

# Enhanced pyrrole polymerization in self-assembled gold nanoreactors

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## ABSTRACT

Poly(styrene-*alt*-maleic acid) (SMA) is an amphiphilic alternating co-polymer which self assembles into highly organized nanostructures in water. These nanostructures include nanotubes or nanosheets creating hydrophobic cavities in the middle and hydrophilic domains on the outside. The nanoreactors generated by SMA are unsupported and induce a confinement effect due to the small size of the cavities (2-3 nm), promoting reactions that are not thermodynamically favored in bulk. Indeed, this template has been used successfully for an environmentally friendly synthesis of organic polymers (polypyrrole) as well as metal nanoparticles (gold and platinum). Pyrrole was found to spontaneously polymerize within the confined hydrophobic cavity of SMA whereas gold was found to form an atomically-thin gold monolayer on the outer hydrophilic surface of SMA. Gold when mixed with SMA was found to produce atomically thin gold crystals (30-50 nm) on the hydrophilic domain and gold clusters (2-3 nm) in the hydrophobic cavity produced by SMA. In this study, we detail the development of gold nanoreactors and demonstrate its catalytic capabilities by the polymerization of pyrrole.

**Keywords:** hybrid polymer-metal systems, pyrrole polymerization, gold nanostructures

## 1. INTRODUCTION

Gold nanoparticles have been extensively used in nanomedicine because of their unique properties and many applications in variety of fields including biology, chemistry, clinical laboratory or biomedicine. [1-5] Interestingly, the non-reactive nature of gold in the bulk is altered at the nanoscale allowing its use as an active center for nanoreactors. Nanomaterials are known to have unique properties leading to advantages including altered catalytic capability or dominating atomic or molecular interaction.[6, 7] Bottom-up approach is commonly suggested for the development of nanoreactors since it enables the reaction to occur in a controlled environment and builds the product from the dominating atomic interactions via self-assembly.[8] Block copolymers are known to self-assemble and produce larger nano structures with larger cavity sizes when compared to alternating co-polymer.[9, 10] The large

cavity produced by block copolymer prevents confinement effects influencing the reactivity inside the template leading to choosing an alternating copolymer.

Poly(styrene-*alt*-maleic acid) (SMA) is an amphiphilic alternating co-polymer which self assembles into highly organized nanostructures in water. [11] These nanostructures include nanotubes or nanosheets creating hydrophobic cavities in the middle and hydrophilic domain on the outside. It has previously been shown that SMA nanotubes are formed from the association between eight SMA polymers through  $\pi$ - $\pi$  stacking with a hydrophobic cavity of 3 nm and a hydrophilic domain on the outside.[12] The nanoreactors generated by SMA are unsupported and induce a confinement effect due to the small size of the cavity, promoting reactions that are not thermodynamically favored in bulk. In this study, SMA<sub>m</sub> instead of SMA is used because it has demonstrated enhanced reactivity with gold. [13] The main structural difference between SMA and SMA<sub>m</sub> is the highlighted methyl group (highlighted in a circle in Figure 1). The presence of this methyl group does not change any properties of SMA itself but instead affects its interaction with gold. [13] The methyl group has been computationally observed to modify the conformation of the molecule such that gold is able to interact with two oxygen atoms instead of one strengthening its interaction. [13]. It is important to note that SMA<sub>m</sub> consists of 85% of SMA structure, without the methyl group highlighted in Figure 1 whereas the other 15% is with the mono methyl ester.

Polymerization of pyrrole and the production of well dispersed and stable platinum nanoparticles (~2nm) have been observed under the confinement of SMA<sub>m</sub> without any reducing agents.[14, 15] Moreover, it was also found that using the SMA-platinum system along with pyrrole led to faster kinetics of pyrrole polymerization and an overall threefold increase in the reaction rates.[16] Polypyrrole was specifically chosen because of its wide range of applications including high conductivity or capacity for energy storage. [14, 17] Therefore using SMA as a template provides an option for environmentally friendly synthesis and reduction of metal salts under confinement effect without the use of any reducing agents.

The modified properties of gold under confinement effect have been observed and studied for various systems such as in SiO<sub>2</sub> cavities or inside siloxane nanocages.[18,

19] Reduction of gold has been conducted using reducing agents such as hydrogen gas or amines.[20, 21] The confined conditions created by SMA makes it possible to reduce gold without any reducing agents as detailed in earlier studies by our group.[15] Production of stable well dispersed gold nanoparticles has proven to be a challenge in research and hence, this study aims to develop a system that allows for a simple method of synthesis of stable and well dispersed gold nanoparticles. Using SMA as a template also enables the reaction of gold with hydrophobic and hydrophilic domains at the same time. The aim of this paper is to develop gold nanoreactors by using a polymeric template, SMA<sub>m</sub> and demonstrate its increased catalytic capabilities by polymerization of pyrrole.

The nanoreactors produced are expected to present improved reactivity's due to the enhanced properties of the metal catalyst at the nanoscale combined with the confinement effect within the cavities. Lastly, the enhanced catalytic capabilities of SMA<sub>m</sub> gold nanostructures are proven by fast pyrrole polymerization. The ability to control the interaction of gold with the hydrophobic or hydrophilic cavity offers tremendous potential on tailoring the hydrophobic and hydrophilic reactive environment for many applications.

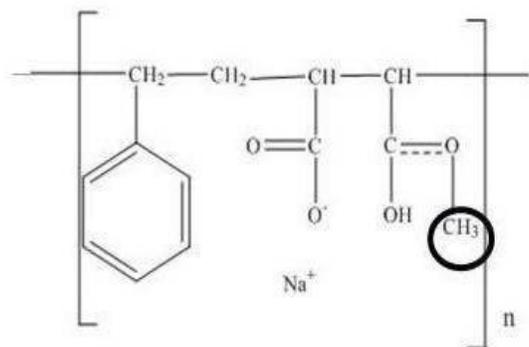


Figure 1: Chemical Structure of SMA<sub>m</sub> with 85% of the structure being without the methyl group (black circle) and 15% of the structure shown in the figure

## 2. MATERIALS AND METHODS

Poly (styrene-*alt*-maleic acid) with monomethyl ester (SMA<sub>m</sub>) was solubilized to make 1% solution and then neutralized to pH 7 with NaOH as required. Gold(I) chloride (AuCl) and pyrrole were used as received. For sample preparation, 5 ml of SMA<sub>m</sub> at pH 7 was mixed with appropriate amounts of gold for the development of nanoreactors. AuCl was added in a 1 to 1 ratio by weight to SMA. After the development of nanoreactors, pyrrole was added in excess to monitor enhanced catalytic capabilities of the developed nanoreactor. The polymerization of pyrrole was monitored via UV/Vis spectroscopy. SMA 350 kDA, Gold (I) chloride 99.9% and pyrrole monomers were

purchased from Sigma Aldrich and used without further purification.

## 3. RESULTS AND DISCUSSION

The growth of the nanoparticles within the confined regions of SMA was followed by UV-Vis using the different peaks generated by the clusters (300nm) and the crystals (560nm). Specifically, AuCl was found to interact with both the hydrophobic and the hydrophilic domains of SMA simultaneously, while producing gold crystals of 30-50nm in contact with the hydrophilic domain and gold clusters of 2-3 nm due to the size restriction of the hydrophobic cavity .[13] The results were then confirmed with IR and TEM (not shown). After the development of gold nanoreactor, pyrrole was added to the system to demonstrate the enhanced catalytic capabilities of the system.

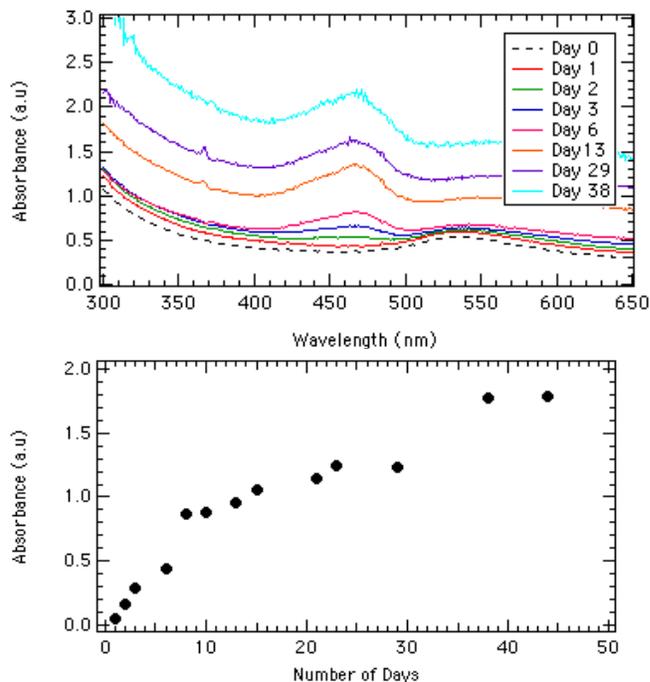


Figure 2: Polymerization of pyrrole observed in UV/Vis spectra of AuCl in 1% SMA<sub>m</sub> solution a) peak at 470 nm develops on day 2 b) pyrrole polymerization vs. the number of days at 470 nm. Reprinted from [13].

The polymerization of pyrrole has been observed earlier as explained in the introduction. Similarly, the polymerization of pyrrole can be observed in Figure 2a with a peak at 470 nm observed to develop on Day 2. Without the addition of any metals the pyrrole with the same SMA template was observed to polymerize after approximately a month. After the addition of platinum nanoparticles to the template the polymerization could be observed on day 8 demonstrating enhanced reactivity with faster reaction kinetics.[16] Comparatively in Figure 2b the

polymerization of pyrrole can be observed on the second day up to day 44. This proves that gold is able to form stable nanoreactors with the polymeric template and demonstrates enhanced catalytic activity. Moreover, the polymerization within the template occurs due to the hydrophobic cavity provided by the SMA template which is able to generate the confinement effect promoting pyrrole polymerization that is spontaneously not favorable otherwise.

#### 4. CONCLUSION

In this study, we developed a simple environmentally friendly method for the development of gold nanoreactors and produced stable gold crystals and clusters at the same time. Moreover, the enhanced catalytic effect produced in SMA<sub>m</sub>-gold was demonstrated with pyrrole polymerization starting on second day. The proven enhanced catalytic activity opens the system to many applications in drug delivery and nanoreactors development.

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