SURFACE COVERAGE OF POLYANILINE-COATED SILICA GELS [*]

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Silica gels of $15\,\mu$m and $130\,\mu$m mean sizes were covered by polyaniline hydrochloride (PANI) nanofilms during polymerisation under different conditions. A surface coverage of the silica gel was determined from the C 1s or N 1s photoelectron spectra by two methods. The first one, the line shape analysis carried out by QUASES-Tougaard software, enables us to recognise also the surface morphology of the samples. The second method accounts for the C 1s or N 1s peak area ratios originating from the PANI-coated silica gels and from the PANI standard. The results indicate that silica gel surfaces are not fully covered by the PANI film. The coverage values are consistent mutually, correlate well with polymerisation conditions and are in good agreement with a PANI content determined independently by burning the PANI-coated silica gel samples.

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1   Introduction

Polyaniline (PANI), a member of an extensive family of conducting polymers, have recently been used in the surface modification of various materials. Particularly, glass surfaces immersed into the aqueous reaction mixture became fully coated with a PANI nanofilm [1–3]. The typical film thickness varied between 50 nm and 400 nm depending on reaction conditions [2]. Surprisingly, silica gels of micrometer dimensions are not fully covered, as indicated from photoelectron spectroscopy (XPS) measurements [4,5]. This method provides promising possibilities for quantitative and non-destructive chemical characterisation of surface nanostructures [6,7].

In this contribution, we have determined the surface coverage of silica gels quantitatively by the C 1s and N 1s photoelectron spectra recorded from the PANI-coated silica gel samples and the PANI standard. Two methods were applied. The intensity ratio method (IRM) is simply based on the peak-area ratios of the C 1s or N 1s peaks recorded from the sample surface and the standard. Next, a more complex method is the line shape analysis of the C 1s or N 1s peak and an extended inelastic background behind the peaks recorded from both the sample and standard surfaces.

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2 Experimental

Two types of silica gel were used for the sample preparation: porous spheres, 15 μm in diameter (Separon SGX, Tessek) and porous fragments, a mean size of 130 μm (Silica gel 100, Fluka). Aniline hydrochloride (2.59 g, 20 mmol) was dissolved in water in a volumetric flask to 50 ml of solution. The same volume of aqueous solution of ammonium peroxydisulfate (5.71 g, 25 mmol) was prepared. Solution of aniline hydrochloride, followed by the solution of ammonium peroxydisulfate, were poured at 20°C, and at 0–2°C in one case, to a beaker containing silica gel, and gently stirred during the subsequent polymerization [4,5]. The reaction mixture thus contained 0.2 M aniline hydrochloride and 0.25 M ammonium peroxydisulfate. The progress of exothermic polymerization was monitored by recording the temperature of reaction mixture [8,9] with a digital thermometer. After the polymerization, which took several minutes, the mixture was left at rest overnight. The compact sediment of PANI-coated substrate was separated next day from the free-flowing PANI precipitate. The coated silica gel was washed three times with 100-ml portions of 0.2 M HCl, similarly with acetone, and separated by filtration. The powders were dried in air and then *in vacuo* at 60°C. Content of PANI in the PANI-coated silica gel was determined from the difference in ash after burning the initial and PANI-coated substrates. The PANI hydrochloride was prepared in the same manner [8] in the absence of silica gel.

The powders of PANI-coated silica and PANI hydrochloride (a standard) were laid on a double-sided adhesive tape, 15×15 mm^2, fixed to a sample holder. The XPS measurements were carried out in the ADES-400 (VG Scientific, UK) spectrometer equipped with a hemispherical angle-resolved energy analyser and x-ray gun. The hemispherical energy analyser was operated with a pass energy of 100 eV and an acceptance angle of $\pm 4.1°$. The XPS spectra were recorded using Al K$_\alpha$ radiation (1486.6 eV). The spectrometer was calibrated by the Au 4f 7/2 line peaked at a binding energy of 84.0 eV. Narrow range spectra of C 1s, O 1s, N 1s, Cl 2p, Si 2p, S 2p and Cl 2p recorded at normal detection angle were used for a current quantitative analysis. Measurements of photoelectron peaks from the PANI standard and from the sample surfaces were made under exactly the same experimental geometry. To avoid expected ion-beam-induced modifications of composition and bonding in the analyzed volume, the sample surfaces were analyzed without sputter-cleaning.

Selected wide-range spectra of the C 1s and N 1s lines with extended inelastic electron background were recorded for the QUASES-Tougaard analysis [10] from specimen surfaces and from standard PANI. Before the QUASES-Tougaard analysis, the spectra were corrected for the spectrometer transmission function [11].

3 Determination of the surface morphology and the coverage

Information about the overlayer morphology and the coverage can be derived from the shape and the intensity of the photoelectron line and an inelastic background behind the line. The method is based on the fact, that due to inelastic scattering of photoelectrons in the solid, the intensity and shape of the peaks and the inelastic background behind the peaks in the electron spectra depend strongly on the depth of origin of the excited photoelectrons. The theoretical framework is described in detail in the literature [12]. The corresponding spectra processing is presently facilitated by the commercial software package QUASES-Tougaard [10]. The method enables us to distinguish between typical cases [13], e.g., uniform overlayer, island-like growth, continuous
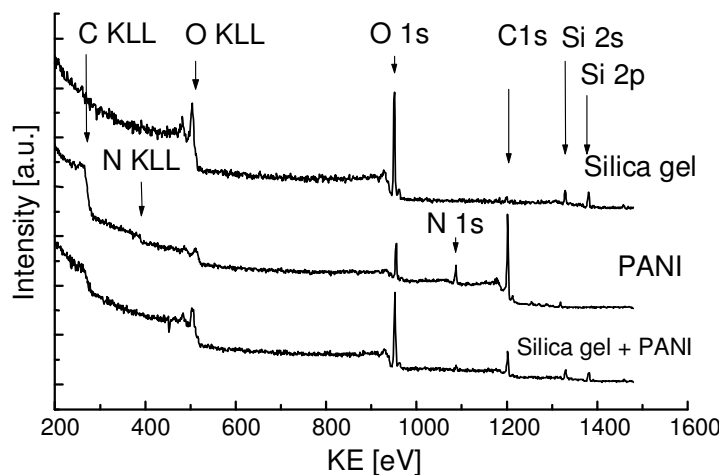
Fig. 1. Typical wide-range photoelectron spectra recorded from silica gel, PANI standard, and silica gel partially covered by PANI. Typical features of the PANI spectra are the C 1s and N 1s lines.

concentration profiles, the buried layer and can be used, for example, as a method of solution of a nanofilm growth mode problem [14]. Due to numerous inelastic electron interactions, electrons forming the background behind a given peak came from much deeper regions of the sample than those contributing to the given peak [10,12]. As shown below, the QUASES-Tougaard analysis resulted in a surface structure model of silica gels partially covered by the PANI thick film.

The intensity ratio method (IRM) is based on the fact that the given photoelectron intensity depends on a sample surface area from which photoelectrons are measured [6]. The IRM compares a photoelectron peak intensity (area) from a sample and a standard. Specifically, the PANI standard should fully cover a substrate and should be sufficiently thick with respect to the information depth of the method used. In the IRM, the surface coverage of the silica gels is estimated from the C 1s and N 1s photoelectron peak areas recorded from the PANI standard, $I_F\infty$, and from the samples, I_F. Supposing that (i) thickness of the PANI film on silica gel particles exceeds the information depth of XPS and (ii) boundaries between the covered and the uncovered surface areas of silica gels are reasonable sharp, the surface coverage θ can be easily calculated from the above mentioned photoelectron intensity ratio

$$\theta = I_F / I_F\infty . \tag{1}$$

It should be noted that the information depth of XPS is defined as a thickness of $3\lambda \cos \alpha$ from which originates 95% of photoelectrons in question. λ is the inelastic mean free path and α is the emission angle measured with respect to the surface normal. For photoelectrons with kinetic energy of 1000 eV passing through a PANI, the value of λ, determined by the elastic peak electron spectroscopy, is about 3 nm [15].
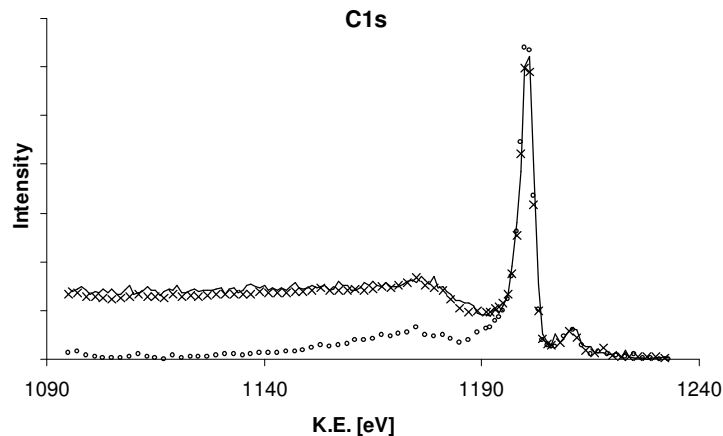
Fig. 2. The line shape analysis of the C 1s line recorded with an extended background at low kinetic energy. The full line represents the measured spectrum — sample S20-3, points display model calculations providing fully covered silica gel ($\theta = 1$) with a 2.1 nm thick PANI nanofilm (circles) and partially covered silica gel ($\theta = 0.38$) with a thickness of 100 nm (crosses).

4 Results and Discussion

Photoelectron spectra of all samples revealed a significant N 1s peak intensity indicating that the PANI is indeed present on silica gel surfaces. Moreover, the spectra of all samples but the PANI standard revealed a significant Si 2p and Si 2s peak intensity. This is illustrated in Fig. 1 where wide-range spectra recorded from the silica gel, the PANI standard and the PANI-coated silica gel surfaces are displayed. The presence of silicon, nitrogen and carbon photoelectron peaks in the spectra recorded from the samples indicate that (i) either silica gels are fully covered by a (very) thin film of PANI with a thickness lower or equal the corresponding value of λ or (ii) the sample surfaces can be characterised by silica gel surfaces partially covered by PANI films. Both possibilities are considered in the following QUASES-Tougaard line-shape analysis.

Fig. 2 shows an illustration of the QUASES-Tougaard line-shape analysis applied to the C1s line recorded from the S20-3 sample. A solid line represents the spectrum recorded from a PANI-coated silica gel surface, data points are the model calculations. The first model examined is the full coverage of silica gel surfaces by the continuous PANI film with a thickness of 2.1 nm. The second one is based on the partially covered silica gel surfaces by the PANI film, $\theta = 0.38$, with a thickness of 100 nm. Evidently, the latter model of surface morphology is in excellent agreement with the C 1s spectral line shape recorded from the PANI sample (S20-3). On the contrary, applying the former model for arbitrary PANI film thickness values, the calculated background spectrum is quite different from the measured one, showing that the full coverage model is not the correct depth-concentration structure model. Similar results were obtained for all samples under study but for 190-S0 and 190-S25 samples where a more complicated two layer model with different thickness had to be applied. The latter indicates a certain PANI film thickness distribution on PANI-coated silica gel samples.

Sample →	S20-1	S20-2	S20-3	S20-10	S20-30	190-S0	190-S25
T [°C]	20	20	20	20	20	0	25
$\Phi[\mu m]$	130	130	130	130	130	15	15
R [g/100 ml]	1	2	3	10	30	10	10
S [cm^2]	1200	2400	3600	12000	36000	100000	100000
IRM (N 1s)	0.44	0.35	0.23	0.21	0.11	0.56	0.64
IRM (C 1s)	0.50	0.38	0.26	0.32	0.17	0.65	0.71
QUASES (N 1s)	0.47	0.34	0.3	0.20	–	0.62	0.85
QUASES (C 1s)	0.55	0.42	0.38	0.31	0.27	–	–
w [wt.%]	23.4	26.3	23.7	14.4	6.1	–	–
t [nm]	1440	813	490	89	13	–	–

Tab. 1. PANI polymerisation conditions and PANI coverage normalised to the unity, calculated from N 1s and C 1s peak areas by using the intensity ratio method (IRM) and from N 1s and C 1s line shape analysis by the QUASES-Tougaard method. T is the polymerisation temperature, Φ is the mean size of silica gels, R is the silica gel amount added to the reaction mixture producing PANI. S is the external surface of silica gels estimated by assuming their spherical shape. Weight fractions of the PANI, w, determined by burning the PANI-coated silica gel samples, are included for comparison. t is the mean thickness of the PANI film estimated by assuming fully covered silica surfaces S and the PANI volume calculated from the weight fraction of the PANI, w, and the PANI density [15].

Results of the surface coverage evaluated by using two above-mentioned methods applied to the C 1s and N 1s photoelectron peak areas (IRM) and their spectral line shapes (QUASES) and PANI polymerisation codnitions are summarised in Tab. 1. For the purpose of comparison, (i) the PANI content of individual samples, determined as an ash by burning the PANI-coated silica samples, (ii) the external surface area values of silica gel used in individual samples, (iii) and the mean film thickness values derived from the PANI percentage, the density and the external surface of silica gel and calculated for the full silica gel coverage, is also included. The coverage values derived by using both methods and by two different photoelectron lines are in good agreement and show clear consistency with the silica gel amount added to the reaction mixture producing PANI. They also correlate with weight fraction of the PANI determined by burning the PANI-coated samples. This correlation is more evident when the mean thickness of a PANI film described above [5] of silica gels and the PANI density [15]. The mean thickness values are rather overestimated since the external surface of silica gel particles differ from that of their total surface due to their porosity [5]. For example, the total surface of the silica gels with a mean size of 130 μm is about 4 000 000 cm^2/g against 1200 cm^2/g valid for their external surface.

The coverage values obtained from the C 1s lines are systematically larger than those derived from the N 1s lines. This phenomenon is likely connected with air-exposition of all samples lasting several days in meantime from their preparation till their insertion into the ultra-high vacuum spectrometer chamber.

The surface coverage decreases as the amount of silica gels added to reaction mixture increases from 1 to 30 g per 100 ml. This behaviour is expected because increasing amount of silica gels in the reaction mixture consumes aniline in the reaction mixture available for the polymerisation.
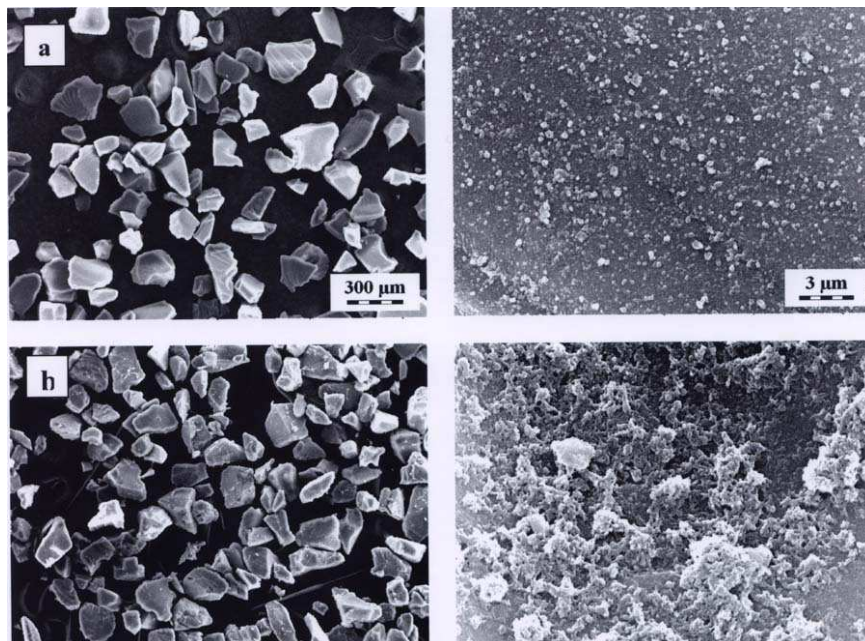
Fig. 3. Scanning electron microscopy: original (top) and PANI-coated (bottom) silica-gel at overview magnification (left) and the detail of the surface (right). 10 g of silica gel per 100 ml of reaction mixture.

Comparing the results obtained by both methods, the coverage values derived from the QUASES-Tougaard analysis are in most cases slightly higher than those from the IRM. This fact may be caused to some extend by their different information depths. The QUASES-Tougaard technique probes depths up to $\sim 10\lambda$, while the IRM sampling depth is only about 3λ. The next reason responsible for the difference may be in a simplified model used. The IRM is in fact purely experimental method, while, the QUASES-Tougaard method is based on simplified models neglecting, for instance, elastic scattering of electrons [16]. This simplification can influence the resulting coverage value due to boundaries between the covered and the uncovered surface areas of silica gel surfaces where some thickness distribution of the PANI film is expected.

Interestingly, the sample prepared at room temperature (190-S25) has higher surface coverage with respect to the sample prepared at 0–2°C (190-S0). This fact indicate an influence of a polymerisation mixture viscosity. There is, however, a more pronounced difference in the surface coverage values determined for samples S20-10 (130 μm size), 190-S25 (15 μm size) with the same amount of silica gel in the reaction mixture which differ in a mean size of silica gels and consequently in an external silica gel surface. Their influence is likely combined with a silica gel porosity and also with silica gel shapes [4,5], as illustrated in Fig. 3 by scanning electron microscopy of PANI-coated silica gels. Unfortunately, all these possible contributions to the surface coverage cannot be separated within this study. Therefore, this topic should be clarified in detail by a near future dedicated experiment.

5   Conclusions

Photoelectron spectra recorded from the PANI-coated silica and the PANI standard were used to determine surface morphology and surface coverage values of silica gel surfaces. For this purpose, the intensity ratio method and the line shape analysis method was applied on the C 1s and N 1s peak areas and the C 1s and N 1s spectral line shapes analysed with an extended inelastic background behind the peaks. The results show that the PANI-coated silica gels are partially covered by the PANI film, the surface coverage has been quantitatively determined by photoelectron spectroscopy and can be to some extend tailored by variation of polymerisation conditions like amount and size of silica gel added to a reaction mixture and the polymerisation temperature.

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