



Polydopamine modified membranes with in situ synthesized gold nanoparticles for catalytic and environmental applications

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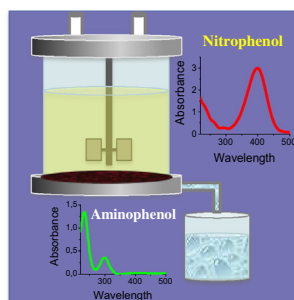
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HIGHLIGHTS

- In situ synthesis of Au nanoparticles over polydopamine modified membranes.
- Membrane reactor was prepared for flow-through mode catalysis and dye degradation.
- High reduction of *p*-nitrophenol and degradation of dyes was obtained at a high flux.
- In continuous flow >98% degradation of Congo red and methylene blue at high flux.

GRAPHICAL ABSTRACT



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ABSTRACT

The versatile ability of dopamine to modify and functionalize surfaces was utilized for the grafting of poly (ethyleneimine) (PEI) and preparation of catalytically active track-etched poly (ethylene terephthalate) membranes. Gold nanoparticles were synthesized by self-reduction of $[\text{AuCl}_4]^-$ ions immobilized on DOPA, whereas for PEI-grafted membranes, the nanoparticles were obtained by in situ reduction using NaBH_4 . The morphological characterization indicated that the gold nanoparticles were synthesized on the surface as well as on the pore walls of the membrane. These membranes were used to fabricate a flow through membrane reactor for continuous flow catalysis and dye degradation. High reduction of *p*-nitrophenol (PNP) and degradation of Congo red and methylene blue dyes at different permeation rates showed promising use of the membranes for such applications. The maximum reduction ($\sim 99\%$) of the PNP to *p*-aminophenol (PAP) was obtained at the permeation rate $\sim 40 \text{ L m}^{-2} \text{ h}^{-1}$, while for the Congo red and methylene blue it was $\sim 95\%$ and 98% at 947 and $473 \text{ L m}^{-2} \text{ h}^{-1}$, respectively. Furthermore the membrane showed sustained catalytic activities for a longer duration and maintained $>99\%$ activity after 11 cycles of dye degradation. These properties confirm the great potential of gold nanoparticle decorated membranes in catalysis and environmental remediation.

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1. Introduction

Metal nanoparticles-based catalysis have attracted great attention in recent past because of the specific catalytic properties, large

surface area-to-volume ratio, and other fascinating chemical and physical properties [1,2]. The high catalytic properties of such materials highly depend on the size and shape of nanoparticles, which cause the origin of easily accessible binding sites on their surface for chemical reactants. However, the very small size of the nanoparticles also complicates their separation and recovery after completion of the reaction. Another problem with pristine

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and free nanoparticles is agglomeration which greatly reduces their catalytic efficiency and dispersion in solution. To prevent the aggregation, the nanoparticles are stabilized with various agents, such as charged molecules [3], polymers [4], dendrimers [5], etc. These stabilizing agents not only protect the nanoparticles but also ensure its dispersion in polar and non-polar solvents. Immobilization of nanoparticles on suitable support is also reported on various substrates to prevent the aggregation such as on alumina [6], silica spheres [7], zeolites [8], SBA-15 [9], graphene [10], polymeric substrates [11], etc.

One of the major challenges in the use of metal nanoparticles as the catalysts is to separate them from the mixture after completion of the reaction. Reports are available, which suggest the coupling of separation with catalysis in membrane reactors where in situ separation of nanoparticles can be achieved [12,13]. However, it is observed in such coupling systems, the nanoparticles adsorption on the membrane surface resulted in a sharp decrease in flux that made the reactor system unusable. One of the most useful ways to solve all the above problems is by immobilization of the nanoparticles on the surface and inside the pores of the membranes by suitable chemical modification using different crosslinking or coupling agents to generate sufficient functional groups or by grafting of polymer brushes, etc. The chemical modifications of membranes are necessary to bind and hold the nanoparticles in harsh and flow through condition. The immobilized nanoparticles can be used for several cycles of operation without the need of separation from the reaction mixture. Highly porous polymeric membranes provide an alternative and efficient support to immobilize different types of nanoparticles and can be significantly used for catalysis in flow through mode [1,14]. Nanoparticle immobilized membranes also avoid the need to disperse the catalyst and of a subsequent recovery by separation from the reaction mixture [1,14]. It is also important to note that in flow through mode of reactions, the membrane pores result in the rapid convective mass transport of reactants to immobilized metal nanoparticles, yielding conversions that often depend on the kinetics or mass flow, rather than diffusion [12,14]. Although the immobilization of nanoparticles on a membrane support offers interesting possibilities for catalysis and membrane reactors in flow through reactions, several other characteristics have to be met for any membrane support to be used for such processes [15]. The most important parameter is that the nanoparticles should be firmly bound to the surface to avoid the leaching problem. The surface properties of the membrane are key factors affecting the mode and amount of immobilization of nanoparticles. Thus, the membrane should possess the functional characters to hold the nanoparticles firmly by electrostatic interaction or by bonding with the groups used for nanoparticle stabilization. Several ways have been reported to modify the membranes for nanoparticle immobilizations such as modification with amino silanes [1], polyelectrolyte multilayers [14], polymer brushes [2], mixing with membrane forming solutions [16] etc. Generally, the immobilization of nanoparticles on solid support tends to show low catalytic activity due to the loss of interaction with the substrate as a consequence of a loss of active sites. One of the other important factors is, size reduction and blocking of pores for this kind of membrane. This could be overcome by modifying the surface with more flexible polymeric materials and surface modifiers which are not only susceptible to immobilization but also can stabilize the nanoparticles.

Recently mussel inspired DOPA coatings have attracted great attention as a biomimetic polymer and universal surface modifying agent for various materials with a broad range of applications [17,18]. DOPA surfaces have been used for further modification via a Schiff base or Michael addition reaction which offers the opportunity to graft amine or thiol containing compounds [17,19]. Recently we have also used the DOPA modification as an

intermediate active layer to graft thermo-responsive poly(*N*-isopropyl acrylamide) to construct thermo-responsive membranes [20]. In the present work, we modified the PET track-etched membranes by dopamine polymerization and further grafted PEI for in situ gold nanoparticle synthesis on both DOPA and DOPA-PEI surfaces. It is reported that the DOPA allows the adsorption of $[\text{AuCl}_4]^-$ and subsequent reduction to gold nanoparticles [9]. Thus the DOPA-modified membrane surface provides dual functions: adsorption of $[\text{AuCl}_4]^-$ anions to amine groups and in situ reduction of the adsorbed anions to gold nanoparticles. Therefore, no reducing agent is required for gold nanoparticle formation on membranes with DOPA at the surface. However, to enable a higher gold nanoparticle loading and stabilization on the surfaces, we further grafted PEI on DOPA-modified membranes. This membrane was also subjected to in situ adsorption and reduction of gold nanoparticles. In this case a reducing agent was also used for gold nanoparticle formation in addition to the in situ reduction over DOPA. Finally, we used both modified membranes for chemical catalysis and environmental remediation in flow through condition. PNP reduction, Congo red, and methylene blue dye degradation were tested as model reactions to assess the suitability of the prepared membranes for the above processes. Almost complete reduction of PNP and degradation of dyes was achieved at a high permeation rate over these membranes in flow through mode.

2. Experimental section

2.1. Materials

The PET track-etched micro-porous membranes (pore diameter: 0.4 μm , pore density: 1.5×10^8 pores/cm² respectively) was obtained from Sterlitech Corporation (Kent, WA, USA). All other chemicals were obtained from Sigma-Aldrich, Inc. (St. Louis, Missouri, USA) and used as received. For all purpose Millipore water was used.

2.2. Membrane modification

2.2.1. Preparation of dopamine coated PET membrane

The DOPA coating and PEI grafting on PET track-etched membranes were carried out as per the previous reports [19,20]. The PET membranes were first soaked in a water-ethanol mixture (1:1) for 3 h and subsequently cleaning with water and ethanol to remove the impurities and contaminations. Dopamine solution was prepared, by dissolving 2 mg mL⁻¹ dopamine [4-(2-aminophenyl)benzene-1,2-diol] in a mixed solvent ($V_{\text{tris}}/V_{\text{ethanol}} = 9:1$) of 10 mM tris-HCl (2-amino-2-hydroxymethyl-propane-1,3-diol) buffer solution, (pH 8.5) and ethanol. Washed membranes were kept under constant shaking at room temperature in the dopamine solution. The self-polymerization of dopamine on the membrane was allowed for different time intervals ranging from 3 to 24 h. The DOPA-coated membranes were carefully washed with ethanol and deionized water to remove unreacted and loosely bound dopamine. The coated membranes were dried at 60 °C in vacuum for 12 h before any further modification.

2.2.2. Grafting of PEI onto dopamine coated PET membrane

DOPA-coated membranes were immersed into a solution of PEI (2 mg mL⁻¹ of 15 mM tris-HCl buffer (pH 8.5), molecular weight $M_w = 25,000$ g mol⁻¹) for 3 h under constant shaking condition at 60 °C. After the incubation, the reaction vessel was cooled down to room temperature and was further kept under shaking for 24 h to allow the maximum grafting. The modified membranes were thoroughly washed with deionized water and dried in vacuum at 60 °C to a constant mass. The amounts of dopamine and

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