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Sorption of aurocyanide and tetrachloroaurate onto resin with guanidine ligand—an XPS approach

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Abstract

The guanidine ligand attached to vinylbenzyl chloride matrix as well as its sorption ability to tetrachloroaurate and dicyanoaurate ions were investigated upon using X-ray photoelectron spectroscopy. The form of metallic gold, Au(0), was not observed on gold loaded resin surface when solutions of tetrachloroaurate or potassium dicyanoaurate were used. Complete elution of gold was achieved for both regeneration media: thiourea solution and mixture of sodium hydroxide and benzoate. The results demonstrate that XPS can also be a powerful technique for the analysis of the oxidation state of sorbed metal and can be a suitable method for the confirmation of functional groups incorporated in the polymer.

Keywords: XPS; Gold sorption; Guanidine resin

1. Introduction

Ion exchange resins are employed in the extraction of valuable metal ions. Gold recovery is mostly based on extraction of chloride, thiourea or, of cyanide complexes. The extraction processes are governed by ion exchange, coordination, or by simultaneous action of both of these processes. X-ray photoelectron spectroscopy is widely used for the investigation of surface functional groups and can show the forms of gold species on the polymer surface [1–8]. It is a popular technique for surface characterisation that has been used extensively to study the chemical composition of surface [1]. To our best knowledge, XPS studies of polymer matrix obtained from vinylbenzyl chloride have not yet become popular. There is a scarce number of contributions on this subject [9,10].

This paper deals with X-ray photoelectron spectroscopy, XPS, study of guanidine modified copolymer of vinylbenzyl chloride and divinylbenzene. For the purpose of simplicity, this material will be called AG3 resin within this paper. The chemical structures of the resin as well as gold loaded forms of obtained complexes were analysed by XPS and FTIR spectroscopy. Such analyses allow assigning the possible structures of sorbed species.

2. Experimental

2.1. Materials

The neat copolymer of vinylbenzyl chloride, VBC, and divinylbenzene, DVB, containing 2 wt% of cross-linker, was obtained in the form of expanded gel according to the procedure described in another paper [11]. This material served as the polymer matrix for modification.

The reaction with guanidine, resulting in the preparation of suitable resin, was carried out in two steps. In the first one, polymer was aminated with the excess of 1,3 diaminopropane. The diamine was added to dioxane swollen copolymer with the molar ration of 10:1, amine:chloride, in order to prevent the matrix from branching or cross-linking. Next, amino groups attached to the polymer matrix were transformed to guanidine ligands in the reaction with cyanamide. This reaction was carried out in DMSO solution by refluxing for 7 h. During the reaction the pH of

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the mixture was adjusted to pH 8–9 using a solution of 5 M NaOH. After that time polymer beads were placed in a column and washed with water and finally with 0.001 M HCl. The scheme of reaction is shown in Fig. 1. The synthetic way resulted in resin AG3 displaying water content equalling 2.73 g/g, nitrogen content 11.9 mmol/g and anion exchange capacity 4.7 mmol/g [12]. Water content was measured using the centrifugation technique in which about 1 g of polymer swollen in water was placed in a glass vial with the glass bottom fritted and centrifuged for 5 min at 3000 rpm. After drying under high vacuum at 60 °C for 24 h the polymer was weighed. Water content expressed as ratio $(m_w - m_d)$ and m_d, where m_w is the weight of the wet polymer and m_d is the weight of the dry polymer. The nitrogen content was determined using Kiejdahl's method applied to polymers [13]. The chlorine content was measured through burning of ca. 30 mg of the dry polymer sample in an oxygen-filled flask. The products of burning were adsorbed in diluted hydrogen peroxide solution. The content of Cl was determined using Volhardt's method of titration [14]. Anion exchange capacity was determined according to Hecker's method [12] i.e. approximately, 1 g of swollen polymer was placed in an ion exchange column and washed in 250 ml of 1 M HCl, about 200 ml of 0.001 M HCl until the final filtrate concentration will equal 0.001 M HCl. Next 500 ml of 4% sodium sulphate in 0.05 M NH_4OH was passed through the ion exchange column and the eluate was collected in a 500 ml volumetric flask and analysed for its chloride concentration.

Aldrich Chemical Co supplied all reagents.

2.2. Sorption and desorption

A batch method was used to examine the sorption and desorption of gold. The gold uptake was performed from hydrochloric solutions at room temperature. The samples were immersed in solution for 48 h. Next, the solutions were removed and Au concentration was determined by Perkin–Elmer Analyst 100 atomic spectrophotometer (242.8 nm wavelength). The mass balance served for calculating the amounts of sorbed and desorbed gold. The same samples of resin AG3 were evaluated in XPS study.

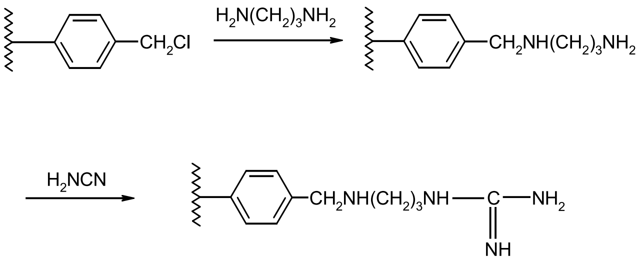

Fig. 1. Scheme of guanidyl ligand incorporation into VBC/DVB copolymer.

The resin samples were preloaded with gold in order to obtain significant signal of Au in the XPS spectra. The first sample (0.746 mg of swollen beads) was put in contact with 300 cm^3 of potassium dicyanoaurate in 0.001 M HCl solution that contained 500 mg/dm^3 of Au. The second sample of the resin (0.378 mg of swollen beads) was put in contact with 150 cm^3 of tetrachloroaurate solution in 0.1 M HCl that contained 478 mg/dm^3 of Au.

Preloaded samples of the resin with gold sorbed to the level of 497 mg Au per 1 g (first sample) and 445 mg of Au per 1 g of dry resin (second sample) were put in contact with two elution solutions. The first one, 150 cm^3 of a 5% thiourea in 0.1 M HCl solution, and the second, 850 cm^3 of 0.5 M mixture of sodium hydroxide and sodium benzoate, were used upon the first and second loaded resins, respectively. More details concerning the parameters for the method of sorption and desorption can be found in our earlier paper [11,15].

2.3. Sample analysis

X-ray photoelectron spectroscopy (XPS) was performed on SPECS UHV System equipped with PHOIBOS 100 spectrometer and SPECLAB software. X-ray source was generated using Mg anode operating at 100 W (wide-range scan) and 200–300 W (high resolution spectra). The spectrometer energy scale was calibrated using Au(4f7/2), Ag(3d5/2) and Cu(2p3/2) lines at 84.2, 367.9 and 932.4 eV, respectively. The analyser mode was set on constant serving of energy of 30 eV (survey scan) and 5 eV (narrow scan). Sample charging was compensated using an electron flood gun with 0.5 mA current and 0.1 eV energy. The detection angle was normal near the surface. The base pressure in the UHV analysis chamber was below 1×10^{-9} mbar. N1s, Au4f and Cl2p peaks of VBC/DVB copolymer, resin AG3 after modification with guanidine ligands, the resin of gold loaded and unloaded from $KAu(CN)_2$ or $HAuCl_4$ solutions were fitted and derived by SPECSLAB and Origin 7.0 professional software packages using Gaussian–Lorenzion curve profile and Shirley baseline.

FTIR spectra in KBr pellets were recorded on a Perkin–Elmer System 2000 spectrophotometer.

3. Results and discussion

3.1. Progress of guanidine modification

The vinylbenzyl chloride copolymer, VBC/DVB, containing 2 wt% of divinylbenzene was obtained in suspension polymerisation in the presence of toluene. These parameters allow to obtain the polymer within a gel expanded structure [16].

The synthesis of the resin AG3 bearing guanidine ligand is represented in Fig. 1. Modification of VBC/DVB copolymer was performed by a reaction of chlorine atom of vinylbenzyl units of polymer matrix with 1,3 diaminopropane and transformation of this derivative to guanidine by attaching cyanamide. The obtained resin bears long chain of guanidine ligand. The analysis of FTIR spectrum, Fig. 2, has confirmed the presence of guanidine functionalities. The fact of guanidine attachment is proved by the disappearance of the band at 1265 cm^{-1} assessed to CH$_2$Cl groups and appearance of the bands at 1549 cm^{-1} and at 1650 cm^{-1}. According to Zhang and co-workers [10] there are the following characteristic peaks for polymeric guanidine: $\nu_{C=N}$ at 1689–1650 cm^{-1} (stretching vibration), δ_{NH} at about 1640 cm^{-1} (scissoring bending), ν_{C-N} at about 1300 cm^{-1} (stretching vibration). A wide, strong intensive band at 3409 cm^{-1} can be attributed to N–H and NH$_2$ bonds [10,11,16–18].

A survey scans of VBC/DVB copolymer, line a, neat resin AG3, line b, and resin loaded from solution of aurocyanide, line c, are presented in Fig. 3. Since polymer matrix was prepared from vinylbenzyl chloride and divinylbenzene they should compose of carbon, hydrogen, chlorine and, for the resin only, nitrogen. XPS surface composition of obtained materials is presented in Table 1. Surprisingly, oxygen was determined in the samples. This fact allowed us to suppose the presence of C–OH groups obtained after hydrolysis of CH$_2$Cl groups [19]. There are also two contamination processes that affected the surface evaluation: adsorption from the surrounding air and from the glassware. Whereas, the first enlarged content of carbon the second one resulted in the appearance of silicon on the surfaces [20]. Due to the presence of Si band and its stable location in all XPS spectra, Si2p3/2 line was used as a supplementary reference line of our XPS study.

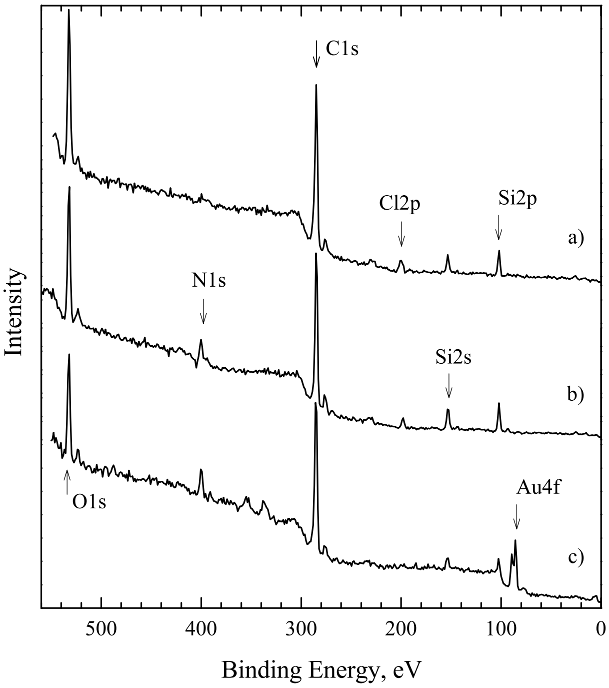

Fig. 3. XPS survey scan of VBC/DVB copolymer (a), AG3 resin (b), AG3 resin gold loaded from KAu(CN)$_2$ (c).

3.2. Narrow scan of N1s region

The spectra of the resin AG3 are shown in Fig. 4. Here, the line a shows a signal near 400 eV that ascribes N1s nitrogen atoms. Deconvolution of this region reveals three peaks. The first one, at 398.85 eV, can be attributed to the neutral imine bonds –CH=N– [21,22,25], the next two peaks at 400.00 and 400.57 eV can be related to –NH– groups and to free amine groups [3], respectively. Partition of areas

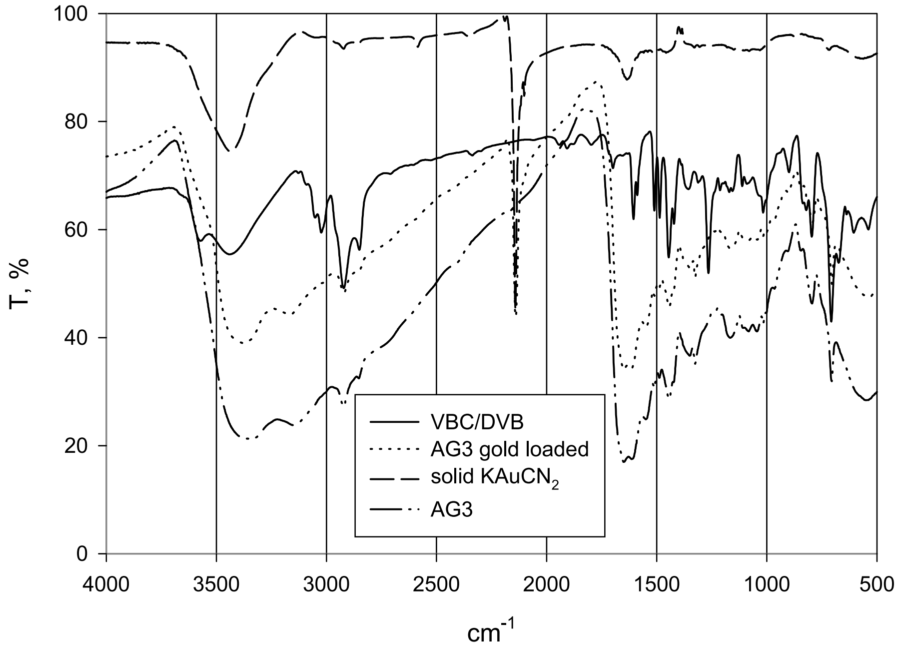

Fig. 2. FTIR spectra of VBC/DVB copolymer, AG3 resin, dicyanoaurate gold loaded AG3 resin and solid KAu(CN)$_2$.

Table 1
XPS surface composition (as % of all elements present) in VBC/DVB matrix and the resin

Sample number	Polymer	Sample composition (%)					
		C1s	N1s	O1s	Si2p	Cl2p	Au4f
1	VBC/DVB copolymer	67.8	–	25.8	8.1	2.3	
2	Neat resin	63.2	5.7	19.4	10.0	1.7	
3 Loaded	Resin $KAu(CN)_2$ loaded	69.4	8.1	15.1	5.9	0	1.5
3 Unloaded	Resin unloaded	67.3	6.5	19.9	5.3	1.0	
4	Resin $HAuCl_4$ loaded	67.5	7.8	14.4	3.0	5.9	1.2
4 Unloaded	resin unloaded	67.4	6.2	19.2	3.9	1.3	

under N1s peaks show that *N*-alkyloguanidine ligand is adequate to the structure containing 4 atoms of N (ratios of nitrogen forms in substituted amine groups: imine groups: free amine groups reaches 2:1:1), Table 2 and Fig. 4. It clearly shows that guanidine groups attached to the matrix can be presented as shown in Fig. 1. As it is given in Fig. 4b, two new peaks at 398.45 and 401.2 eV have appeared. The low energy peak can be assigned to cyanide of gold complex $Au(CN)_2^-$ when aurocyanides were sorbed [3,4,23]. The high-energy peak, which appeared at 401.2 eV, can be related to protonated free amine groups [23]. Aurocyanide loading was performed from 0.001 M HCl solution and some amine groups of resin should be protonated. Fig. 4c, presents the state of resin surface after aurocyanide desorption within 5% solution of thiourea in 0.1 M HCl solution. As one can notice the peak at 398.45 eV has disappeared. The mass balance analysis proved that gold desorption process was completed.

3.3. Narrow scan of Au 4f region

3.3.1. Dicyanoaurate sorption

Sorption of gold complexes, $Au(CN)_2^-$, from potassium dicyanoaurate revealed that binding energy of Au(I) 4f(7/2) 85 eV was invariable. This may suggest that Au(I) was sorbed on resin AG3 in its unchanged oxidation state [2,4,5]. The XPS spectra for potassium dicyanoaurate, line a, the loaded resin from aurocyanide solution, line b, and for unloaded resin, line c, are shown in Fig. 5. One can observe that line Au 4f is unchanged.

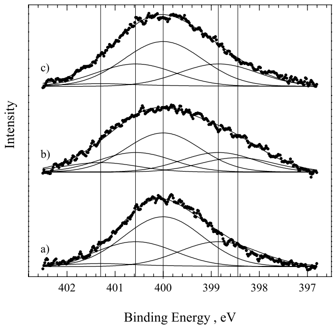

Fig. 4. Deconvolution of N1s spectra of AG3 resin (a), AG3 resin gold loaded from $KAu(CN)_2$ solution (b), AG3 resin state after gold unloaded (c).

As shown in Table 1 samples loaded with gold showed an average N/Au ratio of 1.6. It is possible that it corresponds to possible different gold complexes. Some species of Au(I) can be sorbed on resin surface. Basing on XPS quantitative calculations and literature quote [24] we can suppose that $Au(CN)_2^-$, $Au_2(CN)_3^-$, AuCN or mixture of AuCN and $Au(CN)_2^-$ compounds might be sorbed on to the polymer surface [24]. It is difficult to distinguish between these species, although, some authors tried to do that. Warshawsky has reported that binding energy for AuCN is 85 eV and for $KAu(CN)_2$ is 84.9 eV [4]. This difference of binding energies is too small to distinguish these compounds. Binding energies for gold loaded resins [3–5] and activated carbon were reported [23,25]. Their IR spectra were used to confirm the presence of the $Au(CN)_2^-$ anions and AuCN species. It was observed that characteristic peaks changed from 2530 to 2556 cm^{-1} at different pH [3–5,23,25].

As it is shown in Fig. 4b, the new peak, appearing at

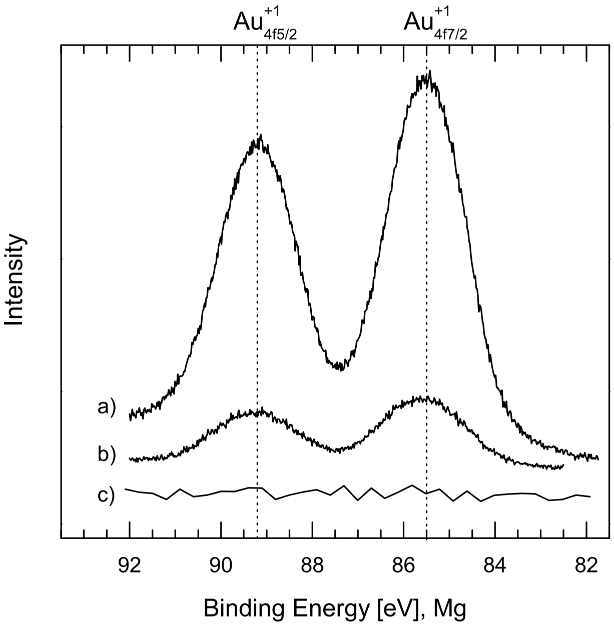

Fig. 5. XPS Au4f spectra of solid $KAu(CN)_2$ (a), AG3 resin gold loaded from $KAu(CN)_2$ (b) and AG3 resin state after gold unloaded (c).

Table 2
Binding energies and related partition of N1s components for the neat, gold loaded from $KAu(CN)_2$ solution and the unloaded resin

Resin sample[a]	−C=N 398.85 eV	−NH− 400.00 eV	NH_2 400.57 eV	$Au(CN)_2^-$ 398.45 eV	$-NH_3^+$ 401.3 eV
Neat 2	0.25	0.5	0.25	–	–
Loaded 3	0.25	0.42	0.25	0.16	–
Unloaded 3	0.24	0.48	0.24	–	0.04

[a] As presented in Table 1.

398.45 eV of N1s, can represent the ion exchange between the protonized resin and $Au(CN)_2^-$ anion. Metallic gold Au(0) was not detected in this case. This is consistent with our FTIR spectrum shown in Fig. 2. The spectrum shows a sharp band at 2540 cm^{-1} assigned to C≡N stretching vibration of $Au(CN)_2^-$ complex after gold loading. Solid dicyanoaurate $KAu(CN)_2$ salt shows peak at 2541 cm^{-1}. There is no appreciable change on location of C≡N group during sorption. Polymeric AuCN showing a CN frequency at 2261 cm^{-1} was not observed on the resin surface [2,3,25]. In the acidic solution, it is possible for the following reaction to appear

$$H^+ + Au(CN)_2^- \rightarrow AuCN + HCN$$

It can take place when temperature raises above 60 °C and when insoluble AuCN is precipitated [2]. However, when hydrophobic adsorbent is present, AuCN precipitation can also occur in the cold solutions. It is postulated that the hydrophobic surface catalyses the reaction since such a reaction takes place extremely slowly in a glass container [2]. In such a case the loaded resin should contain yellow spots of solid AuCN. During our experiments no AuCN was visible on the resin surface. This was confirmed by FTIR spectroscopy that indicates the presence of $Au(CN)_2^-$ anions only. After gold elution by an excess of mixture NaOH and sodium benzoate, XPS spectra showed absence of Au4f signal, Fig. 4c. This is to prove the full elution of gold at Au(I) oxidation state from the loaded resin.

We can conclude that while the uptake of $Au(CN)_2^-$ anions occurs on the resin, Au(I) does not reduce to metallic gold. There is some literature data that has shown such possibility [2–6,25]. Some of it has pointed on reconstruction of surfaces during XPS measurements [26].

3.3.2. Tetrachloroaurate sorption

Fig. 6 shows the deconvolution of Au4f region for gold sorbed from tetrachloroaurate acid solution. It is visible that some peaks of Au(I)4f and Au(III)4f overlap. It was noted; see Table 1, that ratio of Au/Cl close to 4 appears for gold loaded sample. It suggests presence of $AuCl_4^-$ complexes on the resin surface and oxidation state of gold at Au(III). Table 3 compares and presents binding energies of $AuCl_4^-$ anions and resins loaded from $HAuCl_4$ solution with data from studies in the literature described by other authors.

It is worth to emphasise here that during XPS measurements the Au4f peak could have been changing quickly during the long time of measurement [2,20]. Such photo-reduction occurring during XPS measurements has been noted in the literature. We believe that at the beginning of our experiment gold was the predominant form of tetrachloroaurate gold complex with Au(III). Sometimes, the reduction of Au(III) appeared to Au(I) and even to the Au(0) level as metal [2,20,27,28]. Our elution process showed complete removal of gold and we do not consider a possibility of existence of AuCl species. In this experiment, the participation of Au(I) in total gold amount was estimated as 14%, only. Moreover, if AuCl were present in a lot larger amount on the resin AG3, the colour of the resin surface should have changed towards yellow–green. We do not observe such an effect. Despite the possibility of an easy reduction of Au(III) ions to Au(I) and Au(0) form during the XPS analysis, the presence of metallic gold Au(0) was not observed.

4. Conclusion

It might be concluded that during gold sorption from HCl solutions of $HAuCl_4$ and $KAu(CN)_2$ the gold stayed in its oxidation states of Au(III) and Au(I). It was not reduced to the metal form, Au(0). It was observed that the reduction of gold Au(III) to Au(I) can occur easily during the long acquisition time in XPS experiment. Completed elution of

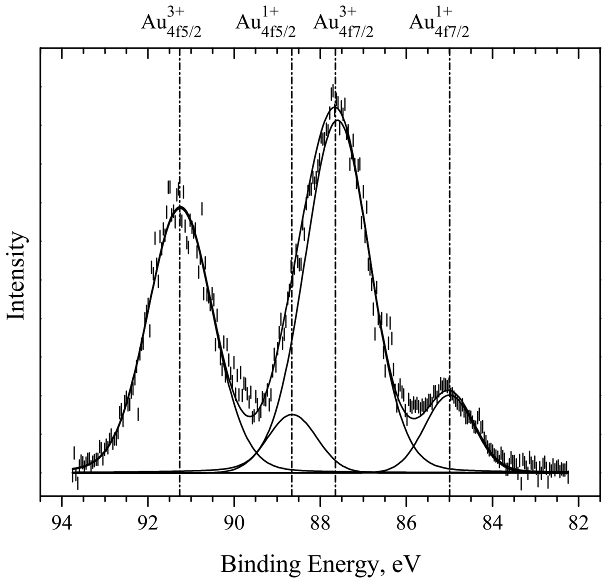

Fig. 6. XPS Au4f spectra for AG3 resin gold loaded from $HAuCl_4$ solution.

Table 3
Binding energy (eV) of AuCl, $AuCl_4^-$ anions and resins loaded with $AuCl_4^-$. Comparison of XPS data obtained in this work with data from studies in the literature

	Au 4f5/2	Au 4f7/2	Oxidation state	Reference
$AuCl_4^-$	90.4	87.0	+3	[6]
$HAuCl_4$	–	87.6	+3	[7,31]
$HAuCl_4$	90.4	87.6	+3	[30]
AuCl	–	86.2	+1	[29]
POD2-Au loaded	87.1	84.2	Not given	[6]
PSD2-Au loaded	89.3	85.6	Not given	[6]
TAPDA-Au loaded	–	86.59	+3	[31]
		85.04		
AEPZR-Au loaded	–	88.85	+3	[7]
PANI-Au loaded	–	84	0	[8]
PC3-Au loaded	88.16	85.32	+3	[30]
AG3-Au	88.65	85.00	+1	This work
	91.3	87.6	+3	

POD2 and PSD2, polymeric pseudocrown ether, TAPDA, poly-Schiff base containing bisthiazole rings, AEPZR, aminoethyl piperazine resin, PANI, polyaniline, PC3, polystyrene supported polymeric thiacrown ether.

gold using thiourea solution and a mixture of sodium hydroxide and sodium benzoate was achieved. The results demonstrate that XPS can also be a powerful technique for the analysis of the Oxidation State of sorbed metal and functional groups incorporated in the polymer. We believe this paper to be one of the first to describe properties of guanidine resin by means of XPS spectroscopy. It can help understand the nature of sorbed gold complexes. We are planning to investigate the effect pH on sorption properties also.

Acknowledgements

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