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# Synthesis and characterization of polymer brushes containing metal nanoparticles

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## Summary

Poly(2-hydroxyethyl methacrylate) (PHEMA) brushes were grown from flat silicon wafers with surface-tethered α-bromoester initiator via atom transfer radical polymerization (ATRP) in aqueous media at ambient temperature first. Kinetics studies revealed an approximate linear increase in thickness with reaction time, indicating that the polymerization process owned some "living" character. Then a kind of polymer-metal complexes (PMCs) were obtained after the introduction of $Cu^{2+}$ cations into the PHEMA brushes by the complexing bond between $Cu^{2+}$ cations and the hydroxyl groups in PHEMA brushes. Finally, the $Cu^{2+}$ cations in PMCs were reduced by $NaBH_4$ and a kind of PHEMA brushes containing metal nanoparticles of $Cu^0$ was formed.

## Introduction

The modification of surfaces with polymer brushes is widely used to tailor surface properties such as wettability, biocompatibility, corrosion resistance and friction [1,2]. Polymerization methods are often used to synthesize polymer brushes including cationic polymerization [3], anionic polymerization [4], ring-opening polymerization [5], nitroxide-mediated radical polymerization [6], reversible addition fragmentation chain transfer polymerization (RAFT) [7] and atom transfer radical polymerization (ATRP) [8,9]. ATRP is a recently developed "living" radical polymerization method, which is particularly versatile for the polymerization of various vinyl monomers, such as styrene, methacrylates, acrylates and acrylonitrile [10,11]. In addition, ATRP does not require stringent experimental conditions and it can be accomplished easily at ambient temperature by using water as the solvent [12,13].

2-Hydroxyethyl methacrylate (HEMA) is a commercially important functional monomer that is widely used in the manufacture of soft contact lenses and intraocular lenses [14,15]. Robinson et al. recently published an account [16] of the polymerization of HEMA via aqueous ATRP at ambient temperature. Bruening and coworkers also reported that thick PHEMA brushes could be grown from flat gold surface by water-accelerated surface-initiated ATRP [17]. Due to the tremendous hydroxyl groups in PHEMA brushes, the derivatization of the PHEMA brushes with various functionalities has gained more and more interests nowadays. Based on Bruening's work [17], Jennings' group has succeeded in the synthesis of fluorinated [18] and hydrocarbon side chains modified [19] PHEMA brushes by the derivatization of the hydroxyl groups in PHEMA brushes. To our knowledge, metal cations including $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$, etc can be bound to polymer chains containing functional groups such as pyridine, pyrrolidone, -OH and –HS, etc to form polymer-metal complexes (PMCs) [20], and the work about the derivatization of the hydroxyl groups in PHEMA brushes on flat surface to PMCs has not been reported yet. Furthermore, by the reduction of the metal cations above, the polymer brushes containing metal nanoparticles [21] can be obtained and they have gained much attention for the unique characters of the metal nanoparticles [22].

In this paper, thick PHEMA brushes (>350nm) on α-bromoester initiator modified flat silicon were obtained by water-accelerated surface-initiated ATRP first. By using the hydroxyl groups in PHEMA brushes as the ligands, $Cu^{2+}$ was introduced by the complexing bond and PMCs were formed. In the end, we used $NaBH_4$ to reduce $Cu^{2+}$ in PMCs and nanoparticles of $Cu^0$ were formed mainly on the surface of the PHEMA brushes.

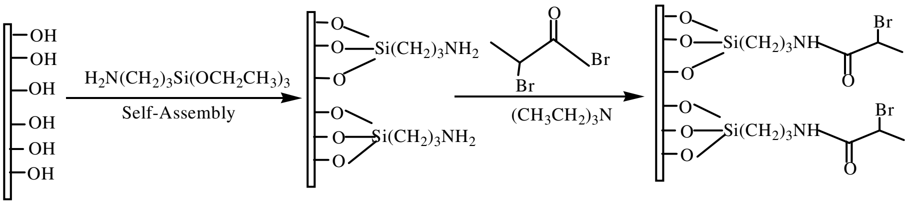
## Experimental

### *Materials*

2-Hydroxyethyl methacrylate (HEMA) was purified by washing an aqueous solution of 25 mol% monomer with hexanes, salting the monomer out of the aqueous phase by addition of NaCl, drying over $MgSO_4$, passing through a column of basic alumina, and distilling under reduced pressure. CuCl purchased from Shanghai Chemical Co. (A.R., 97.0%) was purified by stirring in glacial acetic acid, filtered, washed with ethanol and dried. 3-aminopropyl triethoxysilane (99.0%) (Aldrich), $CuBr_2$ (99%) (Aldrich) and 2-bromopropionyl bromide (2-BPB) (97.0%) (Fluka) were all used as received. 2,2'-bipyridine (bpy) (A.R., 97.0%) provided by Beijing Chemical Co. was recrystallized twice from acetone. Triethylamine (A.R., 99.0%) was dried by $CaH_2$ overnight, then distilled under reduced pressure before use. The water used throughout these experiments was either demineralised or purified using a Millipore Simplicity 185 system at 18.2 MΩ. $CuCl_2 \cdot 2H_2O$ (A.R.) was purchased from Beijing Chemical Co. and used without further purification. The n-type silicon wafers were sliced into rectangular strips of about 1cm×3cm in size. To remove the organic residues on the surface, the silicon substrate was washed with the "piranha" solution, a mixture of 98wt% concentrated sulfuric acid (70vol%) and hydrogen peroxide (30vol%) [23], then washed thoroughly by copious water and dried in vacuum before use. The static water contact angle on the wafers was 15°, revealing the cleanness and uniformity of the surface.

### *Immobilization of the initiator on silicon surface*

The two-step process of immobilization of the surface initiators was shown in Scheme 1. The first step was the aminopropylsilanation of silicon surface: the cleaned wafers were put into the solution of 0.1 ml of 3-aminopropyltriethoxysilane in 5ml of dry toluene for 18 h at room temperature, then the wafers were cleaned under ultrasonic treatment in dry toluene and absolute ethanol successively, finally dried under a flow of nitrogen ($N_2$). The second step was described as following: The above wafers were immersed into the solution of 0.1 ml of triethylamine in 5 ml dry toluene and then cooled in an ice bath (0°C). After 10 min, 0.05 ml of 2-BPB was added dropwise while gently agitating the triethylamine solution to ensure that the surface was well exposed to the incoming 2-BPB. The reaction was carried out at 0°C for 2 h and then at room temperature for 5 h. The wafers were rinsed with toluene and absolute ethanol, respectively, and then dried under a flow of $N_2$. The initiator-immobilized substrates were either used immediately for polymerization or stored in a dry box at room temperature.



**Scheme 1** the two-step process of immobilization of the surface initiators

*Surface-initiated atom transfer radical polymerization*

The condition for preparation of PHMEA brushes on silicon was similar to the literature [17]. CuCl (0.55mmol), $CuBr_2$ (0.16mmol) and bpy (1.56mmol) were together used as the catalyst system. They were dissolved in the HEMA/water (4ml/4ml) mixture. The polymerization was carried out in the oxygen free system at ambient temperature for a predetermined time.

*Preparation of the PMCs of PHEMA brushes*

The PHEMA brushes coated substrates were added to 20 ml of a DMF/water solution (DMF/water, 9:1 v:v) containing excessive $CuCl_2{\cdot}2H_2O$. The reaction was taken at 80°C under the stirring of $N_2$ flow. 24 h later, the substrates were moved out and sonicated cleaned by water to get rid of the physically absorbed $Cu^{2+}$ completely.

*Synthesis of the PHEMA brushes containing metal nanoparticles*

The above PMCs modified substrates were put into 50 ml of water containing $NaBH_4$ at a concentration of 0.5 %. The process of reduction was allowed to proceed at 40°C for 5 h under the flow of $N_2$ stirring.

*Measurements*

The X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCA LAB MK II x-probe spectrometer with Mg Ka X-ray radiation to determine the surface composition of the substrates. The atomic force microscopy (AFM) observations of the surface were carried out with the commercial instrument (Digital Instrument, Nanoscope IIIa, Multimode). All the tapping mode images were taken at room temperature in air with the microfabricated rectangle crystal silicon cantilevers (Nanosensor). The static water contact angles of various surfaces were measured by Krüse DSA 10 MK2 (Germany). For each sample, at least three measurements from different surface locations were averaged. The thickness of the polymer brush was determined by ellipsometry (M-2000 UI J. A. Woollam Co., Inc).

## Results and discussion

To prepare the polymer brush on the silicon surface, a uniform and dense layer of initiators immobilized on the silicon surface is indispensable. Scheme 1 outlines the route to generate the ATRP initiator on silicon wafers. The α-bromoester initiator on the silicon substrate was prepared by the self-assembly of 3-aminopropyl-triethoxysilane, followed by amidization with 2-BPB. XPS was used to confirm the formation of the initiator monolayer. The Br 3d binding energy (BE) peak is observed around 70 eV in Fig. 1, fully indicating the formation of the initiator monolayer. The content of Br is 4% by the calculation of XPS. Furthermore, the static water contact angle was 81.6° at this time, much larger than the cleaned silicon surface (15°) in table 1, which indicated that the surface properties has changed greatly.

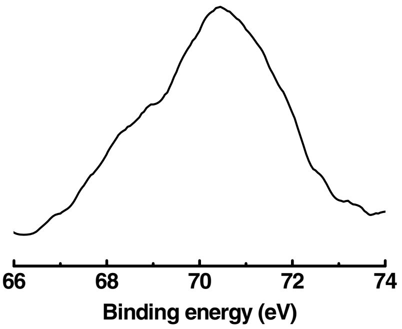


Fig.1. XPS spectra of the initiator modified with self-assemble: the peak of Br 3d

Table 1 static water contact angles of different surfaces

| Different Surfaces | Clean Si | Initiator | PHEMA | PHEMA-$Cu^{2+}$ |
|---|---|---|---|---|
| Contact angle | 15° | 81.6° | 58.1° | 65.2° |

The advantage of ATRP over other living polymerization, such as anionic and cationic polymerization, is the tolerance for various functionalities in the monomers, leading to polymers with functionalities along the chains. HEMA is a kind of very common hydrophilic functional monomer and its polymerization process on gold by surface-initiated ATRP has been proved to be "living" [17]. The deactivator "$CuBr_2$" played a very important role to help the polymerization under controlled [23]. Water acted as an accelerator [13] for the polymerization and it can help to obtain the thick PHEMA brushes. In the present work, surface-initiated ATRP of HEMA was carried out on the initiator modified silicon wafers in water-borne system at ambient temperature. The presence of grafted polymer on the silicon surface was ascertained by XPS analysis. Fig. 2 is PHEMA's C1s core-level spectra and it can be curve-fitted with four peak components having BE's at about 284.4, 286.1, 288.0, 289.2 eV. They are one by one attributable to the (1) aliphatic hydrocarbon (*C*-C/*C*H), (2) an ester-induced,*β*-shifted carbon (*C*-COO), (3) the methylside ester (*C*-O), and (4) the carboxyl carbon(*C*=O) in HEMA molecular structure. Furthermore, it is necessary to point out that the XPS signal of Si (Fig. 3) disappeared after the grafting of PHEMA, which indicates that the PHEMA brush is fairly thick and dense. The variation in water contact angle (at a thickness of 396nm) in table 1 also indicates that PHEMA brushes have been grown on the silicon surface successfully. The water contact angle decreases from 81.6° to 58.1° because PHEMA is a kind of hydrophilic polymer.

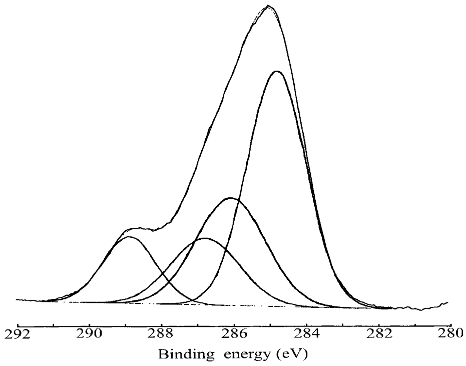


Fig.2. C 1s XPS spectra of PHEMA brush

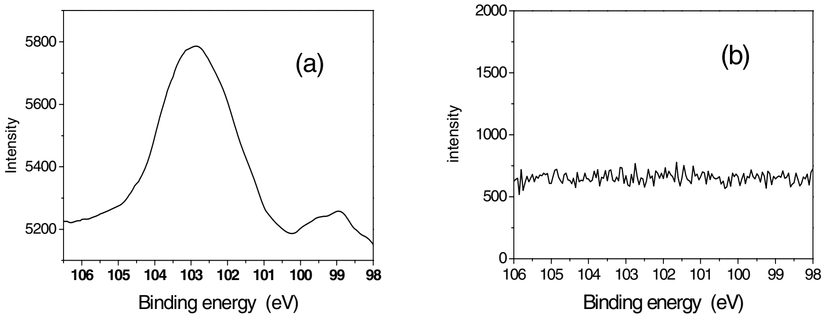


Fig.3. Si 2p XPS spectra of (a) initiator modified and (b) PHEMA brushes modified silicon surfaces

Ellipsometry was used to measure the brush thickness grown on the silicon wafer. As shown in Fig. 4, an approximately linear increase in thickness of the grafted PHEMA layer on the initiator modified silicon surface with the polymerization time is observed, which indicates that the process of surface initiated ATRP of HEMA has a "living" character. The surface coverage of the resulting film (thickness = 396nm) is 43.6mg/m$^2$ (surface coverage = film thickness × density of PHEMA).

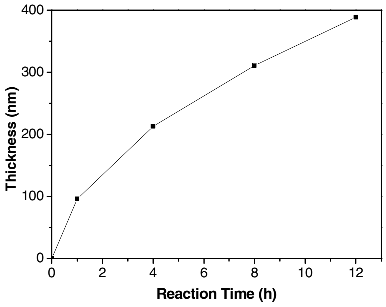


Fig.4. Dependence of PHEMA film thickness on polymerization time

By using the hydroxyl groups in PHEMA brushes as the ligands, PMCs (PHEMA-$Cu^{2+}$) were obtained after the introduction of $Cu^{2+}$. Fig. 5a is the Cu2p XPS spectrum. This is a typical XPS of $Cu^{2+}$ with four peaks. The values of the BE are about $Cu2P_{3/2}$ =934.2eV and the other three are oscillating companion peaks, which indicate that the state of $Cu^{2+}$ is not change. The existing of Cu2p XPS fully indicates that PMCs have formed. Residual metal cations absorbed on the surface are unlikely because the substrates have been ultrasonically cleaned in fresh DMF and water carefully. As shown in table 1, the silicon surface with PMCs layer has a contact angle of 65.2°. Compared with PHEMA modified surface, the data of contact angle increased a little because some hydroxyl groups in PHEMA brushes have complexed with $Cu^{2+}$ leading to the decreasing of hydroxyl groups on the surface. The PMCs modified silicon surface was reduced by $NaBH_4$ in the end and Fig. 5b is the Cu2p XPS spectrum after the reduction. We observe that two oscillating companion peaks have disappeared indicating that $Cu^{2+}$ has been reduced successfully. The content of copper increased much (from 2.37% to 3.96% calculated by XPS) after the process of reduction because the process of reduction was mainly occurred on the surface of the PMCs. The atoms of $Cu^0$ clustered into nanoparticls on the surface and the cations of $Cu^{2+}$ in the deeper region should move to the outer region because the concentration of $Cu^{2+}$ should be a balance and the dispersion of $Cu^{2+}$ should be uniform in the whole PHEMA brushes.

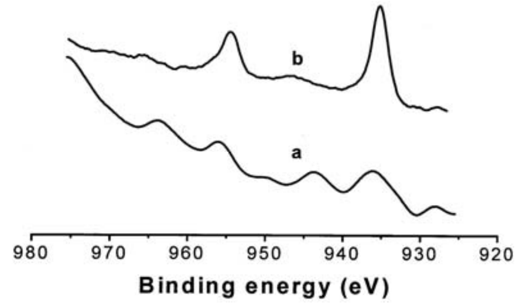


Fig.5. Cu2p XPS spectra (a) before and (b) after reduction by $NaBH_4$

The changes in topography of the silicon surface were studied by AFM. Representative AFM images of the (a) PHEMA, (b) PMCs and (c) after reduction of (b) modified silicon surfaces are shown in Fig. 6. The root-mean-square surface

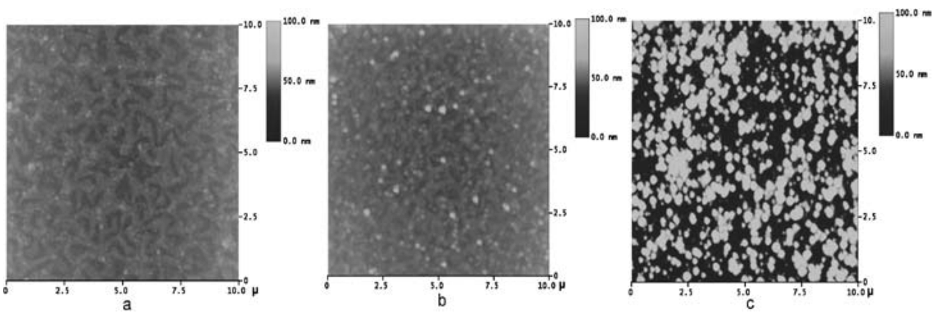


Fig.6. AFM images of (a) PHEMA, (b) PMCs and (c) after reduction of (b) by $NaBH_4$

roughness (RMS) of PHEMA modified surface (at a thickness of 396nm) is 4.10nm, which indicates that the ATRP graft polymerization has proceeded uniformly. Compared with (a), there is no much change in (b), RMS increases a little to 4.45nm due to the introduction of $Cu^{2+}$. After the reduction (c), the nanoparticles with the diameter about 200nm appear on the surface. They are all spherical and almost in the same size. Combined with the results of XPS, these spherical nanoparticles are made up of $Cu^0$ and they almost exist on the surface of the PHEMA brushes.

## Conclusions

In this paper, well-defined and covalently tethered PHEMA brushes were prepared via water-accelerated surface-initiated ATRP of HEMA on pre-α-bromoester functionalized flat silicon surface. XPS and ellipsometry data indicated the formation of PHEMA brushes on the silicon surface. Kinetic study revealed an approximate linear increase in thickness of PHEMA brushes with reaction time, indicating that the chain growth from the surface owned some “living” characteristic. The hydroxyl groups in PHEMA chains can be used directly for complexing with metal ions of $Cu^{2+}$ and the PMCs modified silicon surface were obtained. After the reduction of PMCs modified silicon surface by $NaBH_4$, polymer brushes containing metal nanoparticles of $Cu^0$ were formed by the characterizations of XPS and AFM.

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