

An efficient grafting technique for producing molecularly imprinted film via reversible addition-fragmentation chain transfer polymerization

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Supplementary Materials

1. Control method

The control method for monitoring the growth of film in situ real-time by SPR is described as follow: the fitting parameters of the SPR sensor chip and the films are listed in Table S1. In this simulation, the only variable value is the thickness of the film. As shown in Fig.S1A, a series of SPR angular curves are simulated from line a to line g, corresponding to different thickness of films from 0 to 60 nm. If a film with a certain thickness was need to be synthesized, such as a film with a thickness of 50 nm, corresponding to line f in Fig. S1A. The SPR can be used to monitor the reflectivity changes in situ real-time at 69 degree. It can be clearly see that the reflectivity of the bare Au at 69 degree is about 0.6. The reflectivity will decrease as the thickness of the film is growing as shown in Fig.S1. The incident angle increases at the same time and the minimum value of reflectivity value will be obtained at the resonance angle, in this example, is 69 degree. If the film continuously grows, the reflectivity at 69 degree will increase as shown in Fig. S1 (line f).

In general, the thickness of the film prepared on the SPR sensor chip is unknown before it is detected by other equipments, such as SEM. However, the $\Delta\theta$ of the film can be designed by the researchers. In order to control the thickness (within the SPR detection range) of the film, the researchers can control the $\Delta\theta$. This method is quite useful to control the growth of thin film on the SPR sensor chip. And it is especially suit to prepare film by photo-initiated method for the reaction can be stop as the light source is turn off.

Table S1. Fitting parameters of SPR sensor chip and the film in acetonitrile.

Material	Refractive index= n thickness= d
Glass substrate	n=1.845
Gold layer	n=0.21+3.42i d=50nm
Films	n=1.5 and d=0-60nm
Acetonitrile	1.3441 (20°C)

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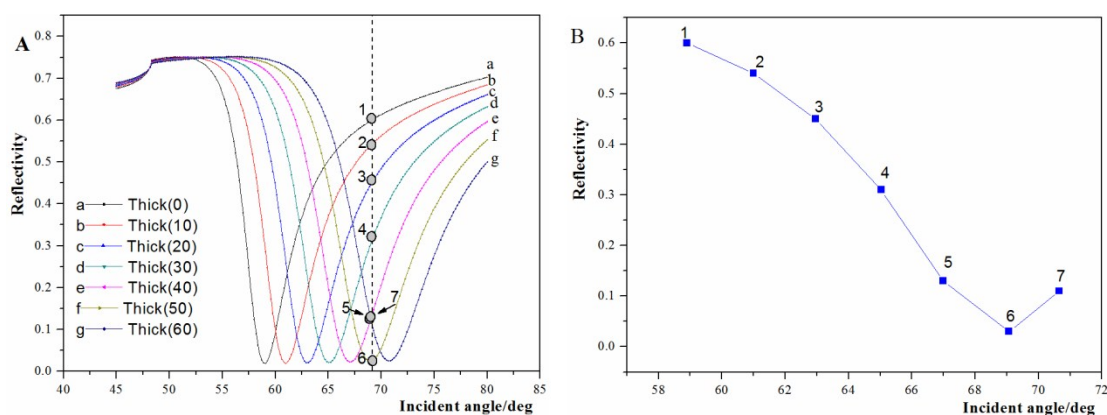


Fig.S1 A The simulated angular curves of SPR as the film grows from 0 to 60 nm in acetonitrile; B the reflectivity changes at 69 degree.

2. Optimization experiments

In this work, a two-step method was used to fabricate the MIP film on the SPR sensor chip. In order to make the MIP water compatible and optimize the properties of the MIP film, different ratio of cross-linker (EGDMA) was used in the preparation process. Lower ratio of cross-linker could not survive in PBS pH 7.4 such as MIP1. The stability in PBS pH 7.4 was improved as the ratio of cross-linker of preparing the second MIP film layer increased, such as MIP2, MIP3, and MIP4. It indicated that the second MIP film could not only apply the recognition sites but also allow the E2 come through the second layer and reach to the imprinted cavities of the first layer. However if the ratio of cross-linker of synthesizing the second MIP film was higher, such as MIP4, it was hard for the E2 to reach the imprinted cavities formed in the first layer and caused the response decrease.

Table S2 Preparing MIP films (T=template, M=monomer, C=cross-linker, T:M:C, molar ratio), stability and working description.

MIP	1 st layer T: M:C	2 nd layer T: M:C	Stability in PBS pH7.4 (Y/N)	Response to E2 (10 ⁻⁸ mol/L, PBS pH7.4), ΔR (%), (n=3)
MIP1	1:4:8	1:4:15	N	-
MIP2	1:4:8	1:4:18	Y	0.46
MIP3	1:4:15	1:4:18	Y	0.87
MIP4	1:4:15	1:4:25	Y	0.54

3. Control experiments

In order to study the role of DDMAT during the photopolymerization, different MIP films were prepared and the details were listed in Table S3. Only one layer of MIP film was synthesized separately in these control experiments. The surface modified for the preparation of MIP3 was according our previous report [1]. The gold chip was immersed in 1 mmol/L 1-dodecanethiol ethanol solution for 24 h to form a self-assemble monolayer.

Table S3 Composition of each solution for preparing MIP film.

MIP	E2 (mg)	MAA (μ L)	EGDMA (μ L)	Initiator (mmol/L)
MIP1	27.2	34	285	1(mmol/L) DDMAT
MIP2	27.2	34	285	10 (mmol/L) DDMAT
MIP3	27.2	34	285	10 (mmol/L) benzophenone

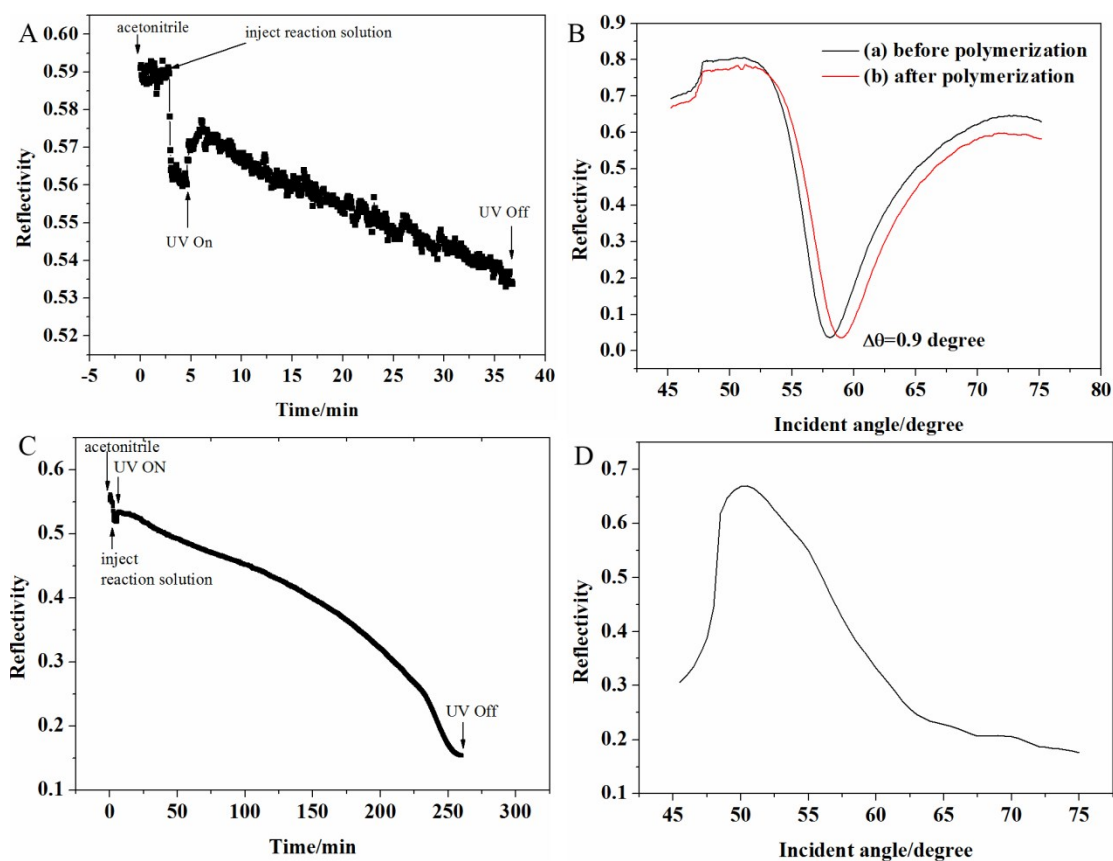


Fig.S2 The preparation of MIP1: (A) kinetics of polymerization with 1 mmol/L DDMAT under UV irradiation for about 32 min; (B) incident angles before and after polymerization; (C) kinetics of polymerization with 1 mmol/L DDMAT under UV irradiation for about 254 min; (D) incident angle after polymerization

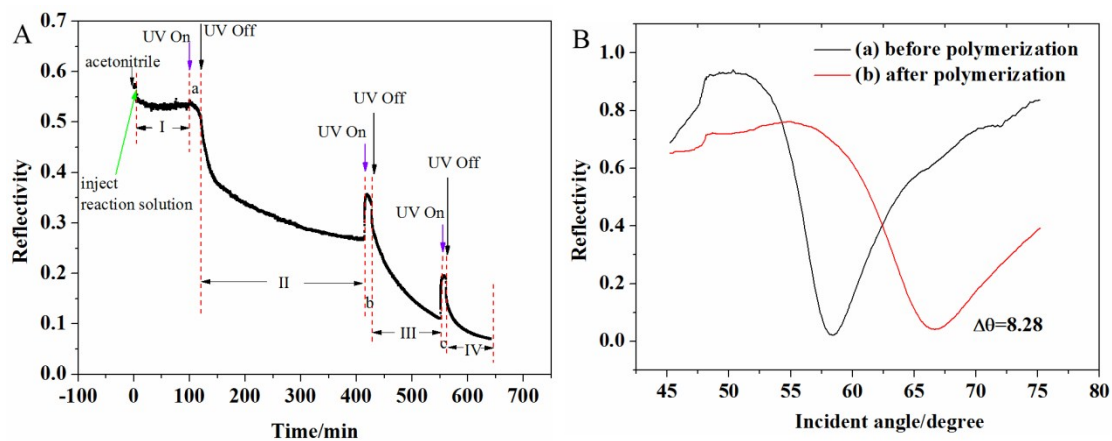


Fig.S3 The preparation of MIP2: (A) kinetics of polymerization; (B) incident angles before and after polymerization

$$\text{R}-\text{S}-\text{C}(=\text{S})-\text{S}-\text{R} \xrightarrow{h\nu} \text{R}\cdot + \cdot\text{S}-\text{C}(=\text{S})-\text{S}-\text{R}$$
$$R \cdot \xrightarrow{\text{monomer}} RP_n \cdot$$
$$\text{RPn}^\cdot + \text{R}-\text{S}-\text{C}(=\text{S})-\text{S}-\text{R} \rightleftharpoons \text{Pn}-\text{S}-\text{C}(\text{S}-\text{R})-\text{S}-\text{R} \rightleftharpoons \text{PnR}-\text{S}-\text{C}(=\text{S})-\text{S}-\text{R} + \text{R}^\cdot$$
$$\text{RPn}-\text{S}-\text{C}(=\text{S})-\text{S}-\text{R} \xrightarrow{h\nu} \text{RPn}-\text{S}-\text{C}(=\text{S})-\text{S}\cdot + \text{R}\cdot$$
$$\dot{\text{R}} + \text{monomer} \xrightarrow{\text{propagation}} \text{RPm}\cdot$$
$$\text{RPm} + \text{RPn} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \\ \text{S} \\ \text{S} \end{array} \text{S-R} \rightleftharpoons \text{PnR} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \\ \text{S} \\ \text{S} \\ | \\ \text{R} \end{array} \text{S-PmR} \rightleftharpoons \text{RPn} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \\ \text{S} \\ \text{S} \end{array} \text{S-R} + \text{RPm} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{C} \\ \text{S} \\ \text{S} \end{array}$$
$$\text{RPn}-\text{S}(\text{S})\text{S}\cdot + \text{RPm}\cdot \rightleftharpoons \text{RPn}-\text{S}(\text{S})\text{S}-\text{PmR}$$

Figure 1 consists of two plots, A and B.

Plot A is a graph of Reflectivity (Y-axis, ranging from 0.48 to 0.64) versus Time/min (X-axis, ranging from 0 to 120). The data is represented by black squares. The plot shows a series of steps: an initial drop from ~0.60 to ~0.55 at t=0 (labeled 'inject reaction solution'), a rise to ~0.59 at t=5 (labeled 'UV On'), a slight dip at t=10 (labeled 'UV Off'), and a final drop to ~0.51 at t=30. The reflectivity then remains relatively constant around 0.51 until t=120.

Plot B is a graph of Reflectivity (Y-axis, ranging from 0.0 to 1.0) versus Incident angle/degree (X-axis, ranging from 45 to 80). Two curves are shown: (a) before polymerization (black line) and (b) after polymerization (red line). Both curves show a minimum reflectivity around 59 degrees. The minimum reflectivity for curve (a) is approximately 0.05, and for curve (b) it is approximately 0.08. The difference in the minimum reflectivity is labeled as $\Delta\theta=0.54$.

Fig.S5 The preparation of MIP3: (A) kinetics of polymerization; (B) incident angles before and after polymerization

4. Contact angle measurements

The contact angles of Au, cysteamine-Au, DDMAT-cysteamine-Au and MIP film modified Au were obtained by one drop of double distilled water (DDW) on the surfaces separately. The graphs were freezed immediately as shown in Fig.S6. The contact angle changes of MIP film along with time variation in DDW and PBS (pH 7.4) were obtained as shown in Fig.S7 A and B. Both experiments were carried out using 1 μ L sample solution (DDW or PBS pH 7.4) at the same temperature (25 $^{\circ}$ C).

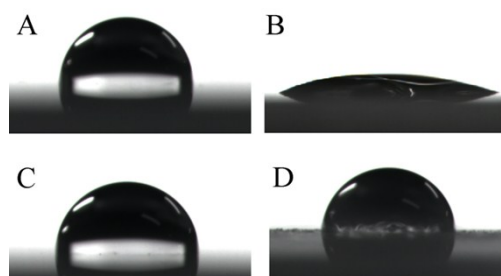


Fig.S6 Contact angle values of (A) Au, (B) cysteamine-Au, (C) DDMAT-cysteamine-Au and (D) MIP film coated.

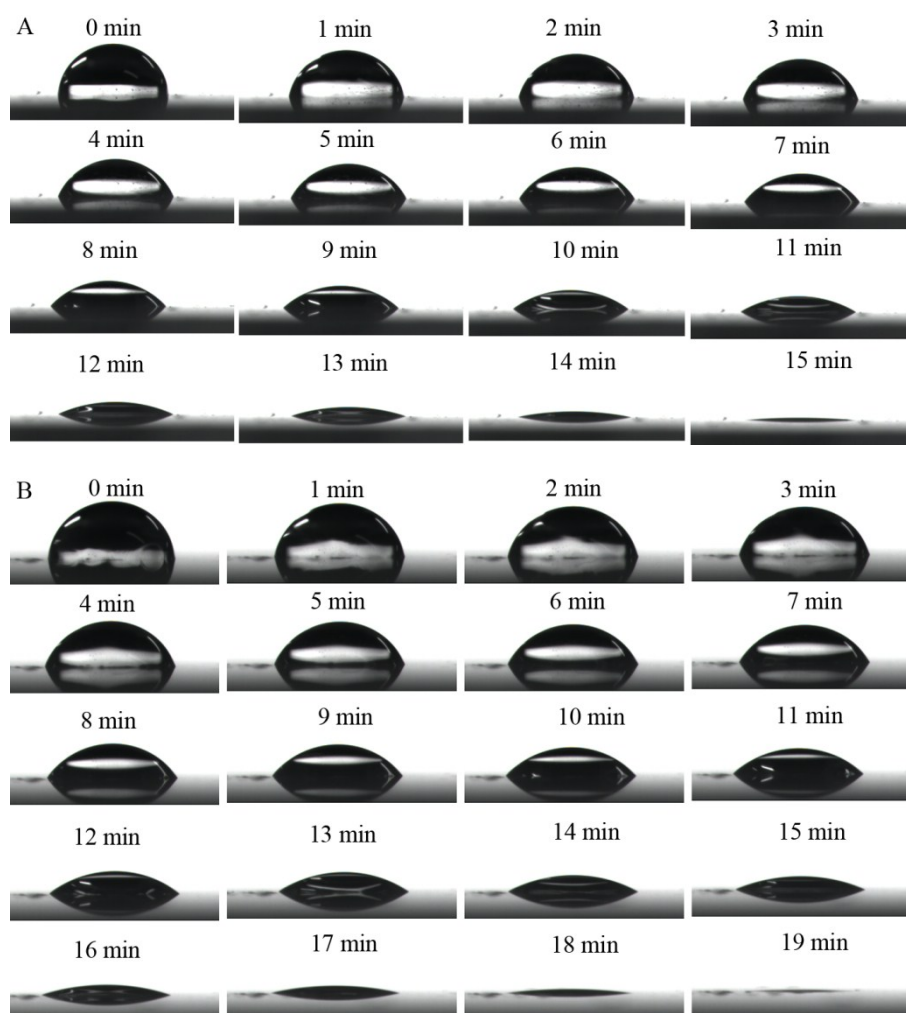


Fig.S7 The profiles of a sample drop on the MIP film: (A) a drop of DDW; (B) a drop of PBS pH 7.4

The changes of contact angle along with time variation were shown in Fig.S8. Results indicated

that the MIP film could be wetted as the contact time increased. The contact angle changed faster with dropping a PBS pH 7.4 as a sample on the MIP film surface compared with that of using DDW as a sample. It may due to the swelling of the MIP film at the PBS pH 7.4, which accelerated the wetting velocity.

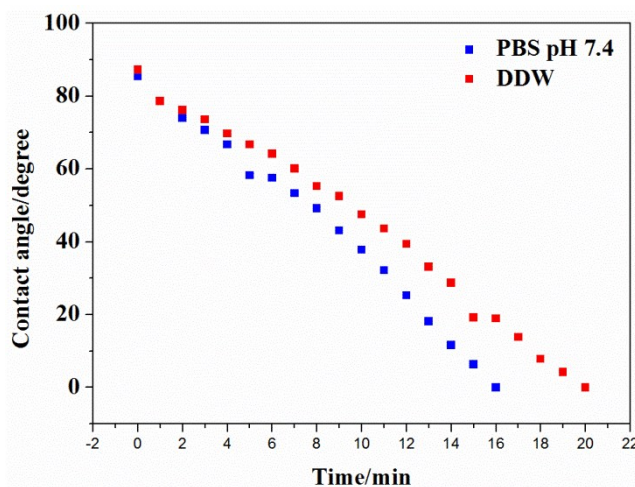


Fig.S8 The contact angles of MIP film along with time variation in PBS pH7.4 and DDW

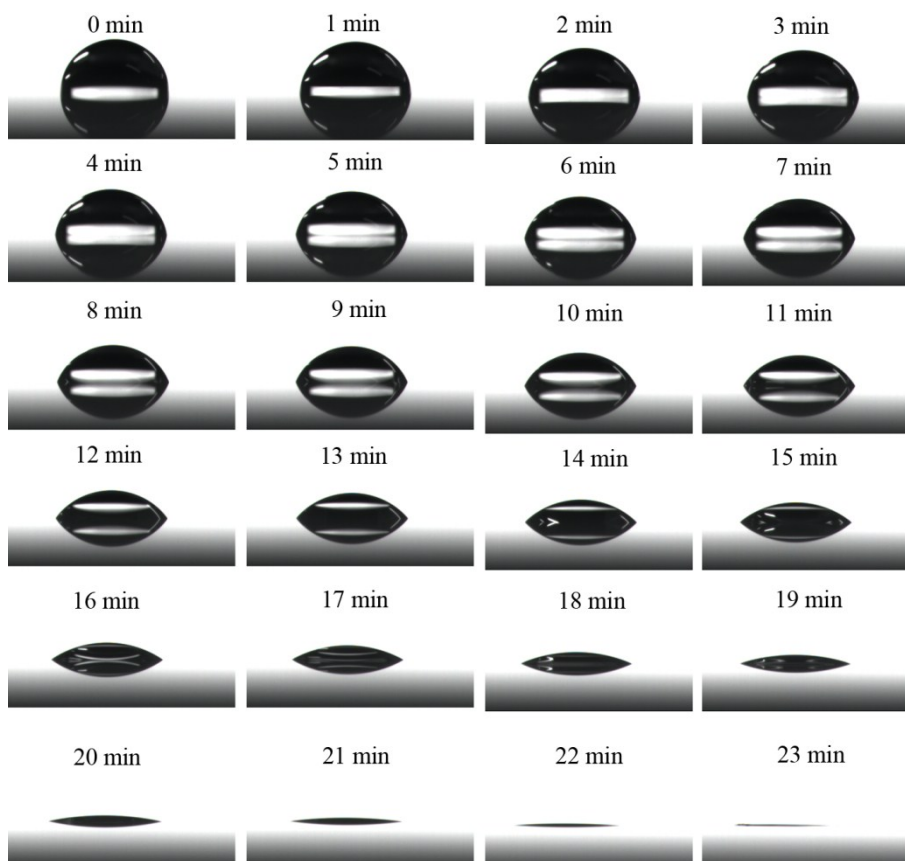


Fig.S9 The profiles of a drop (PBS pH 7.4) on the Au surface

Consider the evaporation of the droplet at room temperature, the change of the contact angle on the Au surface along with time variation was also carried out using PBS pH 7.4 as a sample as shown in Fig. S9. Results showed that the contact angle decreased slowly on the Au surface

because of its hydrophobic surface property. These results also indicated that the decrease of the contact angle on the MIP film was not only caused by the evaporation but also partly caused by the spreading and permeating of the droplet on the MIP film.

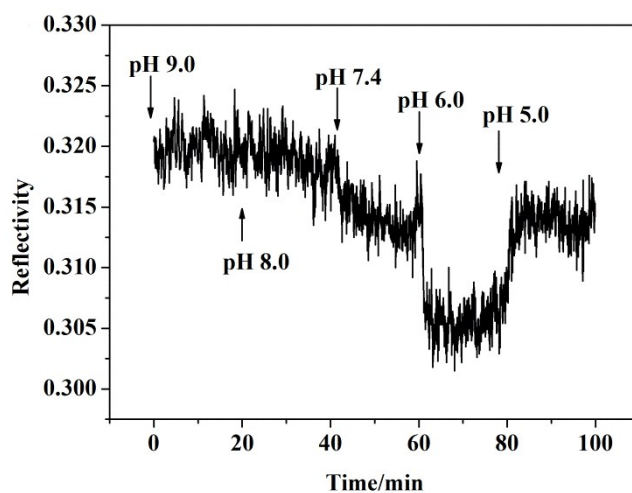


Fig. S10 Reflectivity changes in different blank solutions, from pH 9.0 to pH 5.0

References

- [1] Q. Zhang, L. Jing, J. Zhang, Y. Ren, Y. Wang, Y. Wang, T. Wei and B. Liedberg, *Anal. Biochem.*, 2014, **463**, 7
- [2] R. Ran, T. Wan, T. Gao, J. Gao and Z. Chen, *Polym. Int.*, 2008, **57**, 28