Quantifying the Polymeric Capping of Nanoparticles with X-Ray Photoelectron Spectroscopy

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Abstract

X-ray Photoelectron Spectroscopy was used to characterise silver nanoparticles capped with poly(ethylene) glycol in a room temperature ionic liquid (RTIL), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]). The amounts of oxygen and silver present in nanoparticles capped with different molecular weight thiolated PEG chains were monitored, and the number of thiolated PEG chains per nanoparticle was calculated, an *in situ* characterisation not previously possible.

Main Text

The capping of nanoparticles controls a large number of their properties, including reactivity,[1] stability,[2] and susceptibility to electron transfer.[3] However, there is a lack of detailed understanding of the structure and the extent to which a nanoparticle is capped, particularly *in situ* in solution. The characterisation of the capping agents *in situ* is highly important for the development of the controlled synthesis of nanoparticles and the use of the nanoparticles in a broad range of fields including nanocatalysis[4] and biomedical applications.[5]

X-ray Photoelectron Spectroscopy (XPS) is a powerful surface characterisation technique frequently applied to quantitatively understand solid materials. However, recently XPS has been used to analyse samples of ionic liquids (ILs),[6] which have such low volatilities that they can be used in the high vacuum environment of the instrument, allowing characterisation of both the ionic liquids themselves[7] and any dissolved[8] or suspended[8b, 9] materials *in situ*. As ILs have a number of desirable physicochemical properties such as recyclability, tuneable hydrophilicity and miscibility as well as wide electrochemical windows,[10] ILs have been used as an alternative medium for many processes. In particular, ILs have been demonstrated to enhance the physical and chemical properties of nanoparticles and stabilize the nanoparticle catalysts.[11] The use of ionic liquid in XPS measurement also facilitates studies of metal deposition *in situ*, for example potassium[12] and rubidium[13] deposition, allowing the investigation of the fundamental kinetic and thermodynamic properties of the processes.

This work seeks to use XPS to quantify the polymeric capping of silver nanoparticles suspended in a Room Temperature Ionic Liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]). Thiolated poly(ethlyene) glycol (PEG) is used as a proof-of-concept example to demonstrate the developed technique. PEG has been frequently used as a capping agent due to its acid resistance and customisability.[14]

The amounts of silver and oxygen atoms present are monitored, allowing the first insight into the number of thiolated PEG chains attached to Ag NPs in solution. The wrapping of thiolated PEG around the Ag NP is potentially crucial in protecting the silver core against dissolution and other chemical reactions. In an electrochemical context, the capping molecules are thought to reversibly partially `unwrap' to allow electrical contact to be made between the nanoparticle core and the electrode.[1]
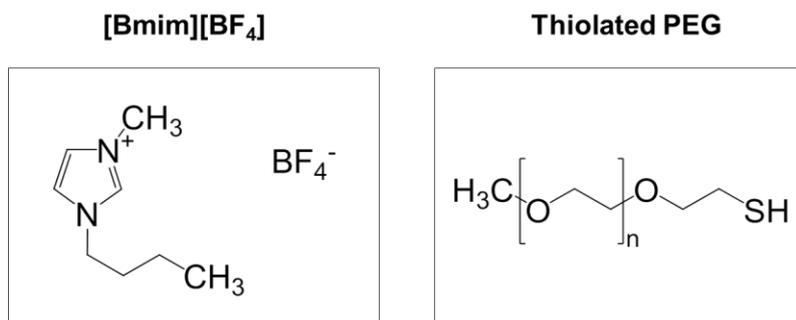
Figure 1: Chemical structures of [Bmim][BF4] and thiolated PEG.

First, the XPS spectra of pure ionic liquid in the absence of nanoparticles were recorded. The survey of the pure ionic liquid across the binding energies shown in Figure 2 shows that all the expected peaks characteristic of the components of the ionic liquid (carbon, boron, nitrogen, and fluorine) are observed. The slight variation in binding energy (± 0.1 eV) between samples was attributed to charging. Notably, in the blank IL only an extremely weak O1s peak is observed at a binding energy of around 530 eV, quantified as 0.6 atomic% oxygen, indicating that the IL has a low surface water content. The atomic% composition of the blank IL is shown in Table 1. The measured values are close to the expected for all elements, and comparable with analyses of this IL performed by others.[7c, 15] We estimate the relative error in compositions as +/- 10%.[6] The sample is found to be slightly richer in F and B and slightly deficient in C and N compared with the expected values from the molecular structure. Since B and F are both found in the anion and C and N both found in the cation, this may indicate that the surface of the IL has a slight preference for the anionic species.
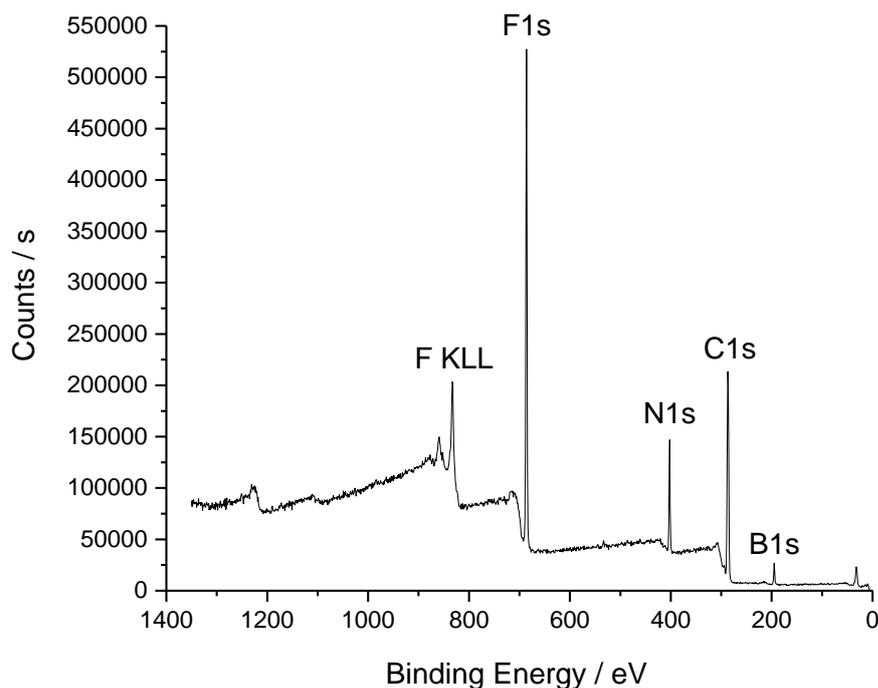
Figure 2: A survey XPS scan of pure [Bmim][BF₄].

Table 1. **Measured compositions of IL samples by XPS. Error is XPS composition estimated as +/-10% of each value.**

Element	Atomic%				
	Molecular structure of IL	Blank IL	IL + PEG 2000 MW	IL + Ag + PEG 2000 MW	IL + Ag + PEG 6000 MW
B	6.7	7.1	8.1	6.9	6.4
C	53.3	49.2	51.8	48.1	48.9
N	13.3	11.8	12.1	11.6	11.9
O	0	0.6	0.6	1.1	1.2
F	26.7	31.2	27.4	31.8	31.4
Ag	0	0	0	0.5	0.2

A sample of IL containing poly(ethylene) glycol methyl ether thiol (thiolated-PEG) with molecular weight 2000 Dalton was prepared by combining 1.8 μL of a 2mg/mL solution of thiolated PEG into 30 μL of [Bmim][BF₄] (99 %, IoLiTec, Germany) and placing it under 0.1 mbar vacuum overnight to remove any water present. XPS of this sample gave spectra very similar to the blank IL. As can be seen in Table 1, the IL containing PEG 2000 MW showed a slightly higher carbon surface content (51.8 atomic% vs. 49.2 atomic% in the blank

IL). However the oxygen level was identical, and if PEG were present at the surface, the oxygen level would be expected to increase. Therefore it seems that addition of PEG 2000 MW to the IL does not result in detectable PEG at the surface of the droplet by XPS. Instead we ascribe the increased C1s signal to environmental contamination which is a common feature for samples analysed by XPS.

Next, the XPS responses of ionic liquid in the presence of Ag NPs were studied. Citrate capped nanoparticles were prepared as described previously,[16] and recapped with poly(ethylene) glycol methyl ether thiol (thiolated PEG, 2000 MW or 6000 MW) by placing 10 μL of a 2 mg/mL solution of thiolated PEG into a 490 μL solution of 20 nm (diameter) nanoparticles, and allowed to sit for three hours. Then, an aliquot of nanoparticles (90 μL) was combined with 30 μL of [Bmim][BF$_4$] (99 %, IoLiTec, Germany) and placed under 0.1 mbar vacuum overnight to remove the water and other volatile impurities, resulting in a solution of 2×10^{-5} mol m^{-3} Ag NPs. All aqueous solutions and nanoparticle suspensions were made using deionized water from Millipore with resistivity not less than 18.2 MΩ cm at 25 °C.

A 5 μL droplet of the NP-containing IL was placed on a borosilicate glass slide and analysed by XPS; detailed in SI. The droplets measured around 3mm in diameter. The resulting XP spectra of the sample showed indistinguishable C1s, N1s, F1s and B1s peaks from the blank IL. Samples containing Ag NPs capped with thiolated PEG (2000 MW or 6000 MW) in [Bmim][BF$_4$] ionic liquid show additional peaks as compared with the pure ionic liquid or the IL containing PEG 2000 MW. Figure 3 shows the O1s peaks in the blank IL and IL containing Ag NPs capped with 2000 and 6000 MW thiolated PEG. The O1s signal clearly increases in intensity on addition of the Ag NPs. This is reflected in the increase in O concentration for these samples shown in Table 1. Figure 4 shows the Ag 3d peaks recorded from the Ag NP containing samples. Ag can clearly be detected. The Ag 3d peaks are observed at binding energies of 375 and 369 eV corresponding to Ag3d$_{3/2}$ and Ag3d$_{5/2}$ peaks from metallic silver. As expected, silver is only detectable by XPS in samples containing Ag NPs. In the case of the 2000 MW PEG, the observed O:Ag ratio was 1.8 ± 0.2, whilst in the case of the 6000 MW PEG, the observed surface O:Ag ratio in the surface layer was 4.3 ± 0.4.
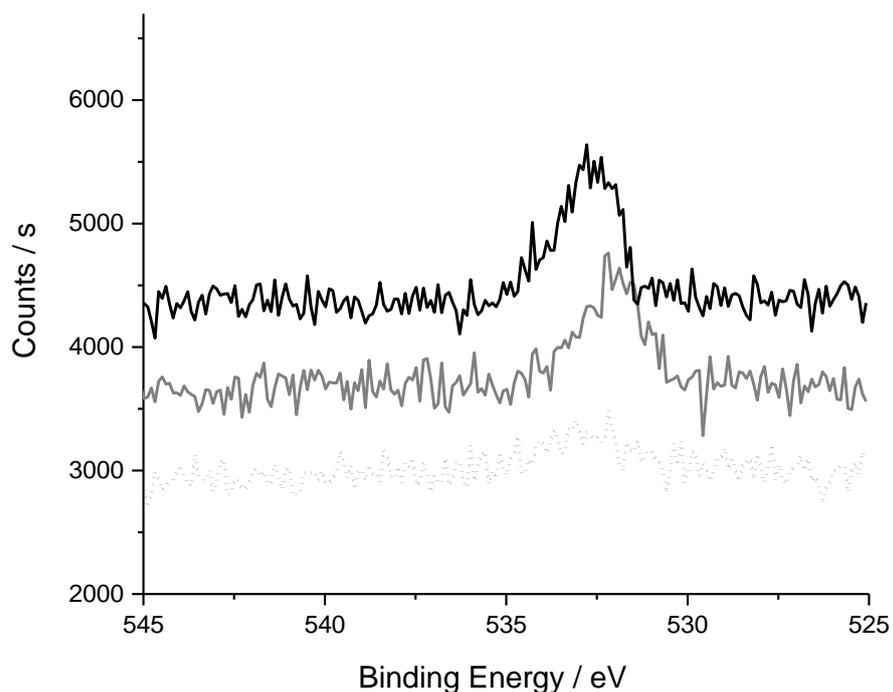
Figure 3: Oxygen 1s signals of blank ionic liquid (dotted line), 2000 MW thiolated PEG capped Ag NPs (grey solid line) and 6000 MW thiolated PEG capped Ag NPs (black solid line) as detected by XPS.
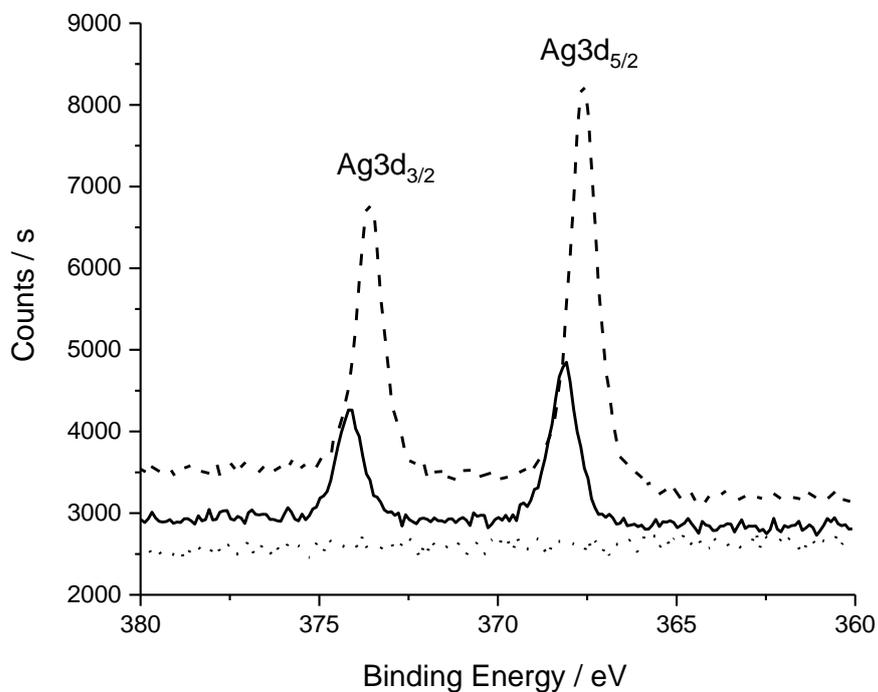

Figure 4: Ag 3d signals of blank ionic liquid (dotted line), 2000 MW thiolated PEG capped Ag NPs (dashed line) and 6000 MW thiolated PEG capped Ag NPs (black solid line) as detected by XPS.

The difference in the ratio of silver to oxygen present reflects the length of the thiolated PEG chain, with each 6000 MW thiolated PEG chain containing 135 oxygen atoms, and each 2000 MW thiolated PEG chain containing only 44 oxygen atoms. We can therefore use the XPS measurement to determine how many thiolated PEG chains are attached to each nanoparticle. This is done by calculating the number of silver atoms in each nanoparticle, multiplying this number by the Ag:O ratio in each case to obtain the number of oxygen atoms present, and dividing by the number of oxygen atoms in each thiolated PEG chain of the given molecular weights. From this, $1.0\pm0.1 \times 10^4$ thiolated PEG chains of 2000 MW and $7.7\pm0.8 \times 10^3$ thiolated PEG chains of 6000 MW are attached to the silver nanoparticles. This determination is an upper limit, as it is possible that some free PEG is present in the samples, although this was not detected in the PEG containing IL in the absence of Ag NPs. A simple estimation of the number of chains that make up a saturated monolayer − calculated by dividing the surface area of a nanoparticle by the van der Waals radius of a sulfur atom − is 1.2×10^5 chains. This suggests that the thiolated PEG chains are not very tightly packed around the silver nanoparticle.

In conclusion, XPS has been used to characterise thiolated PEG capped Ag NPs in a RTIL by quantifying the ratio of silver atoms to oxygen atoms. This analysis allowed the calculation of the number of thiolated PEG chains per nanoparticle as $1.0\pm0.1 \times 10^4$ thiolated PEG chains of 2000 MW or $7.7\pm0.8 \times 10^3$ thiolated PEG chains of 6000 MW.

Supporting Information

The Supporting Information includes the detail of chemical reagents, instrumentation, measurement procedures and the characterisation of Ag NPs.

Acknowledgements

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