B3           | 100             | 0                     | 0.271               |
| B4           | 200             | 0                     | 0.543               |
| B5           | 100             | 0.6                   | 0.271               |
| B6           | 100 + 2.6 g PEG 8000 | 0              | 0.271               |

and possible remnants, and finally was heated to 60°C for 24 h. Table I presents the molar ratio between SDBS and Bi in the preparation solution of the various types of prepared BiOCl. In the preparation of the B6 samples, 2.6 g of poly(ethylene glycol) (PEG) 8000 were added to the SDBS solution.

Characterization.—The surface areas of the various types of BiOCl particles were measured by BET adsorption isotherms at 77 K, using Flowsorb II 2300 (Micrometrics) apparatus. High Resolution Scanning Electron Microscopy (HR-SEM) images were taken using a Zeiss Ultra Plus High Resolution FEG-SEM microscope, equipped with an EDS system. Electron backscattering diffraction (EBSD) analysis was performed by Scanning Electron Microscope - FEI E-SEM Quanta 200 emission scanning electron microscope. The diffuse reflectance spectra of the powders were recorded by a Shimadzu UV 2600 spectrophotometer, equipped with an integrating sphere accessory. X-ray diffraction measurements were performed by a Rikagu MiniFlex X-ray diffractometer. The operation conditions were λ = 0.1541 Å (CuKα), 30 kV and 15 mA and step size of 0.02°/step.

Transient FTIR measurements.—The step-scan FTIR system used for this work consisted of a Bruker V-70 FTIR spectrophotometer. The third harmonic (355 nm) of a Nd:YAG pulsed laser (Quantel, 5 mJ FWHM pulse), operating at 10 Hz, was used for sample excitation. A fast, broad spectral window MCT detector, having a temporal resolution of 2.5 nsec, was used. The measured signal was stored and averaged over 20 pulses prior to setting the mirror in the next position. Care was made to verify that any transient changes were diminished prior to the next laser shot, i.e. within less than 100 msec. Results were recorded at intensity of 20 mJ/pulse and at 10 mJ/pulse by introducing appropriate attenuating filter. The whole IR beams path was under vacuum, in order to improve signal to noise ratio. More details on the experimental SS-FTIR system can be found elsewhere.

The samples were fixed within a pressed KBr pellet (1 mg BiOCl within 200 mg KBr; pressed at 5 tons for 1 h, thus forming 13 mm pellets). The obtained spectra were taken versus that of a background of KBr pellet experiencing exactly the same conditions as the BiOCl-containing samples. In part of the measurements the BiOCl particles were exposed to hole scavengers (propanol) and electron scavengers (methyl viologen) prior to measuring. For ethanol and propanol, a BiOCl-alcohol colloid suspension was prepared by introducing 1 mg of B1 particles and 199 mg of KBr powder into a water-propanol mixture (5 ml of propanol with 5 ml of water). The mixture was then allowed to dry at 40°C and the powder was pressed into a pellet. Similar procedure was used to prepare pellets containing B1 particles that were pre-exposed to methyl viologen. Here, 5 ml water were used to dissolve 5 mg of MV instead of an alcohol-water mixture.

Photocatalytic reduction of hexavalent chromium (Cr (VI)).—A stock solution of 1.28 × 10−5 M Cr (VI) was prepared by dissolving K2Cr2O7 in water. 1 ml of the stock solution was diluted with 49 ml of DI water and a few drops of concentrated H2SO4 were added, the final pH being ~2.85. The photocatalytic experiments were carried out under nitrogen atmosphere in a batch reactor made of glass. Here, 50 mg of a photocatalyst were added to the 50 ml of 2.56 × 10−5 M Cr (VI) solution and were mixed vigorously for 20 min while bubbling nitrogen to remove any dissolved oxygen. The photocatalytic reactor, containing the solution and the photocatalyst, was set overnight to reach a stable equilibrium state. During the photocatalytic experiments a Light Emitting Diode source (LED-R Ltd.) was used, emitting 365 nm light (15 nm FWHM). The impinging flux was 3.17 × 1015 photons sec−1 cm−2 and the exposed area was 12.5 cm².

The concentration of Cr (VI) was measured by taking 0.6 ml aliquots from the solution at different times and centrifuging them for 10 min. To determine the concentration of Cr (VI) a known method was adopted. The method is based on formation of a complex between Cr(VI) and 1,5-diphenyl carbazide (DPC) in strongly acidic solution, which absorbs strongly at 543 nm. Accordingly, 0.200 ml of 0.02 M DPC were added to the clear aliquots, and the concentration of the Cr (VI) was measured by following changes in the absorbance of the solution at 543 nm.

Results and Discussion

Figure 1 presents the SEM images of the six types of BiOCl particles prepared at different nominal molar ratios between SDBS and bismuth. In the absence of SDBS (B1 particles), most of the particles looked like irregular-shaped flakes, while some had a needle-like shape. Particles that were grown in the presence of SDBS were larger in their dimensions (1–3 μm) and had the shape of thick slabs (0.1–0.2 μm in thickness). The higher the concentration of SDBS was, the smoother the slabs. More important, the presence of SDBS had a significant effect on the sidewalls of the particles. In B3 and B4 these sidewalls formed an asymmetric octagon. In many cases the octagons...
Figure 2. HR-SEM images of B3 and B4 particles (left) and the corresponding Kikuchi lines obtained from the marked rectangular areas.

Figure 3. The XRD patterns of the various types of BiOCl particles. The positions of the peaks in (A) were taken from JCPDS file No. 01-065-0861.

Figure 4. HR-SEM image of B3 particles onto which Pt nanoparticles were photodeposited.

The XRD patterns of the various types of BiOCl particles. The positions of the peaks in (A) were taken from JCPDS file No. 01-065-0861. Performing the same measurements on the sidewalls of the samples did not yield any specific orientation.

Figure 2 presents the Electron Back Scattering Diffraction (EBSD) patterns for B3 and B4 particles. The crossing point of the Kikuchi lines indicates that the orientation of the dominant plane (from which the diffraction pattern was taken) was (001) for both types of samples. For all types of samples, the XRD pattern was in line with previous reports on BiOCl, and agreed with the JCPDS data file No. 01-065-0861. While the locations of all peaks were found to be at the expected 2θ angles, the relative intensities of the peaks varied from one sample type to the other. These variations repeated themselves for each sample type (including types made by the same procedure in different batches), demonstrating that the difference in the relative ratios was an inherent property of the preparation scheme. The ratio between the intensities of the (001) peak to the (101) peak decreased upon increasing the relative amount of SDBS (see Table II) from 13.1 to 4.5. Preparation under less acidic conditions or in the presence of PEG 8000 further reduced this ratio to 2.6 and 1.8, respectively. The relative intensity of the (001) peak to that of the (200) peak was hardly changed upon increasing the concentration of SDBS (at constant acidity). This ratio was significantly reduced upon elevating the pH during preparation (B5 type) or using PEG (B6 type).

The typical crystalline sizes were calculated according to the Scherrer equation (while assuming a constant K of 0.9), for all types of samples and for the major peaks. Results are given in Table S1. The calculated typical crystalline size for all types was between 50 nm and 86 nm. This is significantly smaller than the size of the particles as observed by SEM (200–3000 nm), suggesting either multi-crystallinity of each particle, and/or poor crystallinity of large crystallites. Reducing the acidity of the preparation solution or introducing PEG 8000 into the system led to a slight decrease in the Scherrer’s size of the crystallites, i.e. had a deleterious effect on the crystallinity of the particles. No distinct effect of increasing the SDBS/Bi ratio on the size of the crystallites was found, although the crystallites prepared in the absence of SDBS (B1 particles), were among the largest.

The specific surface area of the BiOCl particles (Table II) was found to very low (0.6–4.9 m² g⁻¹), due to the large size of the particles and the absence of porosity. It should be remembered that the use of surfactant per unit of mass does not take into account the high molecular weight of bismuth (209 g mole⁻¹). In general, the higher the SDBS/Bi ratio was, the lower was the specific surface area. These results are consistent with the SEM images, showing some growth in the size of the particles upon increasing the amount of surfactant.

The bandgap energies were calculated by plotting Tauc plots, while assuming indirect band gaps, as claimed for BiOCl. The calculated energy gaps are given in Table II. The calculated bandgaps were quite similar (3.28 ± 0.07), except for the B6 particles, prepared with the PEG8000, where an apparent value of 3.5 was calculated.

Photodeposition of platinum islands on BiOCl particles.— Nanoparticles of platinum were photodeposited on the BiOCl particles in order to monitor the tendency of charge carriers to migrate to specific facets. The deposition was performed by exposing the BiOCl particles to UV light in a mixed ethanol/water solution containing Pt⁴⁺ ions.

Figure 4 presents a SEM image of B3 BiOCl particles, onto which nanoparticles of platinum were photodeposited. As shown, the deposition took place on the (001) facet only. Some platinum nanoparticles were deposited also along faults in the BiOCl particles (not shown here) and also on the edge of two intersecting sidewalls. Nevertheless, most of the area of the sidewalls (some of these had orientations belonging to the {101} family) was free of deposited platinum. In the absence of another source for reduction, the reduction of the Pt ions is...
Table II. XRD intensity ratios and energy gaps of the various types of BiOCl.

| BiOCl sample | SDBS/Bi Molar ratio | pH during preparation | Specific surface Area (m² g⁻¹) | XRD peak ratio (001)/(101) | XRD peak ratio (001)/(200) | Band gap [eV] |
|--------------|---------------------|-----------------------|-------------------------------|--------------------------|---------------------------|----------------|
| B1           | 0.000               | 0                     | 2.6                          | 13.1                     | 40.5                      | 3.15           |
| B2           | 0.128               | 0                     | 1.7                          | 4.5                      | 23.2                      | 3.10           |
| B3           | 0.271               | 0                     | 1.1                          | 7.8                      | 47.7                      | 3.26           |
| B4           | 0.543               | 0                     | 0.6                          | 7.0                      | 32.5                      | 3.22           |
| B5           | 0.271               | 0.6                   | 4.9                          | 2.6                      | 5.6                       | 3.25           |
| B6           | 0.271 (+PEG)        | 0                     | 3.5                          | 1.8                      | 4.5                       | 3.50           |

performed by photoinduced electrons arriving to the BiOCl surface. Therefore, the location of the Pt nanoparticles indicates that following excitation, electrons are present primarily at the {001} facets, and hardly at the sidewalls facets.

**Transient FTIR measurements.**—Figure 5 presents the FTIR spectrum of the B1 BiOCl particles as measured by a conventional measurement. A characteristic peak at 524 cm⁻¹ is assigned to symmetric stretching of Bi-O⁻²⁴ together with very weak two satellite peaks at 610 cm⁻¹ and 437 cm⁻¹. Also shown is a sharp peak at 1384 cm⁻¹, found before in BiOCl particles together with strong peaks originating from adsorbed water (HOH bending at 1640 cm⁻¹ and a strong, wide, envelop at 3475 cm⁻¹ with a shoulder at 3400 cm⁻¹, characteristic of H-bonded OH stretch). Similar spectra were obtained with all other types (Figures S1 – S5).

Figure 6 presents the Step-Scan FTIR measurements of B1, B3, B4, B5 types of BiOCl. The SS-FTIR spectra of B2, B6 can be found in the supplementary data (Figures S6, S7). The spectra clearly show transient changes following excitation. The main changes were an increase in the intensity of the Bi-O stretching mode peak, beginning for all types of particles approximately 10–15 nsec after excitation, reaching a maximum intensity 25–50 nsec after excitation and returning to its original intensity 70–130 nsec from excitation. In general, the larger the increase in intensity was, the more time it took to return to the original pattern. The increase in the intensity followed the following order: B5>B6>B1>B3>B4>B2. Except for B2, the higher the SDBS/Bi ratio during preparation was, the lower was the growth in the intensity of the 523 cm⁻¹ peak. In parallel to the transient increase in intensity, a blueshift to 550–580 cm⁻¹ was observed. This shift was quite correlated with the increase in the intensity: the maximal shift was observed at the same time where the intensity was the highest. Returning to the original position coincided with regaining the original absorption. BiOCl types that revealed the highest change in intensity (B1, B6) also showed the most pronounced shift. In the B1 sample, which was prepared without any SDBS, hence had the largest (001)/(101) XRD peak ratio (i.e. likely to have the highest extent of (001) facets), a growth in the 620 cm⁻¹ peak, leading to coalescence with the symmetric Bi-O peak was observed. Moreover, at a certain point in time (80 nsec from excitation) its intensity was almost equivalent to that of the symmetric Bi-O peak, quite in contrast to its almost negligible intensity in comparison with that of the 525 cm⁻¹ peak (Figure 5). Growth in the intensity of a 640 cm⁻¹ peak was observed also in the B5 sample, prepared under low acidity. Another transient peak was observed in B4 at 770 cm⁻¹. It should be noted that apart of the changes reported herein, there were no repeatable temporal changes in the spectra at other wavenumbers.

In order to better understand the origin of the temporal changes in the spectra and the reason for the effect of the preparation procedure on these changes, a set of transient measurements was performed with B1 samples (Figure 7). In this set of measurements the particles were exposed to various scavengers (propanol, methyl viologen) prior

![Figure 5](image-url)  
**Figure 5.** The FTIR spectrum of the as-prepared B1 particles.

![Figure 6](image-url)  
**Figure 6.** The SS-FTIR spectrum of the BiOCl particles. For clarity the spectra were vertically shifted. The numbers on the left represent the time (in nsec.) elapsed since excitation. The black bar in each type of sample equals to an absorption of 0.25 O.D.
to excitation. A dramatic change in the behavior was observed upon exposure to the hole scavengers propanol: the transient increase in the intensity of the Bi-O peak became much weaker, and in certain re-measurements there was hardly any noticeable peak. Furthermore, no transient blue shifting was observed and the peak remained around 530 cm$^{-1}$. In contrast, exposure of the B1 particles to methyl viologen, a known electron scavenger, prior to the preparation of the pellet, led to a substantial increase in the transient Bi-O peak, relative to the behavior of this peak in the absence of any scavenger.

In addition to that, and in order to assure that the transient effects were not due to the presence of minute amounts of SDBS a second set of measurements was performed with particles that had been exposed to UV light for several days prior to performing the transient FTIR measurements. In general, there was hardly any effect on the temporal behavior of B1-B5 BiOCl particles following long term exposure to UV light.

Photocatalytic reduction of Cr (VI) on BiOCl particles.—The reduction of Cr (VI) to Cr (III) was used as a means to study the effect of faceting on the photocatalytic properties. Figure 8A presents typical changes in the spectrum of the Cr (VI)-DPC complex indicating changes in the concentration of Cr (VI) following exposure to 365 nm light in the presence of B5 particles. As can be observed in the Figure, the only effect of exposure in the presence of BiOCl particles was a reduction in the absorption of the strong, wide, peak around 540 nm. Accordingly, the kinetics of the reduction was then deduced by monitoring changes in the absorption at 543 nm. The kinetic data of the system was found to fit a first order law (Figure 8B). The same first order was found also for the other types of particles (Figures S8−S12 in the supplementary data).

The averaged apparent first order reaction rate constants for the various types of BiOCl samples are summarized in Table III. The values in the Table are average values, and the standard deviation was in general between 4%−8%. To account for the difference in the surface area, normalized rate constants ($k^*$), obtained by dividing the apparent rate constants by the specific surface area, are also given. Here, the normalization was performed to compensate for the adsorption of the Cr(VI) ions in the dark, which, at large, correlates with the specific surface area. As portrayed in the table, the effect of normalizing according to surface area was quite mild, in terms of comparing the activities of the various types of BiOCl particles. The photocatalytic activities can be classified according to the following order: B4>B3>B5>B1>B6>B2>>photolysis, whereas the normalized photocatalytic activities followed the following order: B4>B3>B1>B5∼B6>B2. The differences in the activities are quite

| Sample type       | Rate constant [k (1/min)] | Normalized rate constant ($k^*$) [1/min-m$^2$] |
|-------------------|---------------------------|-----------------------------------------------|
| W/O photocatalyst | ~0                        | N/A                                           |
| B1                | 4.48×10$^{-3}$            | 0.034                                         |
| B2                | 1.24×10$^{-3}$            | 0.015                                         |
| B3                | 5.42×10$^{-3}$            | 0.098                                         |
| B4                | 5.81×10$^{-3}$            | 0.194                                         |
| B5                | 4.73×10$^{-3}$            | 0.019                                         |
| B6                | 3.39×10$^{-3}$            | 0.019                                         |
significant, suggesting that the measured values reflected an effect of the preparation process.

**Discussion**

The step-scan FTIR measurements revealed transient changes in the spectrum of the BiOCl samples, which occurred within 70–130 nanoseconds after excitation. These changes are manifested by growth in the intensity of the Bi-O symmetric stretching peak around 530 cm\(^{-1}\), and in some cases blue shifting or appearance of a new satellite peak around 620 cm\(^{-1}\) as well as around 770 cm\(^{-1}\). The duration of the transient changes, as well as the extent of increase in the absorption, was found to vary between different types of samples that had been prepared under different conditions, i.e. under varying concentrations of a surfactant (SDBS) that affected the morphology, size and faceting of the BiOCl particles. In parallel, the photocatalytic activity of the various types of samples, as measured by monitoring the kinetics of reduction of Cr(VI) ions, was found to change from one type to the other. These changes cannot be attributed to differences in the surface area of the various types of particles, since the same trends are found both with and without normalizing the kinetics according to the surface area.

Although, in principle, it is erroneous to assume a strict correlation between XRD peaks ratio and the ratio between facets, such ratios are often taken as qualitative indications of such ratios.\(^5\) Accordingly, particles having high 001/101 intensity ratio can be regarded as having higher percentage of (001) facets relative to (101) facets, than particles having lower 001/101 intensity ratio. In this context, it should be noted that electrons tend to accumulate on (001) facets (see Figure 4), while holes are likely to accumulate on (101) facets. Figure 9A presents the normalized rate constants (k\(^+\)) versus the 001/101 intensity ratios in the XRD pattern of the various types of particles. A “volcano-like” behavior is observed. The highest rates were observed at a ratio close to 7, obtained for B4 particles. At low ratios, measured for B5, B6 the rates were lower, and likewise at very high ratio, measured for B1.

Like all other photocatalytic systems, the photocatalytic reaction contains two parts: oxidative and reductive. While most of the attention is naturally given to the reductive part (Cr (VI) \(\rightarrow\) Cr (III)) the oxidative part should not be overlooked, as the two processes have to be eventually balanced. A classic example for this need for balancing is given by the photocatalytic oxidation of organic contaminants with TiO\(_2\), where the stripping of electrons is the bottle-neck, hence to achieve high oxidation rates for organic contaminants it is essential to supply sufficient molecules of oxygen to promote the reduction process.\(^2\) Back to the BiOCl case, in the absence of sacrificial oxidized species, the water molecules become the chemical specie responsible for oxidation. Their oxidation should be conceived as the rate determining process. Indeed, addition of an organic material (in particular, performing the reaction in the presence of hole scavengers, like alcohols) significantly increases the reduction rate of Cr (VI).\(^19\) For this reason, in the absence of a sacrificial organic specie, increasing the area at which oxidation of water takes place should contribute to the reduction rate of the chromium. Accordingly, in the B1 samples the rate limiting half-cell reaction was oxidation (lack of surface holes), whereas in the B5, B6 samples the rate limiting half-cell reaction was reduction (lack of surface electrons). Although the volcano plot was demonstrated with a reduction reaction, it is believed (but was not measured in this work) that similar behavior should be expected also in oxidation reactions, provided that the necessary conditions for such a behavior (i.e. shifting from one bottle neck to the other) are fulfilled.

In general, this may require choosing the right counter- reactant and measuring over a large span of concentrations.

Quite surprisingly, plotting the normalized rate constants versus the specific surface area (SSA) of the various types of particles reveals that the rate decreases as the surface area increases (Figure 9B). This result is quite surprising, since, for non-porous particles (as the BiOCl particles are) larger surface area implies shorter average distance for the charge carriers from their generation loci to the surface of the particles, where the redox reactions take place. This apparent discrepancy can be explained by the correlation one finds between the formation of well-defined faceted side-walls and the size of the particles (Figure 1) obtained in the larger particles. Hence, it points to the role of sidewalls, in separating electrons from holes, thus contributing to the activity. The observed transient changes in the intensity of the Bi-O symmetric stretch peak requires an in-depth explanation. In general, the absorption intensity of a specific peak depends on both the concentration of the absorbing functional group and the specific absorptivity of a relevant vibrational mode. Since the number of Bi-O bonds did not transiently increase following excitation, it is obvious that the intensity increase was due to an increase in the specific absorptivity. The specific absorptivity is proportional to the square of the transition moment, which, for vibrational spectra, is proportional to the derivative of the dipole moment with respect to the displacement coordinate, rather than to the strength of the dipole moment at zero displacement.\(^27\) It is known that substantial dipole derivatives arise when charge distribution evolve in response to vibrations or due to vibronic interactions with low lying electronic transitions.\(^28\) Exceptional dipole derivatives arise when charge self-localized in a polaron moves in response to a vibration with appropriate symmetry, generating a strong dependence of dipole moment on vibrational displacement.\(^29\) That way, coupling electrons to vibrational modes may increase infrared activity,\(^30\) as indeed was evidenced in the case of tetracyanoquinodimethane.\(^31\) It should be noted that the strength of the transition moment may be influenced not only by the presence of polarons but also by the presence of excitons,\(^32\) by dipole-dipole interactions\(^33\) and by changing the angle between the electric field vector of the excitation beam relative to the vibrational displacement.\(^34\)
To better understand the ways by which the transition moment, i.e. the intensity of the peak, is effected, the relations between the normalized rate constants, the transient duration, the maximal peak intensity and the specific surface area were plotted. Figure 10A clearly shows a negative correlation between the duration of the transient signal and photocatalytic activity. Here, the duration of the transient signal was taken as the time elapsed between excitation and the diminishing of the transient effects. The diminishing of the transient effects was taken as the point in time where 90% of the transient change in intensity in the main peaks disappeared. A negative correlation (with the exception of B2) was also found between the maximal intensity of the transient signal and the specific surface area of the various types of BiOCl. In other words, strong signal reflects large concentration of charge carriers. This reduction in concentration may be due to recombination, the lifetime of excitons in BiOCl is very short, in the order of 1–10 nanoseconds has to reflect the effect of electrons or holes rather than that of excitons. The fact that the maximal signal was delayed, i.e. was observed some 40 nanoseconds after excitation, suggests that it was provoked by the presence of trapped carriers rather than by free carriers.

The negative correlation between transient duration (and intensity) and $k^*$ is then can be explained if one accepts a notion, according to which the transient FTIR signal in the described measurements was caused by (or actually reflected the presence of) species that were doomed to disappear without causing any surface reaction, for example species that were trapped in deep traps, whether in the bulk or on the surface. In other words, strong signal reflects large concentration of charge carriers in deep traps. The opposite effect of propanol, a hole scavenger, was to diminish the transient signal (in terms of both duration and intensity), whereas electron scavengers acted to increase the intensity and duration of the transient signals. The opposite effect of propanol versus that of methyl viologen indicates that the transient changes in the intensity of the Bi-O peak was caused not by trapped excitons (as proposed based on PL measurements\textsuperscript{39}) but rather by one type of charge carrier. The increase in the signal upon using an electron scavenger and the decrease in the signal upon using a hole scavenger suggest that the deep trapped charges are holes rather than electrons. Thus, the finding that the duration of the deleterious transient signal was longer in particles having large specific surface area (hence, on the average, smaller than particles having small SSA) evidently shows that the length that the carriers have to cover in order to participate in redox reactions occurring at the surface, hence the negative correlation between the intensity and duration of the transient signal and the photoactivity of the samples.

The transient measurements performed with samples exposed to charge scavengers shed light on the type of charge carriers that are responsible for the transient FTIR signal. Here, the effect of propanol, a hole scavenger, was to diminish the transient signal (in terms of both duration and intensity), whereas electron scavengers acted to increase the intensity and duration of the transient signals. The opposite effect of propanol versus that of methyl viologen indicates that the transient changes in the intensity of the Bi-O peak was caused not by trapped excitons (as proposed based on PL measurements\textsuperscript{39}) but rather by one type of charge carrier. The increase in the signal upon using an electron scavenger and the decrease in the signal upon using a hole scavenger suggest that the deep trapped charges are holes rather than electrons. Thus, the finding that the duration of the deleterious transient signal was longer in particles having large specific surface area (hence, on the average, smaller than particles having small SSA) evidently shows that the length that the carriers have to cover in order to participate in redox reactions occurring at the surface, hence the negative correlation between the intensity and duration of the transient signal and the photoactivity of the samples.

BiOCl is known to be a p-type semiconductor, however, there are rare reports claiming n-type behavior, depending on the preparation conditions. While the type of conductivity in our samples was not measured, we believe, upon comparing the preparation procedures to those in the literature that all samples were of p-type character. Still, our results cannot rule out the possibility that the capping agents had some effect in this direction.

It should be pointed out that many works on transient absorption and transient photoluminescence in photocatalysts describe time-decay curves in terms of electron-phonon interactions or phonon-phonon interactions, even when there is no direct measurements of phonons. The results presented above do not relate directly to phonons but rather to localized vibrations in the photocatalyst.
Conclusions

Step-scan IR measurements that monitored transient changes in the intensity of the Bi-O symmetric stretch signal of BiOCl following excitation, were found to be sensitive to processes occurring on the photocatalyst at the first 100 nanoseconds after excitation. The observed intensity increase was found to be negatively correlated with the activity toward the reduction of Cr(VI), and was explained as representing the presence of deep traps, most likely located at un-faceted sidewalls.

The observation of a clear correlation between attributes belonging to the transient FTIR phenomena (increased intensity for a limited time of a specific peak) and the photocatalytic activity/surface area clearly demonstrates the potential of the step-scan FTIR technique as a tool for understanding, rationalizing, or even predicting the activity of photocatalytic materials.

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