Preparation of Gold Nanoparticles on Ultrathin Films of Polythiophene and Polythiophene Derivatives

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Two different methods were used to immobilise gold nanoparticles on ultrathin films of polythiophene and polythiophene derivatives. The first method utilised ultrathin films of polythiophene to prepare gold nanoparticles by direct reduction of $HAuCl_4$. A uniform coverage of the polythiophene films with randomly distributed gold nanopraticles possesing a polydisperse size distribution was obtained. Size and size distribution of the gold nanoparticles could be controlled by time, concentration of Au^{3+}, and the addition of a cosolvent. With the second method, ultrathin films of polythiophene derivatives were esterified with thioctic acid, using either Steglich or Yamaguchi conditions. The dithiolane moiety of the thioctic acid was utilised to immobilise gold nanoparticles from a monodisperse gold sol. The gold nanoparticles were adhesive on the polymer films and were not removed by scotch tape tests. The samples with the obtained gold nanoparticles of both methods were analysed by scanning electron microscopy (SEM).

Introduction

Composite materials consisting of conducting polymers and metal nanoparticles are of great interest. Ordered structures as shown in Figure 1 would be the final goal because they are promising for further applications in micro- and optoelectronics.

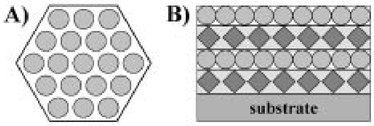

Figure 1. A) lateral hexagonal arrangement, B) sandwich layout.

Some review articles are available on gold nanoparticles, but it would be beyond the scope of this work to give a complete record. For the synthesis the work and reviews of Schmid et al.,[1,2] and for the assembly of gold nanoparticles the review of Daniel et al.[3] should be mentioned.

Holdcroft et al.[4,5] examined the oxidation of poly(3-hexylthiophene) (PHT) with gold trichloride in water-free solvents. The use of thick polymer films (>1 μm) yielded sandwich structures consisting of an oxidised PHT film, covered with a continuous gold layer. However, thinner polymer films (<0.25 μm) yielded only an irregular, nonuniform covering with gold. Holdcroft et al.[5] proposed the following reaction [Equation (1)].

$$3\,[P^0] + 4\,AuCl_3 \rightarrow 3\,[P^+][AuCl_4^-] + Au^0\downarrow \qquad (1)$$

P is a sequence of four monomer units (thiophene rings) in the polymer.[5]

To obtain gold nanoparticles rather than nonuniform gold films, the polymer film has to be even thinner than the 0.25 μm that Holdcroft et al. used. For micro- and optoelectronic applications it is necessary to chemically deposit adhesive films especially on insulating substrates. Ultrathin, adhesive, and smooth polythiophene films were described by Fikus et al.[12–14] (Figure 2). These films can be chemically deposited on a variety of substrates, preferentially insulating, with the adhesion promoter 11-(thien-3-yl undecyl) trichlorosilane (TUTS) and are about 100 nm thick.

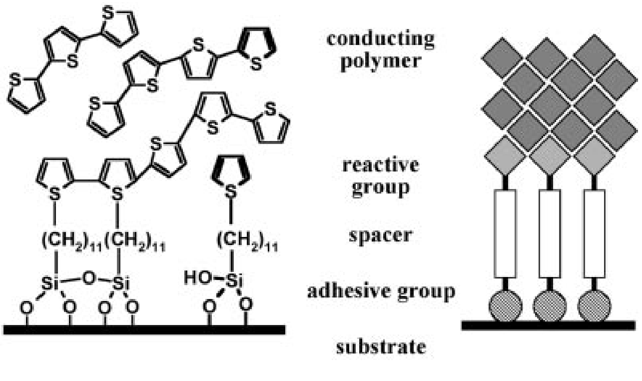

Figure 2. Layout of ultrathin polythiophene films using the adhesion promoter TUTS.

To circumvent complications with the use of water-free solvents it was of interest to determine whether the deposition of gold nanoparticles onto polythiophene films would

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also be possible from aqueous solutions of $HAuCl_4$. Then the following reactions would be possible Equation (2) and Equation (3).

$$3\,[P^0] + HAuCl_4 \rightarrow 3\,[P^+][Cl^-] + Au^0\downarrow + HCl \qquad (2)$$

$$3\,[P^0] + 4\,HAuCl_4 \rightarrow 3\,[P^+][AuCl_4^-] + Au^0\downarrow + 4\,HCl \qquad (3)$$

Equation (2) was proposed by Freund et al.,[6] while Equation (3) was derived from Equation (1), which was proposed by Holdcroft et al.,[5] assuming that $HAuCl_4$ can be regarded as the hydrochloride of $AuCl_3$. The reduction of $HAuCl_4$ requires the incorporation of a dopant anion into the oxidised polymer to achieve charge neutrality. In the case of an excess of polythiophene, all of the $HAuCl_4$ is reduced and only Cl^- is available as a dopant anion, which is described in Equation (2). On the other hand, in the case of an excess of $HAuCl_4$ all of the polythiophene is oxidised, but not all of the $HAuCl_4$ is reduced. A combination of Equation (2) and Equation (3) is then an appropriate description of the polymer doping, as both anions Cl^- and $AuCl_4^-$ are available in solution and can be incorporated into the oxidised polymer.

The immobilisation of gold nanoparticles can be achieved by different ways,[3] but the most promising approach is the utilisation of the strong interaction between thiols and gold, where a gold–sulfide bond is formed.[10] In this work the dithiolane moiety of thioctic acid (Figure 3) is used to immobilise monodisperse gold nanoparticles. This moiety is a cyclic disulfide, which can be regarded as an equivalent of two thiol moieties and was utilised to form self-assembled monolayers (SAMs)[7,8] or as a stabilising agent for gold nanoparticles.[9] To achieve the immobilisation of the gold nanoparticles out of a gold sol, polymer films containing the thiophene derivative 3-methoxy thiophene (MOT) were prepared. The hydroxyl groups in the polymer (ROH) were then esterified with thioctic acid, as depicted in Figure 3.

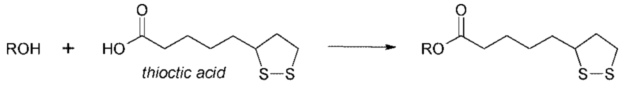

Figure 3. Reaction scheme: esterification with thioctic acid.

Figure 4 shows the layout of the polymer substrates with immobilised gold nanoparticles after the two steps of esterification (1) with thioctic acid and subsequent immobilisation of the gold nanoparticles (2) from a gold sol.

Two different methods were used to immobilise gold nanoparticles on ultrathin films of polythiophene and polythiophene derivatives. With the first method, ultrathin films of polythiophene were utilised to prepare gold nanoparticles by direct reduction of aqueous $HAuCl_4$, to yield polydisperse gold nanoparticles. Size and size distribution of the nanoparticles could be controlled by time, concentration of Au^{3+}, and the addition of a cosolvent. With the second method, ultrathin films of polythiophene derivatives were esterified with thioctic acid, using either Steglich or Yamaguchi conditions. The disulfide moieties of the thioctic acid were utilised to immobilise gold nanoparticles from monodisperse gold sol. The samples with the gold nanoparticles, obtained from both methods, were analysed by scanning electron microscopy (SEM).

Results and Discussion

1) Direct Process

The examined parameters were time, concentration of Au^{3+} and effects of the cosolvent, which are to be discussed. The results are summarised in Figure 5. A continuous gold

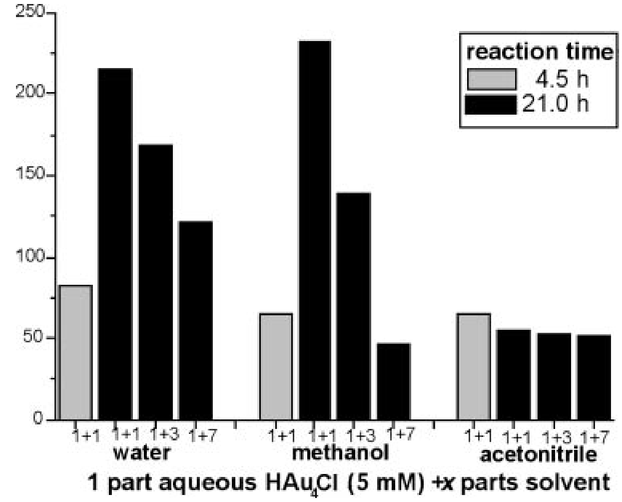

Figure 5. Direct process: mean gold nanoparticle size in relation to concentration, cosolvent, and time.

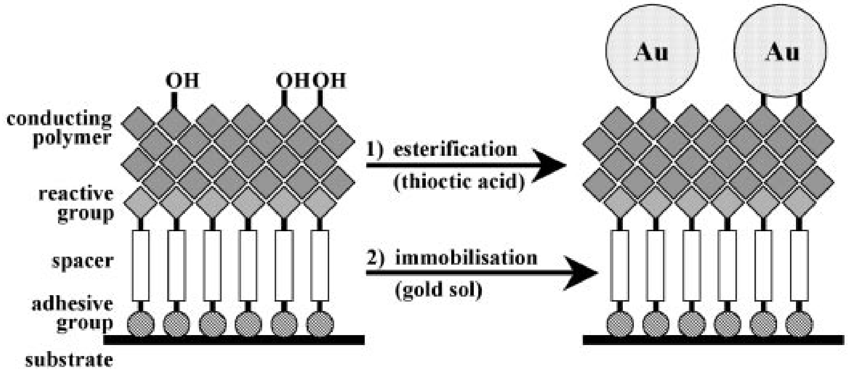

Figure 4. Polymer modification.

layer on the polythiophene films could not be observed, however, gold nanoparticles were visible on the surface of these films (Figure 6). This outcome was expected from the observations of Holdcroft et al.[4,5] with thin polymer films. The gold particles that were obtained were polydisperse and randomly distributed on the polythiophene films. It could be corroborated that undoped polythiophene was able to reduce aqueous gold salt solutions.

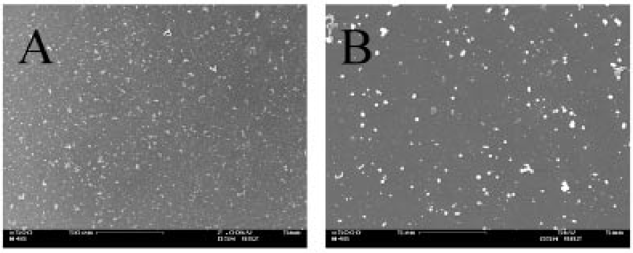

Figure 6. Direct process: typical SEM micrographs: A) 500×. B) 5,000× (5.08 mM of $HAuCl_4$, 4.5 h).

Concentration Dependence

The amount of Au^{3+} in the solutions was the same for all the experiments, because each experiment started with 0.5 mL of an aqueous $HAuCl_4$ solution (5.08 mM) and dilution was achieved by adding, either 0.5 mL, 1.5 mL, or 3.5 mL of solvent into the reaction flask. A decreased concentration of Au^{3+} resulted in smaller particles with a narrower size distribution (parts B and D in Figure 7). This trend could be observed when diluting with water, methanol, and acetonitrile and it was most pronounced with methanol.

Cosolvent Dependence

The presence of a cosolvent (methanol, acetonitrile) resulted in smaller particles with narrower size distributions (parts A and C in Figure 7). The dilution series with methanol yielded results that were little different from the dilution series with water, but were more pronounced, i.e. the decrease in particle size with increasing dilution was larger. The addition of acetonitrile, on the other hand, had a more significant effect on the deposition behaviour of the gold particles. The reduction of Au^{3+} to Au^0 proceeded via Au^+, which is stabilised by acetonitrile. Hence, the deposition of Au was very slow. At a constant number of nucleation centres and nuclei, the size of the nuclei was smaller after a constant time, as the rate of gold deposition was lower, resulting in very small gold particles. The influence of acetonitrile on the deposition was so substantial that there was little change of particle size in the dilution series.

Time Dependence on Particle Size

An increase in reaction time resulted in an increased particle size and a broader size distribution of the particles (parts A and B in Figure 7). Increasing the reaction time from 4.5 h to 21 h and therefore by almost a factor of four, yielded an increase in the particle size of four times.

Summary: Direct Process

The particle size (Figure 5) was increased by the factors, time and concentration. As the particles got larger, the size distribution (Figure 7) also broadened. Adding a second solvent other than water yielded in most cases smaller particles, an effect that could be explained with stabilising effects of the solvent molecules on the different gold species in solution. As a second effect of the solvent addition, the

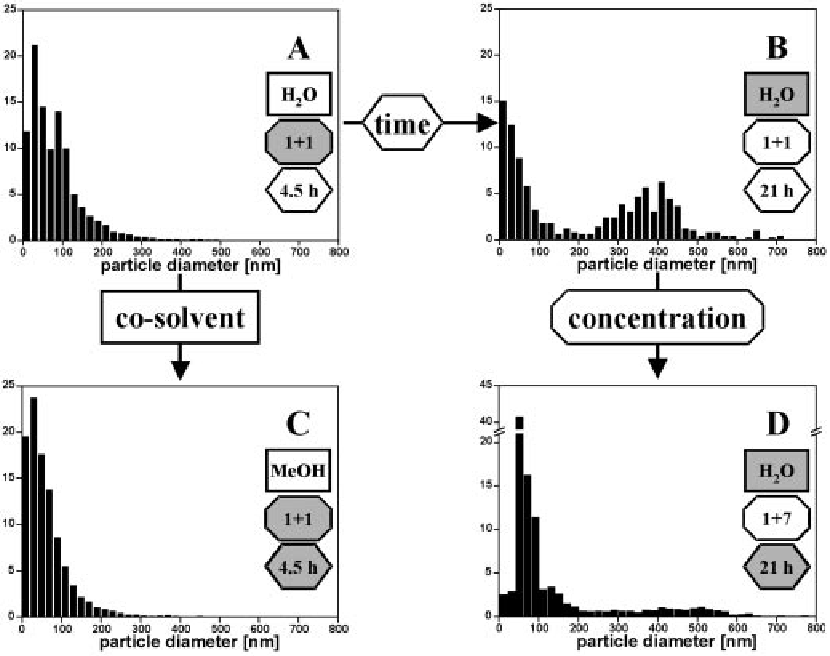

Figure 7. Direct process: particle size distributions.

size distribution became more homogeneous. To conclude this: Particle size and distribution could be positively influence by the addition of the solvents methanol and acetonitrile.

Polymer Modification

In a second set of experiments the polymer was modified by derivatising it with adhesion groups for the immobilisation of gold nanoparticles out of gold sols. The success of the polymer modifications was checked by adsorption experiments with gold sols. Gold sols of Roche Diagnostics were used. These gold sols were prepared with the citrate reduction method[18] with no further stabilising agent used other than citrate and had a mean particle size of 40 nm. For adsorption of the gold nanoparticles the modified polymer films were immersed into the gold sols. Immobilisation of the gold nanoparticles was achieved by cleavage of the disulfide bond of the thioctic acid and formation of two gold sulfide bonds, which was due to the high affinity of gold to sulfur.[9,10]

Polymer Film Modification through Esterification – Steglich Conditions

In Figure 8, as in all of the SEM micrographs, the gold nanoparticles appear as white to light grey dots, while the substrate with the modified polymer film appears in a dark grey. Figure 8 shows the different affinities of the modified polymer films towards the gold nanoparticles: on the unmodified polythiophene film (Figure 8, A) just a few gold nanoparticles were immobilised. The polythiophene film was used as blank test as it could not be esterified with thioctic acid and had a very low affinity to gold.[11] The modified polymethoxythiophene film (Figure 8, B) on the other hand was densely covered with gold nanoparticles, indicating a successful polymer modification.

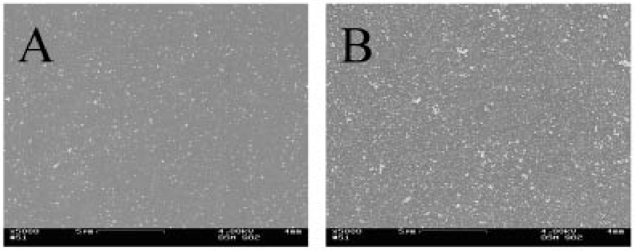

Figure 8. SEM micrographs of immobilised gold nanoparticles on modified polymer films (magnification 5,000): A) polythiophene, B) polymethoxythiophene (modified, Steglich conditions).

The differences in morphology of the copolymer films were examined. The copolymers were prepared from methoxythiophene with thiophene P(T/MOT) and methylthiophene P(MT/MOT), respectively. The films with thiophene (Figure 9, A) had a more homogeneous appearance, than those prepared with methylthiophene (Figure 9, B). This could be explained with a better coupling of the adhesion promoter TUTS with the thiophene, because of a minor steric hindrance of the monomers during polymerisation, due to the absence of the 3-methyl group. Polymer films with regions of different morphology could be observed with the methylthiophene containing copolymers, as shown in part B of Figure 9. These films had a rougher surface, so that more methoxy groups were accessible for esterification with thioctic acid. Thus, locally increased concentrations of dithiolane groups through the thioctic acid ester were available to immobilise more gold nanoparticles on these films. In Figure 9 (see part A) single gold nanoparticles were spread over the unmodified polythiophene film, while in Figure 9 (see part B) inhomogeneities lead to the formation of larger agglomerates of gold nanoparticles. Between the agglomerates regions of homogeneous coverage with single gold nanoparticles were allocated. The regions in the SEM micrograph that had a lighter appearance did not have a higher affinity to the gold nanoparticles compared with the darker regions.

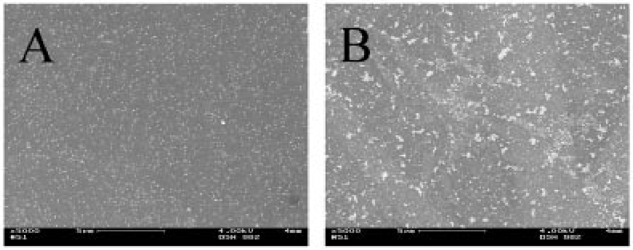

Figure 9. SEM micrographs of immobilised gold nanoparticles on modified polymer films (magnification 5,000): A) P(T/MOT), B) P(MT/MOT) (both modified, Steglich conditions).

The influence of different monomer ratios on the resulting polymers was examined with the copolymers from methoxythiophene with thiophene P(T/MOT). The morphology of the homopolymer films was smooth and homogeneous, as can be seen in Figure 8. With the addition of only small amounts of the other monomer to the polymerisation mixture the copolymer films were still homogeneous, e.g. methoxythiophene in thiophene T/MOT = 90:10 (v/v) (Figure 9, A).

As the monomer ratios were changed further until an equal mixture of the monomers was reached, the morphology of the copolymer films exhibited an increasing roughness. Also, the appearance of regions on the polymer film with different morphologies was observed, which could be indicating that these areas correspond to different segregated copolymers or even homopolymers, respectively.

Adhesion of the gold nanoparticles on the modified polymer films was tested with a scotch tape test. For this, one half of a substrate was covered with scotch tape, which was then quickly removed. SEM was used to examine the samples before and after the test, and no significant loss of gold nanoparticles was detected. Therefore, it can be concluded that the immobilised gold nanoparticles are covalently bound to the modified substrate.

Polymer Film Modification through Esterification – Yamaguchi Conditions

In the experiments examining the Yamaguchi esterification, the quality of the adhesion promoter allowed only the deposition of TUTS films with a high coverage of polysiloxane particles originating from the condensation of TUTS molecules. Thus, resulting in inhomogeneously deposited polymer films, as shown in Figure 10. Figure 11 shows that the polymer morphologies could be reproduced, although their surface structure was more coarse than previously described for the Steglich-modified polymer films in Figure 9. The defects in the polymer films (Figures 10 and 11) are due to the film preparation conditions and could not be eliminated. The immediate detection of the gold nanoparticles was impeded by the numerous polymer particles, but with careful examination the gold nanoparticles became apparent.

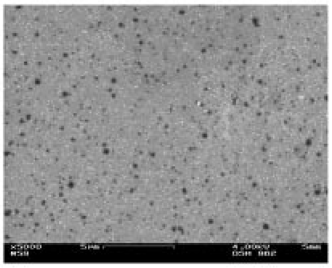

Figure 10. SEM micrograph of immobilised gold nanoparticles on modified polymer film (magnification 5,000): polymethoxythiophene (modified, Yamaguchi conditions).

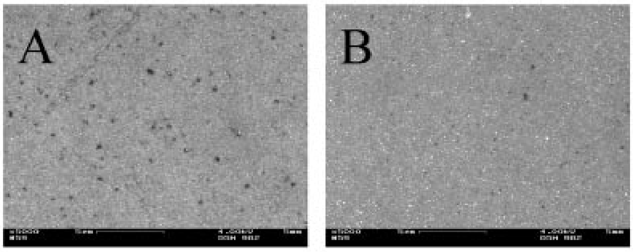

Figure 11. SEM micrographs of immobilised gold nanoparticles on modified polymer films (magnification 5,000): A) P(T/MOT), B) P(MT/MOT) (both modified, Yamaguchi conditions).

When comparing e.g. Figure 8B (Steglich conditions) with Figure 10 (Yamaguchi conditions) in the case of modified polymethoxythiophene, it became obvious that the two pathways for the esterification yielded either agglomerated or separated gold nanoparticles upon subsequent immersion into a gold sol. Also, the coverage of the Yamaguchi-modified polymer films with gold nanoparticles was lower than with the Steglich-modified films. The Yamaguchi-modified polymer films were more porous due to the defects in the pristine polymer films. Therefore, less thioctic acid ester moieties were accessible on the surface by the gold nanoparticles of the gold sol, resulting in a lower coverage of separated gold nanoparticles.

Conclusions

It was shown that gold nanoparticles could be immobilised by two different methods. A direct reduction process, utilising the polymer film of the substrate yielded polydisperse nanoparticles. The particle size of the nanoparticles and their size distribution could be controlled by the factors time, concentration, and the addition of a cosolvent. Monodisperse gold nanoparticles could be immobilised on further modified polymer films. These films were prepared by using thiophene derivatives bearing hydroxyl groups, which were then esterified with thioctic acid using either Steglich or Yamaguchi conditions. The latter method allows the immobilisation of a huge variety of nanoparticles, because those can be prepared ex situ. The only prerequisite for the nanoparticles is that they interact strongly with the dithiolane group of the thioctic acid ester to allow the immobilisation.

Experimental Section

1) Preparation of Ultrathin Films of Polythiophene and Polythiophene Derivatives: The polymer films were chemically deposited on silicon substrates, which were modified with the adhesion promoter 11-(thien-3-yl undecyl) trichlorosilane (TUTS).[12–14]

The pretreatment of the substrates and subsequent modification with TUTS was described in the literature.[12–14] Chemical deposition of the thiophene polymers was carried out in the following manner: the TUTS-modified substrates were placed in a solution of 1.0 g of $FeCl_3$ (anhydrous, Fluka, p.a.) and 25 mL of acetonitrile (<50 ppm water, Fisher Scientific, p.a.), then 100 µL of the respective premixed monomers were added. After 1 h of reaction time, the samples were cleaned in an ultrasonic bath with methanol (Merck, purum). The monomers (Aldrich, p.a.) were thiophene (T), 3-methylthiophene (MT), and 3-methoxythiophene (MOT), the monomer mixtures T/MOT = 90:10 (v/v) and MT/MOT = 90:10 (v/v).

2) Direct Process: Polythiophene substrates were immersed into an aqueous Au^{3+} containing solution: 0.5 mL of $HAuCl_4$ (5.08 mM) + $x \times 0.5$ mL of solvent ($x = 0, 1, 3, 7$; solvent = dist. water, methanol, acetonitrile). Immersion time was 4.5 h and 21 h, respectively. The examined parameters were time, concentration of Au^{3+} and effects of the cosolvent. After reaction, the substrates were rinsed with copious amounts of distilled water and subsequently dried with argon.

3) Polymer Modification: All the glassware used for the reactions was heated in vacuo and subsequently “aerated” with argon.

Polymer modification reactions were carried out in 100 mL Erlenmeyer flasks, each equipped with a rubber septum. The flasks were moved on a one-dimensional shaker during the reaction. Solvents were freshly dried prior to use, and all other chemicals were used as received.

3a) Polymer Film Modification through Esterification – Steglich Conditions: The esterification was carried out according to Steglich et al.[15] following the working procedure of Echegoyen et al.[16] Each solution was premade and then divided into five parts, which were then added to the different polymer substrates. The thioctic acid (9.4 mmol, 1.94 g) and DMAP (0.65 mmol, 0.08 g) were dissolved in 50 mL of dichloromethane and added to the polymer substrates. After 30 min a DCC solution (11.2 mmol, 2.32 g) in 25 mL of dichloromethane was added. After another 22 h, under gentle movement with the one-dimensional shaker, the modified substrates were cleaned in an ultrasonic bath with distilled water and ethanol for 5 min each and subsequently dried with argon.

3b) Polymer Film Modification through Esterification – Yamaguchi Conditions: The esterification was carried out according to Yamaguchi et al.[17] Each reaction mixture was divided into four parts: three parts for modification of three individual substrates and one part for reaction control with GC-MS. The thioctic acid (1.2 mmol, 245.2 mg) was dissolved in 8 mL of THF, then triethylamine (1.2 mmol, 121.8 mg, 166 µL) was added after which the mixture was stirred for 10 min at 0 °C. 2,4,6-Trichlorobenzoyl chloride (1.2 mmol, 292.8 mg, 457 µL) was then added and stirred for another 10 min at 0 °C, followed by 2 h at room temperature. After removal of triethylamine hydrochloride by filtration through a syringe filter (PTFE, 0.2 µm pore width), the filtrate was evaporated in vacuo and the yellow, viscous residue was dissolved in 8 mL of dichloromethane. A solution of DMAP (2.4 mmol, 293.2 mg) in 8 mL of dichloromethane was then added to this. A polymer substrate was treated with a portion of 4 mL of this resultant solution for 48 h under gentle movement with the one-dimensional shaker. Finally the modified substrates were cleaned in an ultrasonic bath with distilled water and methanol for 5 min each and subsequently dried with argon.

3c) Gold Nanoparticle Adsorption: The modified polymer substrates were immersed in a gold sol for 1 h at 4 °C. The gold sol was prepared by Roche Diagnostics with the citrate reduction method[18] with no further stabilising agent used other than citrate. In the first experiments the substrates were placed face up in the adsorption flask, while later on the substrates were placed slightly tilted upside down in reaction tubes for adsorption. This orientation avoided the deposition of gold nanoparticles, which were destabilised from the gold sol during the progressing experiments. After adsorption the substrates were rinsed with copious amounts of distilled water and subsequently dried with argon.

Acknowledgments

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