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Adsorption kinetics of gold nanoparticles on [P(HEMA-*co*-HEA)] swollen hydrogels

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Abstract
Two kinds of hydrogels were synthesized and made in contact with gold nanoparticles (AuNPs) in a colloidal solution to investigate their adsorption properties. These hydrogels were made either of the homopolymer Poly(2-hydroxyethyl methacrylate) (PHEMA) or the copolymer poly(2-hydroxyethyl methacrylate-*co*-2-hydroxyethyl acrylate [P(HEMA-*co*-HEA)]. Several compositions were used and the polymerization was induced by UV irradiation in the presence of the initiator Darocur and the crosslinker 1,6-hexanediol diacrylate (HDDA). AuNPs with a well defined dimension were synthesized by reduction of Au(III) salt solutions in the presence of tannic acid according to a procedure described in a previous work. The adsorption kinetics of the AuNPs on a [P(HEMA-*co*-HEA)] hydrogel was monitored by UV-visible spectroscopy and the experimental data were well fitted with a sigmoidal function.

Keywords: Gold nanoparticles; copolymers; hydrogels; photopolymerization; kinetics, adsorption.

1. Introduction
The chemistry of AuNPs has been the subject of active research for more than a couple of decades because of the wide opportunities of applications in a variety of domains. Because of the large surface area accessible for modification with the possibility of binding targeting molecules or specific biomarkers, these AuNPs [1] have received a considerable attention for applications in biomedicine [2,3], drug and gene delivery [4-6], biodiagnostics [7-9], targeted therapies [10] and medical imaging [11]. Most of these applications are based on the high degree of biocompatibility of AuNPs [12] and their low toxicity towards healthy tissues. Functionalization of AuNPs promotes their stability and delivery to specific target cells in disease areas allowing a high selectivity of interaction with cells and biomolecules. AuNPs were also used to develop sensors for detecting metals in water such as copper, mercury, lead and arsenic [13]. Among the numerous options of drug delivery systems that have been developed in order to improve efficiency and biocompatibility, hydrogels are extremely promising due to their characteristic properties such as swelling in water, biocompatibility, and non-toxicity [14-17]. Hydrogels are made of biocompatible hydrophilic networks that can be prepared from both synthetic and natural molecular species. In the present work, we are interested on the interaction of AuNPs with PHEMA hydrogels focusing specifically on the kinetics of adsorption of the NPs on the polymer network. The hydrogels are able to swell admitting large amounts of water uptake undergoing changes in shape and volume in response to physical or biological stimuli such as temperature, pH, ionic strength or salt concentration [18-20].
A particular interest is given in the literature to the dispersion of AuNPs within homopolymer media, block copolymers in the bulk or on and thin films as well as on the formation of continuous films on polymer substrates[21-23]. Polymer supported metal or metal oxide based on AuNPs represent a new class of hybrid materials exhibiting unprecedented properties with application opportunities not known for polymers or nanoparticles alone [24]. The unusual optical, electronic, magnetic, of organic/inorganic hybrid materials can be used in a large variety of applications, including high-density information storage systems, sensors, magnetic fluids, medical diagnosis, membranes, catalysts, and many other devices.
Among the procedures developed for the formation of continuous nanoparticulate metal films on polymer subtracts, one finds the metal vacuum evaporation [25], the adsorption of metal AuNPs from their colloidal solutions [26], and the transfer of densely packed assemblies of metal AuNPs from liquid surface by Langmuir Blodgett technique [27,28].

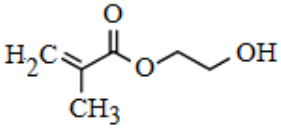
The kinetics of adsorption of nanosized particles has been the subject of a large number of theoretical and experimental studies [29,30], and more or less sensitive methods have been developed to better apprehend their adsorption mechanisms. Among the most sensitive methods, one can invoke for example quartz crystal microgravimetry (QCM) [31,32] and atomic force microscopy (AFM) [33,34]. The former technique enables one to measure drops in the fundamental resonance frequency for a piezoelectric crystal due to deposition of gold AuNPs. Studies of adsorption of AuNPs on poly(2-vinylpyridine) (PVP) using this technique were reported in ref [35] in addition to the AFM image analysis of the polymer surface at increasing adsorption times indicating a progressive coverage.
The present work goes along the same lines using AuNPs / copolymers [P(HEMA-*co*-HEA)] hybrid materials and UV-visible spectroscopy to monitor the kinetics of adsorption.

2. Materials and methods

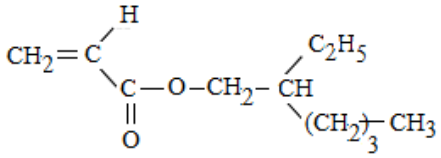
2. 1 Materials

The AuNPs were prepared from trisodium citrate ($(Na_3C_6H_5O_7\cdot 2H_2O)$) and hydrogen tetra-chloroaurate tri-hydrate reagent ($HAuCl_4.3H_2O$) in the presence of tannic acid ($C_{76}H_{52}O_{46}$). All these products were purchased from Sigma-Aldrich.
The hydrogels were made from the monomers 2-hydroxyethyl methacrylate HEMA and 2-hydroxyethyl methacrylate (HEMA), the crosslinker 1,6-hexanediol diacrylate (HDDA) which were purchased from Aldrich, and the photoinitiator 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) purchased from Ciba, Rueil Malmaison (France) (Table 1). All other chemicals used were of the highest available purity and were supplied by Aldrich, Fluka and Sigma.

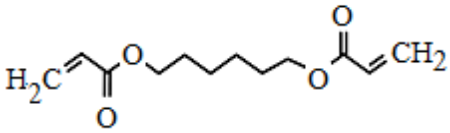
Table 1: Chemical formula of the component used for the polymerization mixture. EMA and EHA are the monomers, HDDA the crosslinker and Darocur is the initiator.



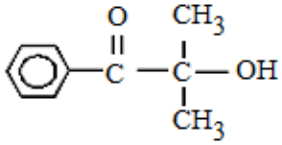
EMA



EHA



HDDA



Darocur

2. 2. Synthesis of the AuNPs

AuNPs were synthesized following the procedure described in ref [36] which is briefly summarized here. A quantity of 10 mg (1.24×10^{-5}mol) of tetrachloroauric (III) acid trihydrate was dissolved in 80 mL of deionized water in a round flask of 0.5 L equipped with a condenser. Another 0.1 L round flask was used to dissolve 40 mg (1.35×10^{-4}mol) of sodium citrate dihydrate and 10 mg of tannic acid in 20 mL of pure deionized water. Both solutions were heated at 60°C before mixing. The obtained mixture was moderately stirred, heated during 1 hour at 60°C, heated to reflux during 10 min before being cooled to room temperature under continuous stirring to yield a mother colloidal solution with a concentration of 2.6×10^{15} AuNPs/mL. The yellow solution turned to deep red indicating the formation of Au clusters in the presence of tannic acid.
Colloidal AuNPs were stabilized to avoid aggregation by grafting hydrocarbon ligand chains with different functional groups. One end of these chains was adsorbed on the AuNPs while the other end was immersed in the solution. The stabilization of the AuNPs was due to electrostatic and steric repulsions [37]. Following the procedure of ref [38], the three ligands, 2-mercaptoethane sulfonate (MS), thiomaleic acid (TA) and 4-mercaptophenol (MP) were used (see Figure 1). Different solutions of MS, TA and MP at 1.22×10^{-7}, $1.22 \times$

10^{-7} and 2.44×10^{-7}mol/L, respectively were added successively every 30 min to 30 mL of the mother solution at room temperature, in the dark and the obtained mixture was stirred during 30 min. The nature and the concentration of thiol solutions were adjusted as a function of the accessible surface sites of AuNPs [36]. The stability of the final colloidal solution was controlled during a period of two months.

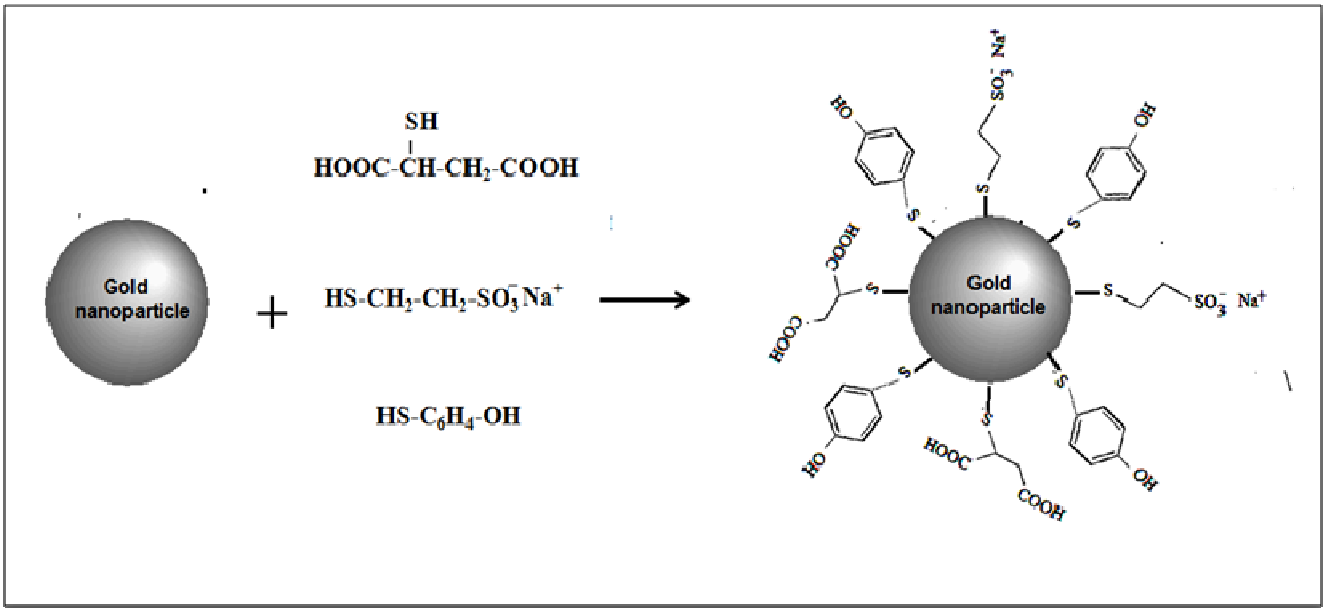


Figure 1: Functionalization of AuNPs using 2-mercaptoethane sulfonate (MS), thiomaleic acid (TA) and 4-mercaptophenol (MP) chains.

2. 3. Preparation of the PHEMA copolymers hydrogels

Five hydrogels referred to as A, B, C, D, E with different compositions were prepared by photopolymerisation. The monomers 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) were mixed with water in different weight fractions while the amount of photoinitiator Darocur 1173 was kept constant at 0.3 w%, the concentration of crosslinker 1,6-hexanediol diacrylate (HDDA) was varied from 0.3 to 1 wt%. Compositions of the five hydrogels A to E are given in Table 2.

Table 2: Composition of the five hydrogels used for the AuNPs adsorption experiments. The concentration of the initiator Darocur was kept constant at 0.3 wt%. All concentrations are expressed in wt %.

	Monomers		Solvent H_2O	Crosslinker HDDA
	HEMA	EHA		
A	34	14.1	51.3	0.3
B	34	14.1	51	0.6
C	34	14.1	50.6	1
D	66.3	0	33.1	0.3
E	65.7	0	33	1

The initial solutions were stirred mechanically during few minutes before transfer into covered glass holders in order to limit the effect of oxygen. Then the solution was put inside a reaction chamber and irradiated by a UV lamp (Philips TL08, wavelength λ = 365 nm, Intensity = 365 mW/cm^2) during 45 min under nitrogen atmosphere. After irradiation, the initial transparent solutions became a translucent rubbery gel which was removed from the holder mold and cut into square pieces of 5cm length and 3 mm thickness. The square gels

were first rinsed thoroughly with distilled water and then dried slowly in air at room temperature before conservation into covered glass containers at 4°C.

2. 4. Adsorption kinetic experiments

The PHEMA membranes were immersed in 5 mL of colloidal solutions, in glass-stoppered Erlenmeyer flasks under stirring at 100 rpm, during 24 hours in order to form PHEMA-AuNPs layer. The number of AuNPs adsorbed on the PEHA membrane was determined using UV-visible spectroscopy. It was easy to check by direct observation the adsorption of AuNPs on the polymer hydrogel because of a characteristic color change leading to a variation of the absorbance. According to the Beer-Lambert law, a linear correlation relationship exists between the absorbance and the concentration of the colloidal solution yielding a calibration curve, representing the absorbance (λ_{max} = 525 nm) versus concentration of the solution. This curve was used to get the concentration of the solution and deduce N_{ad} the number of adsorbed AuNPs from

$$N_{ad} = (C_0 - C) \times V \quad (1)$$

where C_0 and C are the initial and final concentration of AuNPs in a colloidal solution of volume V.

2. 5. Techniques

UV-visible spectra were recorded at room temperature with a Shimadzu UV-2401 PC spectrometer. Absorption measurements were made in the 400–700 nm range.

The homogeneity and diameter distribution of the synthesized AuNPs were characterized using a high resolution transmission electron microscope (TEM) (JEOL 2010) operating at 200 kV. A Zetasizer Malvern 3000 HSA equipped with a He–Ne laser (633 nm) granulometer was used to detect the aggregation of colloidal AuNPs. Deionized water was used throughout the whole procedure and all gold solutions were prepared and stored in clean glass vials.

3. Results and discussion

TEM images revealed that the synthesized AuNPs had a spherical shape with a narrow diameter distribution. Their functionalisation led to a good dispersion in a stable colloidal solution. Figure 2 gives typical micrographs obtained by TEM confirming the spherical shape, size and good dispersion indicated above.

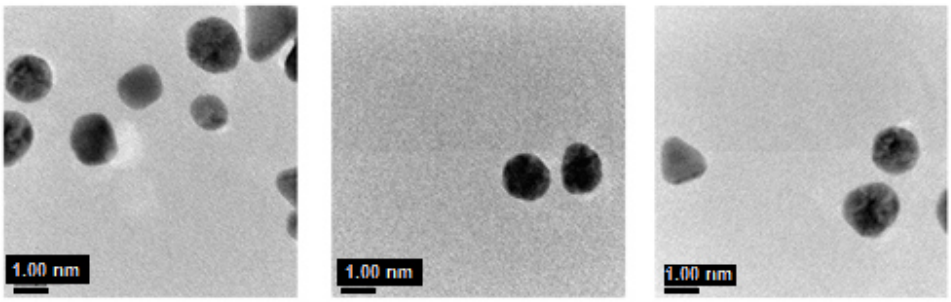


Figure 2: Typical TEM micrographs of AuNPs with average diameter of 1.1 ± 0.2 nm.

The TEM data are displayed in the form of histograms for the diameter distribution considering both volumes and numbers as shown in Figure 3. We found an average diameter of AuNPs of 1.1 nm and a standard deviation of 0.2 nm.

These results are compared with those reported in ref [39] and obtained for two different samples (Table 3). In the first column, sample 1 was obtained by mixing $HAuCl_4 \cdot 3H_2O$ boiling solution with a solution containing ($Na_3C_6H_5O_7 \cdot 2H_2O$) dissolved in water. In the second column, sample 2 was prepared by mixing an aqueous solution of gold chloride with a preheated aqueous solution containing 1% $Na_3C_6H_5O_7 \cdot 2H_2O$, 1% tannic acid and 25mM potassium carbonate. One can clearly note reduction in the size of AuNPs prepared in the presence of tannic acid in sample 2.

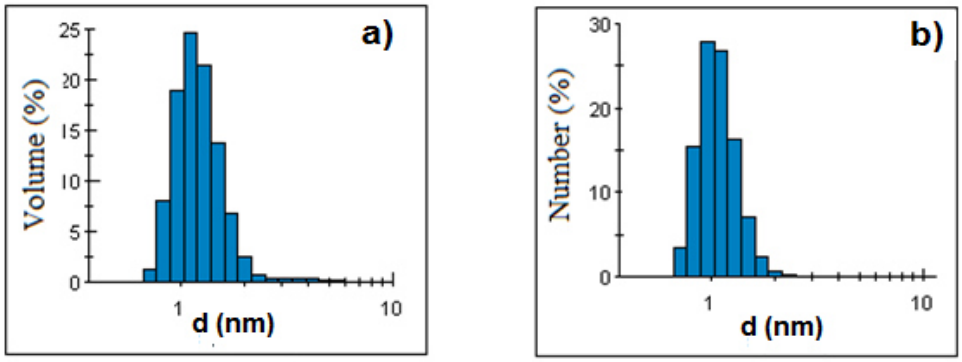


***Figure 3**: Typical* histograms giving the diameter distribution of the AuNPs by a) volume b) number.

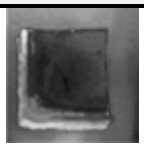
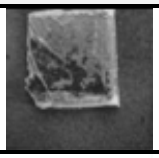
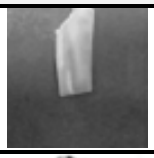
Table 3: Characteristics of AuNPs, the first two columns are data taken from ref [39], the last column are results of the present work.

Characteristics	Sample 1 Ref [39]	Sample 2 Ref [39]	This work
Average diameter (nm)	14.2	6.9	1.1
Standard deviation (nm)	2.6	1.3	0.2
Average weight of the AuNPs (g)	2.9×10^{-17}	3.3×10^{-18}	1.3×10^{-20}
Number of gold atoms per particle	8.8×10^{4}	10^{4}	43.4
Number of particles per ml of solution	8.6×10^{11}	2.8×10^{13}	2.6×10^{15}

We should point out that the number of gold atoms N in a single particle was computed as in ref. [39] using the formula $R = N^{1/3}r_s$, (R is the particle radius, r_s, the Wigner- Seitz radius (r_s = 3 au for gold, R = 0.55 nm gives N = 43.4)). (See also refs [40-42])

When hydrogels were immersed in the colloidal dispersion, one could see with neck eyes the change in color from transparent (before immersion) to deep blue after immersion in the solution (Table 4).

Table 4: Photographs of the five hydrogels (see Table 2) before and after immersion in the colloidal solution.

Hydrogel	***A***	***B***	***C***	***D***	***E***
Before adsorption					
After adsorption					

Micrographs given in Figures 4a and b show the morphology of hydrogels A and E (see Table 2) after immersion in the colloidal solution.

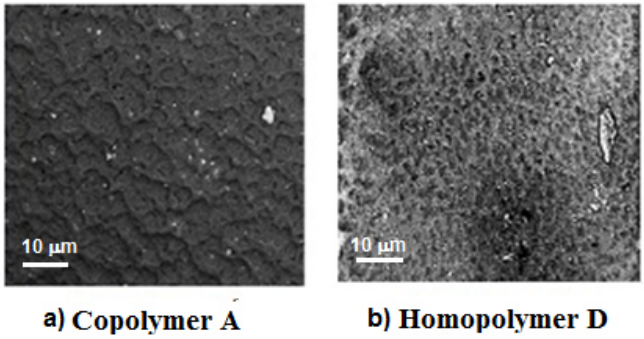


Figure 4: Micrographs of a) copolymer A and b) homopolymer D (see Table 1) after immersion in the colloidal solution.

All the hydrogels were immersed in the solution under constant stirring for 24 hours and their adsorption efficiency ε(%) was calculated using the formula

$$\varepsilon = \frac{C_0 - C}{C_0} \times 100 \qquad (2)$$

We noted that sample A yielded the best efficiency (100 %) and for this reason, it was chosen to perform a kinetic study of AuNPs adsorption using UV–visible spectroscopy. The number of AuNPs adsorbed on the polymer was recorded at different time intervals from 1 to 24 h. The kinetic results are displayed in Figure 5 giving the number of adsorbed AuNPs relative to the unit surface of PHEMA hydrogel. One observes a slow increase at the initial stages followed by a steeper enhancement at intermediate stages and finally a slowing down of the adsorption process at final stages before nearly a daylong experiment was completed.
The maximum adsorption capacity was achieved after 20 hours of immersion of the hydrogel in the solution.

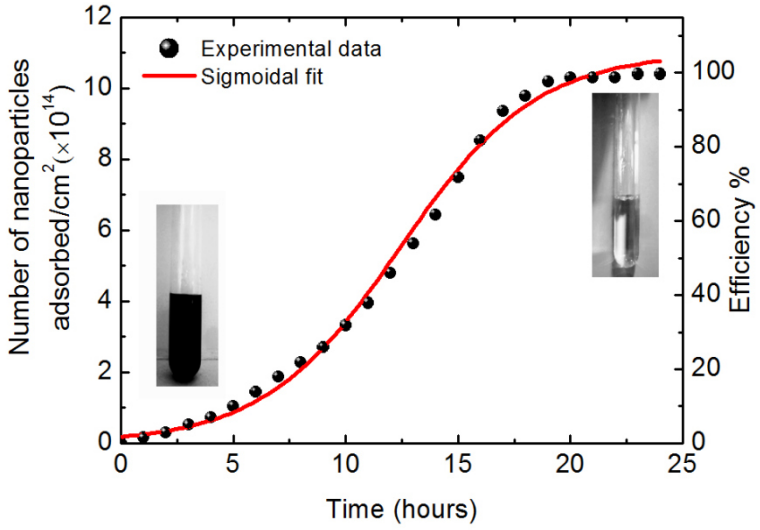


Figure 5: Kinetics of Adsorption of AuNPs on [P(HEMA-*co*-HEA)] hydrogels. Dots represent experimental results while the continuous line represents a fit according to Eq. 3 (α = 11.00, β = 58.91, κ = 0.325). The insets show the colored solution before immersion (left hand side) as opposed to its transparent state at the end of experiment (right hand side).

The measurements were made within accuracy near 4%. They were fitted with the following equation characterized by a sigmoidal shape with a correlation coefficient $R^2 = 0.99604$:

$$N_{ad} = \frac{\alpha}{1+\beta\exp(-\kappa t)} \quad (3)$$

where α and β are constant factors and κ is a parameter describing the kinetics of adsorption. The parameter α is dictated by the saturation level of the adsorbed concentration of AuNPs. The parameter κ is related to the rate of kinetic adsorption while parameter β should be large enough to comply with the initial condition imposing that there are no AuNPs adsorbed on the polymer network at the beginning of the kinetic experiment.
Let us point out that we have also conducted desorption experiments under similar conditions replacing the AuNPs colloidal solution by deionized water. Hydrogel A was immersed in distilled water under vigorous stirring during 24 hours. The obtained solution was tested by UV-visible measurements and permitted to conclude that the adsorption of AuNPs was irreversible. These results meant that the AuNPs were tightly attached to the hydrogel with a strong interaction mechanism which we would like to characterize in more details in the near future.

Conclusion

The aim of this study was to prepare and characterize hybrid materials based on PHEMA and P(HEMA-*co*-HEA) hydrogels as substrate for the adsorption of AuNPs from a stable colloidal solution. The kinetics of adsorption was monitored by UV-visible spectroscopy and the experimental data were nicely fitted with an analytic equation involving a characteristic time $\tau = \kappa^{-1}$ which will be the subject of a future investigation. It would be interesting to determine the system parameters that influence most the kinetics and mechanism of adsorption through a detailed analysis of τ. The question of whether AuNPs were partially embedded into the hydrogel or totally attached to the network surface forming monolayers is still open and requires more experimental data. Note that the hydrogel mesh size is less than the particle diameter, but in view of the strong electrostatic attraction between the anionic polymer surface and the cationic particles, the adsorption is fast and irreversible under the present experimental conditions. The situation could of course change by changing either the pH and / or the ionic strength of the colloidal solution to produce screening of the electrostatic interaction. The adsorption of charged colloidal particles on an oppositely charge surface is an interesting problem which is the subject of a particular attention in the literature from both experimental and theoretical points of view. This question could be addressed in more details in a future work. We hope that the present work paves the way for further achievement in this subject and in particular the development of novel synthesis methods of AuNPs/hydrogel hybrid materials dedicated to biomedical applications.

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