Copper microreactors for O_2 tolerant SI-ATRP synthesis of polymer brush films

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Highlights

- Microreactors fabricated from CNC and 3D printing methods used for SI-ATRP synthesis.
- Polymer brush synthesis dependent on heterogeneous transport of O_2 and Cu species.
- Discussion of how PB synthesis depends on Péclet number and microreactor aspect ratio.
- Polymer brush films having gradients in thickness achievable via controlled boundary layers.

1. Introduction

The tailored control of the physical and chemical characteristics of a surface – from the milimeter down to the nanometer scale – remains a sought-after goal in a variety of disciplines across the physical, chemical, and biological sciences. One method for such control is to coat a surface with an ultrathin (~100 nm) polymer brush (PB), a term describing a densely packed collection of individual polymer chains, each with one end attached to a surface. By changing the molecular properties of the monomer components that compose each polymer chain, one can fine-tune the physical and chemical characteristics of the PB itself. The most effective PB surfaces (i.e., those with high chain density and high uniformity) are synthesized via surface-initiated atomic transfer radical polymerization (SI-ATRP): a heterogeneous method that involves the polymerization of vinyl-containing monomers via an aqueous catalyst (here, Cu^{I}). Standard SI-ATRP methods, however, require an oxygen free environment for optimal synthesis, where the presence of dissolved oxygen will both oxidize the catalyst to an inactive form ($Cu^{I} \rightarrow Cu^{II}$) and furthermore, attack the radical intermediates during polymer chain growth, both of which act to terminate PB growth. Due to this, SI-ATRP methods are typically carried out in Shlenk-line apparatuses with deoxygenated solvents, a strenuous process that often takes hours to complete.

Recent work has shown that the placement of metallic copper plate (Cu^{0}) in close vicinity (< 100 μm) to the substrate of interest will allow for repeatable SI-ATRP synthesis in an ambient environment [1]. In this case any free oxygen will oxidize the metallic copper, thus acting to both deoxygenate the solution while simultaneous forming active catalyst directly in the region of PB synthesis. All following work based on this method has focused on the same principles using static conditions, with the only active control being over both the spacing between the copper plate and polymerization substrate and concentration of various catalyst and monomer components.

Here we extend this work to include the use of copper based microreactors for PB synthesis via two separate approaches. In the first approach we design a variety of copper microreactors for the direct PB synthesis of biointerface coatings (onto gold-coated chips) for use in optical biosensing. We show that these microreactors can be fabricated using traditional CNC processes as well as more modern 3D metal printing methods, where such Cu-microreactors are able to synthesize PB films (via stop-flow) having superior characteristics with respect to synthesis via conventional means. In addition, we will present the use of 3D printed copper microfluidic architectures for the preconditioning of polymerization solutions. We examine how changes to both the channel aspect ratio (diameter/length) and Péclet number affect both the total rate of oxygen digestion and the formation of active Cu^{I} catalyst.

2. Methods

Substrates for polymerization consisted of gold-coated glass slides, where we followed standard protocols to synthesize a self-assembled monolayer of Br-terminated alkanethiols on each surface following a previous protocol [2]. Microreactors were fabricated via CNC machining of copper or alternatively 3D metal printing using a TruPrint 1000 using copper micropowder. Microreactors were

sealed to each substrate via an o-ring along with a soft barrier to control the distance between the substrate and metal surface. 3D printed preconditioners were designed with internal microchannels of 500 µm diameter and variable length. Flow of inactive Cu^{II} catalyst and monomer solutions were accomplished via standard syringe pumps.

3. Results and discussion

Single cell microreactors fabricated using both CNC (Fig. 1b) and 3D printing methods (Fig. 1c) have been used to synthesize ultrathin 100nm thick polymer brush films that have superior properties with respect to films synthesized using traditional methods. These flow cells have been utilized in a stop-flow manner, where inactive catalyst/monomer solutions are injected into the microreactor, after which flow stops for a given time to allow for polymerization to occur (Fig. 1a, [1]).

Similar reactors operated in a flowing environment will produce a boundary layer of both O^2 and Cu^I whose thickness grows in the direction of flow in a controlled manner (Fig. 1d). Such boundary layers can be utilized to synthesize PB films having variable thickness in the axial direction of the flow cell. Likewise, a flow cell containing a longer (high aspect ratio) microchannel can be used to precondition an inactive polymerization solution for direct use with other reaction vessels (Fig. 1e); the rate of O_2 deoxygenation and Cu^I production is a function of both the channel aspect ratio as well as the channel Péclet number.

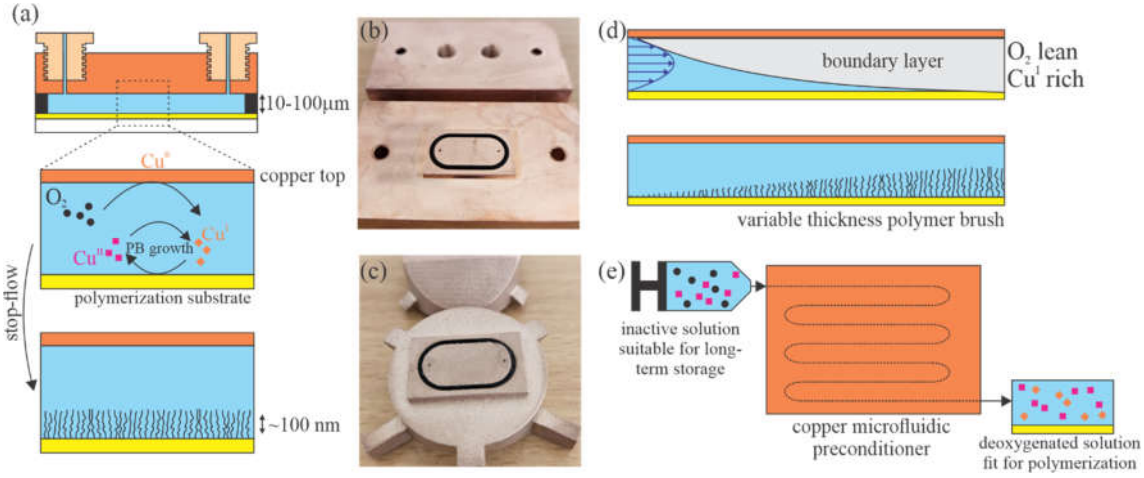

Figure 1. (a) Schematic of the use of metallic copper to allow for the SI-ATRP based synthesis of PB films [1]. Single chip microreactors fabricated from (b) CNC and (c) 3D printed methods. (d) Schematic of the use of such microreactors under flow, which results in the formation of a boundary layer to synthesize PB films having variable thickness. (e) Schematic of the use of a high aspect ratio copper microreactor to precondition an inactive polymerization solution.

4. Conclusions

The use of copper based microreactors, fabricated using traditional CNC or modern 3D printing methods, can lead to massive increases in user-friendliness and polymerization efficiency with respect to traditional static immersion-based methods.

References

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Keywords

Microreactor; polymer brush; heterogeneous catalysis; SI-ATRP; biosensing;