X-ray photoelectron spectroscopy of trihalide ionic liquids: comparison to halide-based analogues, anion basicity and beam damage

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Abstract

X-ray photoelectron spectroscopy is used to investigate two 1-octyl-3-methylimidazolium trihalide ionic liquids, with anions including triiodide and iododibromide. The electronic environment of each element present in ionic liquids studied herein is analysed and compared to their halide-based analogous. The anion basicity is compared based upon the measured N 1s binding energy. The iododibromide ionic liquid is studied as a representative sample to illustrate the beam damage effect. Due to the beam damage, there is a new formed bromine component observed. This effect is calculated and demonstrated for all elements present within the ionic liquid. It suggests that the beam induced decomposition caused a stoichiometric loss of bromine atom and iodine atom, within the experimental error.

Introduction

Ionic liquids, which are composed of entirely cations and anions, exhibit a host of fascinating physico-chemical properties, making themselves desirable alternatives for use in a large range of research areas, such as catalysis [1], synthesis [2, 3], CO_2 capture [4] and electrochemistry [5, 6]. Their intrinsic low-volatility also allows ionic liquids to act as potential solvents for the replacement of commonly used traditional organic solvents [7, 8]. Ionic liquids can also play a key role in the immobilisation of catalysts which allows ease of separation of products and possible recycle of the catalyst [9, 10].

Attributing to their hydrophobic nature, high stability and low viscosity, trihalide ionic liquids have been widely used in the area of electrochemistry [11-13], particularly triiodide ionic liquids, which contain potential redox ion couple, *i.e.* $I^-/[I_3]^-$. To date, many investigations have been conducted to describe the diffusion coefficient and the effect of viscosity on the electrochemical behaviour of triiodide ionic liquids [14, 15]. Apart from that, trihalide ionic liquids have also been used as reagent-solvent in many reactions, *e.g.* stereospecific halogenations of alkenes and alkynes [16]. It has been concluded that ionic liquids with anions, such as $[Br_3]^-$, $[I_3]^-$, $[IBr_2]^-$ and $[ICl_2]^-$, are stable; whereas $[ClBr_2]^-$, $[ClI_2]^-$ and $[BrI_2]^-$ are rather unstable [17].

Since 2005, X-ray photoelectron spectroscopy (XPS) has been effectively used to analyse ionic liquids [18, 19], simply because of their non-volatile nature. XPS investigations can reveal many information, such as surface composition, subtle change of the electronic environment for a certain component present in an ionic liquid [20, 21], the cation-anion interaction [22-24] and the solute-ionic liquids interaction [25, 26]. To aid further understanding of physico-chemical properties of ionic liquids, binding energy derived from XPS has also been correlated to NMR data [27] and Kamlet-Taft parameters [22]. It concludes that both the basicity of the anion [22] and the acidity of the cation [28] can have significant electronic effect on the charge transferred from the anion to the cation. Over the past decade, a large range of ionic liquids have been successfully studied by

XPS, including imidazolium [22, 27, 29], pyrrolidinium [23, 30], pyridinium [24], guanidinium [31], ammonium and phosphonium [32].

Spectroscopic analysis of trihalide ions has been conducted employing a variety of techniques, *i.e.* NMR [16], Raman spectroscopy [33], steady-state UV absorption spectroscopy [34] and XPS [35]. In particular in the latter XPS study, a brief demonstration of the I 3d spectrum of $[I_3]^-$ anion is given indicating non-stoichiometric ratio of the two iodine components and the presence of the shake-up feature. Bonomo *et al.* also measured I 3d spectra for $[I_3]^-$ at a nanoporous NiO/acetonitrile interface aiming to illustrate the adsorption behaviour of $I^-/[I_3]^-$ [36]. Moreover, Odelius group used XPS to show the electronic structure of four LiI_3 solutions by the interpretation of I 4d XP spectra [37, 38]. These results inspire the idea of the systematic investigation of trihalide ionic liquids by XPS.

In this study, we investigate two 1-octyl-3-methylimidazolium trihalide ionic liquids, *i.e.* $[C_8C_1Im][I_3]$ and $[C_8C_1Im][IBr_2]$, using XPS, together with $[C_8C_1Im]I$ and $[C_8C_1Im]Br$. The electronic environment of each element present in ionic liquids studied herein is analysed and compared to their halide-based analogous. Comparisons of the anion basicity, which can be correlated to N 1s binding energies, are also made. It concludes that $[I_3]^-$ and $[IBr_2]^-$ are both the least basic anions. The beam damage is demonstrated for $[C_8C_1Im][IBr_2]$ over a long period of time. It suggests that a stoichiometric loss of Br atom and I atom can be observed due to the beam-induced decomposition

Experimental methods

Materials: All chemicals were obtained from Sigma-Aldrich or Alfa Aesar and were used as received except for 1-methylimidazole, which was distilled over calcium hydride prior to use. All ionic liquids investigated in this study were prepared in our laboratory using established synthetic protocols (see Supplementary Information).

XPS Data Collection: All XP spectra were recorded using a Kratos Axis Ultra spectrometer employing a focused, monochromated Al Kα source ($h\nu$ = 1486.6 eV), hybrid (magnetic/electrostatic) optics, hemispherical analyser and a multi-channel plate and delay line detector (DLD) with a X-ray incident angle of 30° and a collection angle, θ, of 0° (both relative to the surface normal). X-ray gun power was set to 100 W. All spectra were recorded using an entrance aperture of 300 × 700 μm with a pass energy of 80 eV for survey spectra and 20 eV for high-resolution spectra. The instrument sensitivity was 7.5×10^5 counts s^{-1} when measuring the Ag $3d_{5/2}$ photoemission peak for a clean Ag sample recorded at a pass energy of 20 eV and 450 W emission power. Ag $3d_{5/2}$ full width half maximum (FWHM) was 0.55 eV for the same instrument settings. Binding energy calibration was made using Au $4f_{7/2}$ (83.96 eV), Ag $3d_{5/2}$ (368.21 eV) and Cu $2p_{3/2}$ (932.62 eV). The absolute error in the acquisition of binding energies is ± 0.1 eV, as quoted by the instruments manufacturer (Kratos); consequently, any binding energies within 0.2 eV can be considered the same, within the experimental error. Charge neutralisation methods were not required (or employed) in the measurement of these data. Sample stubs were earthed *via* the instrument stage using a standard BNC connector.

Samples were prepared by placing a small drop (≈ 20 mg) of the ionic liquid into a depression on a stainless steel sample stub (designed for powders) or on a standard stainless steel multi-sample bar (both Kratos designs). Ionic liquid samples were presented as thin films (approx. thickness 0.5-1 mm), thereby avoiding experimental complications associated with variable sample height. Initial pumping to high vacuum pressure was carried out in a preparation chamber immediately after thin film preparation to avoid significant absorption of volatile impurities. Pumping of ionic liquids was carried out with care as the high viscosities associated with these samples meant that significant bubbling due to removal of volatile impurities was observed. The pumping down process was consequently carried out slowly to avoid contamination of the UHV chamber by bumping/splashing of the ionic liquid samples. The preparation chamber pressure achieved was ≈ 10^{-7} mbar. Pumping-times varied (1-3 hr total) depending upon the volume, volatile impurity content and viscosity of the sample, *i.e.*, viscous ionic liquids were found to require longer pumping times. The samples were then transferred to the main analytical vacuum chamber. The pressure in the main chamber remained below 1×10^{-8} mbar during all XPS measurements, suggesting that all volatile impurities, such as water, are removed, leading to high purity samples [39].

XPS Data Analysis: For data interpretation, a spline linear background subtraction was used. Relative Sensitivity Factors (RSF) were taken from the Kratos Library and were used to determine atomic percentages [40]. Peaks were fitted using GL(30) lineshapes; a combination of a Gaussian (70%) and Lorentzian (30%) [41]. This lineshape has been used consistently in the fitting of XP spectra, and has been found to match experimental lineshapes in ionic liquid systems.

To aid visual interpretation of the XP spectra presented here, all spectra are normalised to the fitted area of N 1s peak of $[C_8C_1Im][IBr_2]$. This peak was selected to be used for normalisation as nitrogen atoms are present in all ionic liquids studied here in the same amount. This normalisation is applied to all XP spectra for a particular ionic liquid, and therefore does not affect the relative ratios of different elements within a definite ionic liquid.

Fitting procedure for C 1s of all ionic liquids studied herein was carried out using a four-component model developed by Licence group [22, 25]. For a thorough explanation of how the fitting model was developed in more detail, see ref. [22]. XP spectra for all ionic liquids were charge corrected by setting the measured binding energy of the aliphatic C 1s component ($C_{aliphatic}$ 1s) to 285.0 eV [22, 25].

Results and Discussion

Comparison to halide-based analogues

Figure 1 shows the survey XP spectra for $[C_8C_1Im][I_3]$ and $[C_8C_1Im][IBr_2]$. XPS signals were observed for all expected elements, carbon, nitrogen, iodine and/or bromine. It indicates that no silicon or oxygen impurities were detected, as has been observed previously for ionic liquids using XPS [18, 20, 21, 42]. In addition, no additional hydrocarbon signal was observed, indicating that the samples were of high purity. Take the spectrum of $[C_8C_1Im][IBr_2]$ as an example. The elements present in $[C_8C_1Im][IBr_2]$ are iodine, nitrogen, carbon and bromine. I 3d, N 1s, C 1s and Br 3d are the most probable ionization orbitals, as shown in Figure 1. In addition, 3p, 4p and 4d signals for iodine, as well as 3s and 3p signals for bromine are also found in the spectrum. Apart from the photoelectron emissions, KLL carbon and MNN iodine auger lines are also paralleled observed.

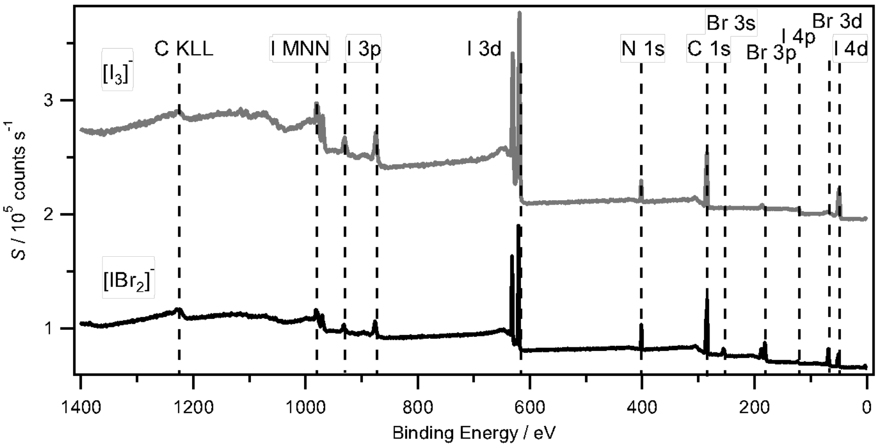

Figure 1 Survey XP spectra for $[C_8C_1Im][I_3]$ and $[C_8C_1Im][IBr_2]$.

The Br 3d XP spectra for $[C_8C_1Im][IBr_2]$ and $[C_8C_1Im]Br$ are shown in Figure 2a. The Br 3d high resolution spectrum is composed of an unresolved doublet peak which originates from the 3d orbital with a spin-orbital coupling energy difference of 1.05 eV [43], and area ratio of $3d_{5/2}$: $3d_{3/2}$ is 3:2, as expected from theory. In the case $[C_8C_1Im][IBr_2]$, there is also a shake-up satellite peak showing binding energy at 74.5 eV [41, 44]. This is due to the delocalisation of the negative charge as a consequent of the formation of $[IBr_2]^-$. The Br $3d_{5/2}$ peak for $[C_8C_1Im][IBr_2]$ shows binding energy at 68.7 eV, which is 1.2 eV higher than that of $[C_8C_1Im]Br$. It confirms that the negative charge within $[IBr_2]^-$ is spread over three atoms. It must be noted that after normalisation, the intensity of the Br 3d spectrum for $[C_8C_1Im]Br$ is only half as much as that of $[C_8C_1Im][IBr_2]$, as expected as there is only one bromine atom within $[C_8C_1Im]Br$.

The typical I 3d spectrum is composed of a doublet peak which is originated from 3d orbital with a spin-orbital coupling energy difference of 11.5 eV [43] and area ratio of $3d_{5/2}$: $3d_{3/2}$ is 3:2. In this paper, unless otherwise stated, the $3d_{5/2}$ component is selected to ensure valid comparisons, simply because the intensity for this component is larger. Figure 2b demonstrates I $3d_{5/2}$ XP spectra for both of $[C_8C_1Im][IBr_2]$ and $[C_8C_1Im][I_3]$. In order to give visual comparison, the spectrum for $[C_8C_1Im]I$ is also included. As shown in Figure 2b, there is only one iodine electronic environment for $[C_8C_1Im]I$ as there is only one peak for I 3d$_{5/2}$, 618.5 eV with a FWHM value of 1.0 eV, and no shake-up feature, as expected, as I$^-$ contains no delocalised π-system. In the case of $[C_8C_1Im][IBr_2]$, there is only one iodine electronic environment as well with a binding energy at 620.9 eV and a FWHM value of 1.1 eV. It must be noted that due to the formation of the electronic delocalised $[IBr_2]^-$, a shake-up feature showing binding energy at 626.2 eV can also be observed. The I 3d$_{5/2}$ binding energy for $[C_8C_1Im][IBr_2]$ is significantly higher (2.4 eV) than that of $[C_8C_1Im]I$. Therefore, the iodine atom in $[C_8C_1Im][IBr_2]$ is significantly more electropositive than the iodine atom within $[C_8C_1Im]I$. This observation is as expected as the negative charge in $[C_8C_1Im]I$ traditionally drawn as being located solely on one atom, whereas for $[C_8C_1Im][IBr_2]$ the negative charge is spread over three atoms.

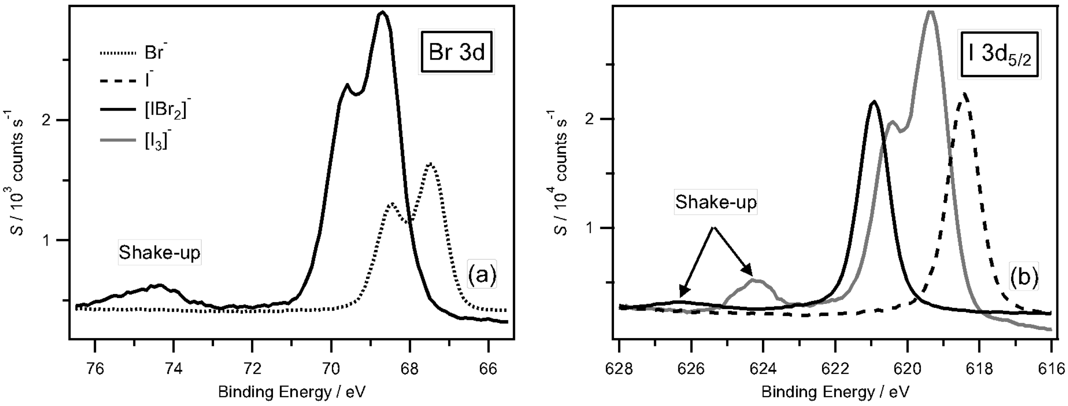

Figure 2 XP spectra of $[C_8C_1Im]Br$, $[C_8C_1Im]I$, $[C_8C_1Im][I_3]$ and $[C_8C_1Im][IBr_2]$ for: (a) Br 3d and (b) I 3d$_{5/2}$.

The I 3d$_{5/2}$ spectrum for $[C_8C_1Im][I_3]$ is composed of a shake-up satellite feature as $[I_3]^-$ contains delocalised π-system as well, and an unresolved doublet peak showing binding energy between 622.0 eV and 618.0 eV. Clearly, iodine atoms within $[I_3]^-$ are in two different electronic environments. A satisfactory fitting can be carried out by using two components, *i.e.* I$_{central}$ and I$_{terminal}$, as shown in Figure S2d. For a more detailed description of the I 3d spectrum for $[C_8C_1Im][I_3]$, see ref. [45]. The binding energy of I$_{central}$ 3d$_{5/2}$ for $[C_8C_1Im][I_3]$ is found at 620.4 eV (see Table S1), which is 0.5 eV lower than that of $[C_8C_1Im][IBr_2]$. It is apparent that bromine atom is more electronegative than iodine atom and has more electron withdrawing effect on the I$_{central}$ atom. Consequently, when compared to that of $[IBr_2]^-$, the I$_{central}$ atom within $[I_3]^-$ is more negatively charged, and thus exhibits lower binding energy.

Anion basicity

The direct data of Kamlet-Taft hydrogen bond acceptor ability (β value), as an indicator of the anion basicity, for trihalide ionic liquids are insufficient due to the strong absorbance of trihalide anions in the UV-vis region, which makes it impossible to determine the basicity through the use of dyes. In this study, comparisons of the anion basicity for two trihalide ionic liquids have been obtained from measured N 1s binding energies, as there is a linear correlation between them and β values [22, 25, 29]. A brief demonstration is shown in Table 1. It concludes that $[I_3]^-$ and $[IBr_2]^-$ can be both considered as the least basic anions. It must be noted that, due to the different technique for the calculation of the basicity of anions (β value), it is better to cite these values from the same literature to avoid introducing errors.

Table 1 N 1s binding energies and β values for all ionic liquids.

Ionic liquids	N 1s binding energy / eV	β [46]
$[C_8C_1Im][Tf_2N]$	402.1 (402.101) [22]	0.47
$[C_8C_1Im][I_3]$	402.1 (402.096)	
$[C_8C_1Im][PF_6]$	402.1 (402.070) [22]	0.53
$[C_8C_1Im][IBr_2]$	402.1 (402.051)	
$[C_8C_1Im][BF_4]$	402.0 (401.980) [22]	0.63
$[C_8C_1Im][TfO]$	402.0 (401.966) [22]	0.64
$[C_8C_1Im]I$	401.8	0.81
$[C_8C_1Im]Br$	401.7	0.89
$[C_8C_1Im]Cl$	401.6 [22]	0.98

Beam damage

The investigation of ionic liquids by XPS sometimes requires a sufficiently long period of acquisition time. Therefore, the stability of ionic liquids under prolonged exposure to X-ray irradiation has to be addressed. Previous works have shown that the surface beam-damage will occur to some ionic liquid systems [47, 48]. In this study, $[C_8C_1Im][IBr_2]$, as a representative sample, was studied over an extended period of time by XPS. The Br 3d, I $3d_{5/2}$ and N 1s spectra are presented in Figures 3a, 3b and 3c respectively.

As shown in Figure 3a, it is apparent that after 700 min irradiation under X-ray beam, there is a shoulder observed at the lower binding energy region which indicates that bromine atoms are in two electronic environments. A satisfactory fitting could be achieved by setting both of the bromine environments with the spin-orbital coupling energy gap of 1.05 eV, as shown in Figure 3e. The component of the main photoelectron peak showing higher binding energy (Br $3d_{5/2}$ = 68.6 eV) corresponds to the Br atom present in $[IBr_2]^-$. Unexpectedly, the other component shows $3d_{5/2}$ binding energy at 67.5 eV which is the same as that obtained for $[C_8C_1Im]Br$ (see Figure 2a for a comparison), meaning that $[C_8C_1Im]Br$ is formed in the system by X-ray irradiation. It must be noted that Br^- has never been involved in the preparation of $[C_8C_1Im][IBr_2]$.

From another point of view, as shown in Figure 3c, it is clear that over the period of the acquisition time, t ≈ 680 min, there is no significant change in intensity for the N 1s peak. However, the measured binding energy for N 1s is found shifted to lower value by 0.1 eV. It has to be emphasized that the experimental error associated with XPS is of the order ± 0.1 eV, meaning that this measured shift in binding energy is negligible. However, in this study, as there is Br^- formed during XPS measurement, the sample become a mixture of $[C_8C_1Im][IBr_2]$ and $[C_8C_1Im]Br$. Due to the high basicity of Br^-, the binding energy of N 1s should shift to lower value. As a result, we may expect that by irradiating the sample for longer period of time, the shift of the measured binding energy of N 1s would be more noticeable with the increasing of the amount of Br^- formed in the mixture.

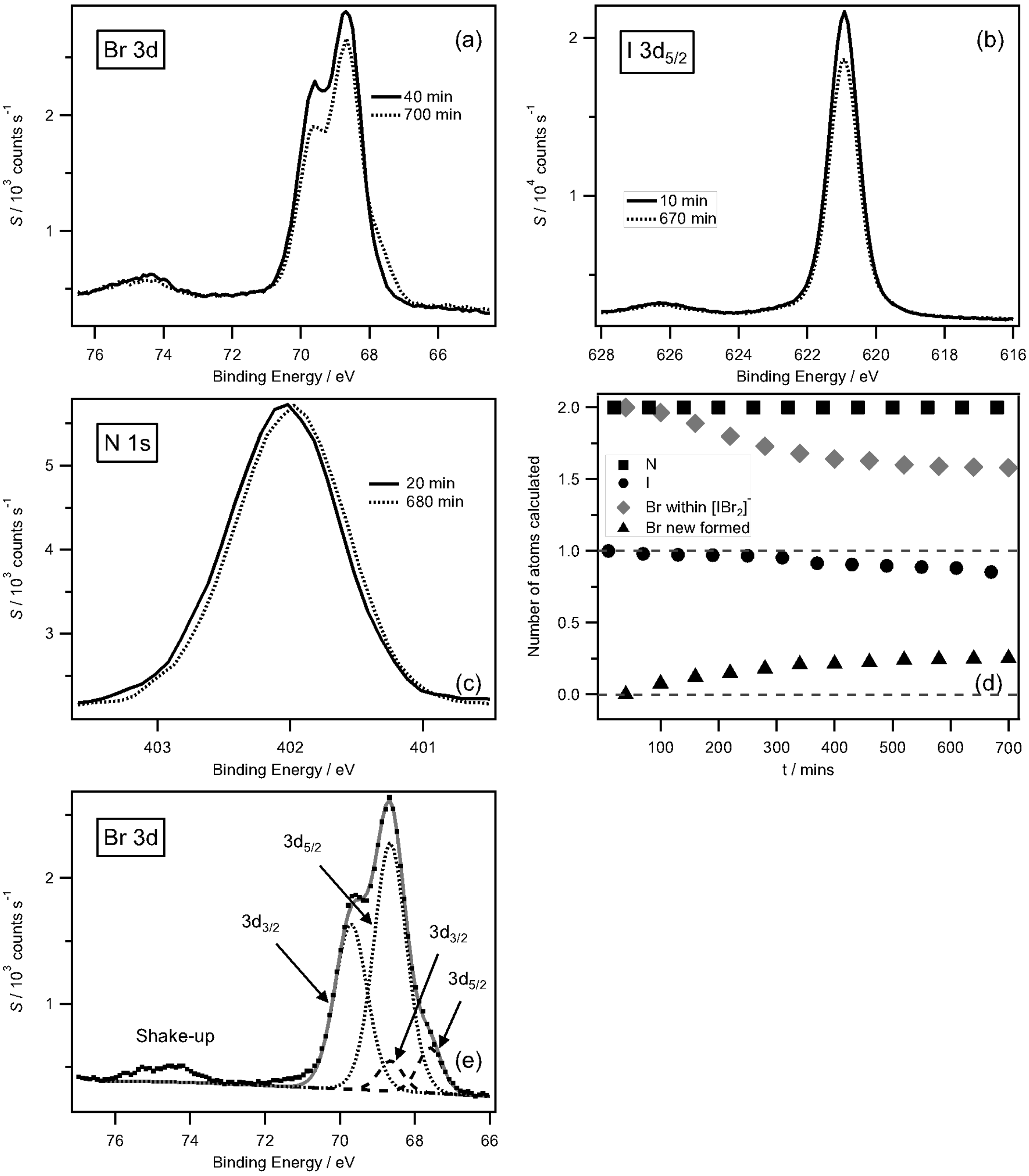

Figure 3 XP spectra of $[C_8C_1Im][IBr_2]$ (the first acquisition and the last acquisition) for: (a) Br 3d, (b) I $3d_{5/2}$ and (c) N 1s. (d) Number of atoms for N, I, Br within $[IBr_2]^-$ and Br (new formed) from XPS as a function of X-ray exposure time (STDEV available in Table S2). (e) Br 3d XP spectrum with fittings for $[C_8C_1Im][IBr_2]$ after 700 min of X-ray irradiation.

On the contrary, an intensity loss in both of the Br 3d and I $3d_{5/2}$ components of the anion can be observed, as shown in Figures 3a and 3b. It was calculated that after about

700 min of X-ray irradiation, the total numbers of bromine atom and iodine atom in loss are 0.17 and 0.15 respectively (see Table S2 in Supplementary Information). A detailed presentation of the intensity changes is illustrated in Figure 1d. It suggests that the beam-induced decomposition caused a stoichiometric loss of Br atom and I atom, taking the 20% experimental error of XPS in semi-quantitative analysis into account. Meanwhile, the intensity of the new formed Br peak increased along with the exposure time. It proposed that due to the beam damage effect, a portion of the $[IBr_2]^-$ anion has been decomposed to form Br^- and IBr, the latter of which left the ionic liquid system subsequently under the high vacuum condition.

Conclusions

We have successfully measured XP spectra for $[C_8C_1Im][I_3]$ and $[C_8C_1Im][IBr_2]$. The electronic environment of each element present in ionic liquids studied herein is analysed and compared to their halide-based analogous. Comparisons of the anion basicity, which can be correlated to the N 1s binding energy, are also made. It concludes that $[I_3]^-$ and $[IBr_2]^-$ can be both considered as the least basic anions. The beam damage is demonstrated for $[C_8C_1Im][IBr_2]$ over a long period of time. It suggests that the beam-induced decomposition happened which gave rise to a stoichiometric loss of Br atom and I atom.

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