Nanoporous block copolymer membranes immobilized with gold nanoparticles for continuous flow catalysis†

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Nanoporous polymers with functionalizable surfaces are desired in the preparation of reactors for continuous flow catalysis. Here, a facile approach for the fabrication of flow reactors is developed by immobilizing Au nanoparticles (AuNPs) on nanoporous membranes derived from block copolymers (BCPs). We synthesized the BCP of poly(2-dimethylaminoethyl methacrylate) and polystyrene (PDMAEMA-b-PS) where the PDMAEMA minority blocks contain tertiary amine groups so as to anchor the Au precursors. Simply soaking the BCP in hot ethanol generated interconnected nanopores with PDMAEMA chains enriched on pore walls following the mechanism of selective swelling induced pore generation. The nanoporous BCP membranes were used as supports to immobilize the AuNPs via in situ reduction of the Au precursors, producing catalytic reactors with the amount of AuNPs conveniently tunable by changing the concentration of the Au precursors. The nanoporous BCPs provided tortuous channels to host more AuNPs and to increase the chances of contact between the reactants and the AuNPs in flow reactions. Thus-produced AuNP-anchored BCP membranes were used as flow reactors to catalytically transform nitrophenol to aminophenol, and a catalytic efficiency up to 100% was reached. We also demonstrated that the membranes were highly efficient in the catalytic degradation of organic dyes.

1. Introduction

As one of the most widely studied metal nano-materials, Au nanoparticles (AuNPs) have been popular for decades because of their prominent performance in catalysis, sensing, biomedicines, etc.5-8 AuNPs have large surface areas and unique crystal facets, which are critical for their practical properties, especially for the catalytic activity when employed as catalysts. However, the high surface energy of AuNPs usually leads to unexpected aggregation during applications, significantly weakening their performances.4 In order to avoid aggregation, AuNPs are frequently anchored on organic or inorganic matrices to enhance their stability. Consequently, both the matrices and AuNPs constitute the catalytic reactors, such as Au–polymer hybrid microgels and silica/Au nanocomposites.5-8 Although the dispersibility and high catalytic activities can be maintained by the support of matrices, these reactors still have disadvantages in catalysis in liquid reaction systems. The separation and recycling of Au compounds from the liquid reaction systems are always necessary after each batch of catalytic reactions, which makes the reaction process tedious and time-consuming and obviously unfavorable for industrial applications.

Recently, continuous flow catalysis has emerged as a promising system for catalytic reactions.9-12 Generally, the flow reactors are constructed by anchoring nanocatalysts on porous supports. Reaction liquids flow through the channels existing in the porous supports. Meanwhile, the reactants can be catalyzed by nanocatalysts anchored within the reactors. Therefore, continuous flow nanocatalysis presents unique advantages of good recyclability, continuous operation and no contamination by catalysts in the products compared with the traditional batch-type catalysis.13-15 In this regard, the development of continuous flow reactors with high catalytic efficiency has attracted wide interest, and a variety of flow reactors based on the combination of AuNPs and porous materials, basically including porous membranes and monolithic columns, have been investigated lately.16-21 To achieve homogeneous and robust anchoring of AuNPs, surface modification of the support materials with amine, thiol or other functional groups that have strong affinity for AuNPs is a common and efficient...

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strategy. For example, Chen and co-workers attached AuNPs on the surface of amino-functionalized polystyrene (PS) microspheres, forming core–shell PS@AuNP hybrid microspheres, and assembled the hybrid microspheres into close-packed porous microsphere membranes followed by deposition of PAA-coated CNTs. The achieved catalytic composite membranes showed good catalytic efficiency of nitrophenol in oily water. For the design of flow-through reactors based on monolithic capillaries, Droumaguet et al. grafted an amine-containing compound, histamine, onto an N-hydroxysuccinimide-functionalized monolith for specific adsorption of AuNPs. The produced AuNP hybrid capillary columns exhibited good catalytic activity with excellent yields for nitrophenol and a series of dinitroaromatic compounds. Nevertheless, multi-step synthetic operations including pretreatment, reaction and purification are inevitably involved in the post-modification of support materials with the bonding sites of AuNPs. Therefore, more convenient approaches for the preparation of continuous flow reactors are highly desired.

In this work, block polymers (BCPs) are used as precursors to construct a porous support for building continuous flow reactors. BCPs have been demonstrated to be a type of preeminent material to fabricate nanoporous membranes with tunable pore sizes and pore geometries. In particular, by the process of selective swelling induced pore generation, the minority blocks in BCPs would migrate and be enriched on the pore walls along with pore formation. Our previous work reported the nanoporous BCP membranes derived from polystyrene-block-poly(2-vinylpyridine) (P2VP) by selective swelling and used them for the size fractionation of nanoparticles. For this work, BCPs of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and PS are synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization and used to prepare nanoporous membranes. After selective swelling treatment, PDMAEMA chains containing tertiary amine groups that have strong affinity to Au precursors would be present along the surface and pore walls of membranes, and thus-produced membranes possess tortuous pore structures and multi-tertiary amine surfaces. Using these membranes as porous supports, AuNPs can be immobilized on them by in situ reduction of Au precursors, forming continuous flow catalytic reactors conveniently without any post-modification. On account of the dense and homogeneous coverage of tertiary amines on the supports, the immobilized AuNPs can be uniformly distributed on the produced membranes. Moreover, the nanoscale pore structure is beneficial for the sufficient contact of reactant solutions with AuNPs, and the hydrophilic nature of PDMAEMA makes the membranes suitable for applications in aqueous systems. The AuNP-immobilized BCP membranes are employed for the reduction of nitrophenol to aminophenol and the degradation of organic dyes in flowing aqueous solutions, and the excellent catalytic activity indicates their great potential in catalytic production of chemicals and degradation of organic dyes in polluted water.

2. Experimental

2.1 Materials

2-Dimethylaminoethyl methacrylate (DMAEMA, Aldrich, 99%) was purified by passing through an alumina column and then distilled under reduced pressure prior to use. Styrene (Sinopharm Chemical Reagent Co., >99%) was passed through an alumina column to remove the inhibitor and stored at −20 °C. 2,2′-Azobis(isobutyronitrile) (AIBN, Aladdin, 98%) was recrystallized from ethanol. 2-Cyano-2-propylidithiobenzoxoate (CPDB, Aladdin, >97%), tetrahydrofuran (THF, Aladdin, ≥99.9%), hydrogen tetrachloroaurate trihydrate (HAuCl4, Aladdin, Au 23.5–23.8% in dilute HCl), sodium borohydride (NaBH4, Sinopharm Chemical Reagent Co., ≥96%), 4-nitrophenol (4-NP, Sinopharm Chemical Reagent Co., ≥99%), rhodamine B (RhB, Sigma, ≥95%) and methyl orange (MO, Aladdin, 96%) were used as received. Macroporous polyvinylidene fluoride (PVDF) membranes with a diameter of 25 mm and a nominal pore size of 0.22 μm were supplied by Millipore as the supporting substrates. Deionized water was used in all experiments. All other reagents including ethanol, chloroform, etc., were of analytical grade and obtained from local suppliers.

2.2 Synthesis of PDMAEMA-b-PS

The synthetic procedure of PDMAEMA is as follows: CPDB (66.3 mg, 0.3 mmol), DMAEMA (7.065 g, 45 mmol), AIBN (9.84 mg, 0.06 mmol), and THF (8 mL) were added into a 40 mL polymerization tube with a magnetic bar. After dissolving thoroughly, the mixture was degassed through three freeze–pump–thaw cycles. Then, the tube was sealed under vacuum and placed in an oil bath at 70 °C for polymerization. After 11 h, the reaction was stopped by cooling the mixture to room temperature rapidly and opening the tube to air. The unreacted DMAEMA monomer was removed by adding the polymer solution dropwise into an excess of n-hexane. The precipitate was collected and dried under vacuum at room temperature to obtain the solid polymer. In order to eliminate the residual monomer completely, this precipitation process was repeated three times to purify the product.

The resultant PDMAEMA was used as the macro-chain transfer agent to synthesize the di-block copolymer of PDMAEMA-b-PS, and the procedure is as follows: PDMAEMA (348 mg, 0.016 mmol), styrene (4.16 g, 40 mmol), AIBN (0.524 mg, 0.0032 mmol), and methanol (2.4 g) were added into a 10 mL polymerization tube with a magnetic bar. Similarly, the tube was degassed by three freeze–pump–thaw cycles and sealed under vacuum. Polymerization was conducted at 80 °C for 78 h. The product was obtained by precipitating the polymer solution into an excess of n-hexane three times, followed by sufficient drying in a vacuum oven at room temperature.

2.3 Preparation of nanoporous PDMAEMA-b-PS membranes

The BCP of PDMAEMA-b-PS was dissolved in chloroform with a concentration of 2 wt%. The obtained solution was filtered.
through PTFE filters with a pore size of 0.22 μm three times to remove any big aggregates that existed. The composite membranes were prepared by spin-coating the BCP solutions onto the PVDF substrates. To prevent the leakage of the coating BCP solutions, the PVDF substrates were immersed in deionized water for a few minutes to make water fill into the pores of the PVDF substrates prior to spin-coating. After removing from water, the water-filled PVDF substrates were placed on a clean glass slide. 200 μL of the BCP solution was added dropwise on the PVDF substrate, followed by spin-coating at 1500 rpm for 30 s with a speed of 5000 rpm. Subsequently, the membrane was heated at 60 °C for 20 min to evaporate the solvent and water completely. To cavitate the BCP layers, the BCP-coated composite membranes were then soaked in ethanol at 70 °C for pre-determined durations, followed by drying in air at room temperature.

2.4 Immobilization of AuNPs on PDMAEMA-b-PS membranes

A certain amount of HAuCl4 aqueous solution was taken out and diluted with deionized water to 0.5, 1.25, 2.5 and 5.0 mg mL⁻¹, respectively. The BCP membranes after swelling treatment were immersed in HAuCl4 aqueous solutions with different concentrations for 12 h. After withdrawing the membranes from the HAuCl4 solutions, redundant solutions on the surface of the membranes were gently wiped with filter paper. Subsequently, the membranes were soaked in the NaBH4 solution (1 mg mL⁻¹) to reduce the Au precursor to AuNPs. After washing with deionized water three times and drying at room temperature, the AuNP-immobilized BCP membranes were obtained.

2.5 Characterization

Nuclear magnetic resonance (NMR) measurements were performed on a Bruker AV400 NMR spectrometer using CDCl₃ as the solvent to characterize the structure of the polymers. A Waters 150C gel permeation chromatograph (GPC) equipped with ultra-styragel columns (500, 103 and 104 Å) and an RI 2414 detector was employed to evaluate the molecular weight (Mₙ, Mₘ) and molecular weight distribution (Mₘ/Mₙ) of the polymers. The measurements were conducted at 30 °C using dimethyl formamide (DMF) as the eluent with a flow rate of 1.0 mL min⁻¹, and monodisperse polystyrene standards were used in the calibration. The surface and cross-sectional morphology observations of the membranes were performed on a field emission scanning electron microscope (FESEM, Hitachi S-4800) at an accelerating voltage of 5 kV. The samples for SEM were treated by spray-gold under vacuum to enhance the conductivity prior to examination. X-ray photoelectron spectroscopy (XPS) was utilized to reveal the distribution of PDMAEMA chains on the surface of the membrane during swelling. The XPS analyses were performed on an ESCALAB 250 XPS system (Thermo Scientific) using an Al Kα X-ray source (hν = 1486.6 eV). Transmission electron microscopy (TEM) observations were conducted on a Philips Tecnai 12 TEM at an accelerating voltage of 120 kV to characterize the sizes of AuNPs anchored on the BCP membranes. To prepare the samples for TEM, the AuNP-immobilized BCP membrane was immersed in dichloromethane under ultrasonication to dissolve the BCP layer and disperse the AuNPs into the solvent. Then a drop of the AuNP dispersion in dichloromethane was deposited on copper grids for the TEM observation. An energy-dispersive X-ray spectrometer (EDX-Noran) was used to analyze the Au content of the prepared AuNP-immobilized BCP membrane at an accelerating voltage of 30 kV.

2.6 Continuous flow catalytic reactions

To study the catalytic properties of the AuNP-immobilized BCP membranes, the reduction of 4-nitrophenol (4-NP) by NaBH₄ was chosen as a model reaction. The continuous flow catalytic tests were conducted with a dead-end filtration cell (Amicon 8010, Millipore Co.). The typical experiment was carried out as follows: A piece of the AuNP-immobilized BCP membrane was fixed in the filtration cell with an effective area of 4.15 cm². The aqueous solution containing 4-NP (10 ppm) and NaBH₄ (500 ppm) was preloaded and continuously flowed through the membrane at a constant flow rate under pressure. The flow rate can be tuned by changing the trans-membrane pressures. UV-vis spectroscopy was used to calculate the conversion of reduction reaction by analyzing the content of 4-NP in the initial aqueous solution and the filtered solution. For the continuous flow catalytic degradation of organic dyes, the initial aqueous solution of RhB (10 ppm) and NaBH₄ (500 ppm), or MO (10 ppm) and NaBH₄ (500 ppm) was used, and operation similar to the reduction of 4-NP was conducted for the catalytic tests.

3. Results and discussion

3.1 Morphology and surface properties of PDMAEMA-b-PS membranes

The BCP of PDMAEMA-b-PS was prepared via two-step RAFT polymerization according to a previous report. Typically, CPDB-terminated PDMAEMA was first synthesized and then used as the macro-chain transfer agent to conduct polymerization of styrene, forming the desired BCP of PDMAEMA-b-PS as shown in Scheme S1†. The chemical structures of the obtained PDMAEMA and PDMAEMA-b-PS were verified by ¹H NMR spectra (Fig. S1†). The characteristic signals of PDMAEMA appearing at 4.07, 2.57, 2.28 and 7.32-7.90 ppm are attributed to the ester methylene protons, methylene protons adjacent to nitrogen, methyl protons adjacent to nitrogen and phenyl protons in the CPDB groups, respectively. The mean degree of polymerization (DP) of PDMAEMA can be determined to be 137 based on the integral values of signals at 4.07 and 7.32-7.90 ppm (eqn (S1)) for the spectrum of PDMAEMA-b-PS. The proton signals appearing at 4.07 and 6.20-7.21 belong to the ester methylene protons of the DMAEMA units and the phenyl protons of the styrene units. According to the integral ratio of the proton signals and the DP of PDMAEMA, the DP of PS is calculated to be 674.
Thus, the molecular weights of PDMAEMA and PDMAEMA-b-PS are 21,500 and 91,600 g mol\(^{-1}\), respectively, and the weight ratio of PDMAEMA in the produced BCP is 23.5%. GPC was also used to characterize the resultant polymers. As shown in Fig. S2, the traces of PDMAEMA and PDMAEMA-b-PS are both symmetric and unimodal, and their molecular weight distributions are narrow (1.17 and 1.16, respectively), which evidence the good control of molecular weights during the RAFT polymerizations.

PDMAEMA-b-PS was coated on the PVDF substrates to form the composite membrane. The BCP layer atop the PVDF substrate was nonporous with a smooth surface and exhibited a completely dense state across the whole thickness (Fig. S3†). In order to cavitate the BCP layer, the composite membrane was immersed in ethanol, which is a selective solvent to PDMAEMA chains, at 70 °C for different durations. Ethanol has a strong affinity to PDMAEMA, but can only slightly swell the PS matrix. Based on the mechanism of selective swelling, ethanol prefers to be enriched in the PDMAEMA domains when it diffuses into the BCP layer. PDMAEMA chains are swollen and expand their volumes, leading to the plastic deformation of the PS matrix. After withdrawing the membranes from the ethanol bath, the swollen PDMAEMA chains collapse with the rapid evaporation of the solvent. Meanwhile, the volumes previously occupied by the swollen chains are converted to pores, as shown in Scheme 1a. Upon swelling treatment for 1 h, the morphology of the BCP membrane was observed by SEM. It is obvious that the BCP layer was changed from nonporous to nanoporous. Elongated and interconnected nanopores appeared on the surface of the membranes (Fig. 1a). Furthermore, this nanoporous structure spanned the entire thickness of the BCP layer, as indicated by the cross-sectional SEM image of the membranes (Fig. 1b).

Apart from the pore formation, the other notable phenomenon that occurred during the selective swelling process was the enrichment of the PDMAEMA chains on the surface and pore walls of the membranes. Before swelling, the PDMAEMA domains were predominately embedded in the PS matrix in the BCP layer. As the volumes occupied by the swollen PDMAEMA phase were converted into pores, the PS matrix constituted the framework of the BCP layer, and the collapsed chains of PDMAEMA, which was covalently linked to the PS chains, covered along the pore walls, primarily determining the surface properties of the membranes. In order to trace the migration of the PDMAEMA chains, XPS was employed to analyze the change of surface compositions of the membranes during the swelling treatment. As shown in Fig. 2, the peak at the binding energy of 400 eV is attributed to N 1s in the PDMAEMA chains. The membrane prior to swelling had a N content of 4.26% in surface composition. After swelling in ethanol for 0.5 and 1 h, the content of N was increased to
4.80% and 4.87%, respectively, evidencing the progressive enrichment of the PDMAEMA chains on the surface with extended swelling durations. This enrichment process happened in parallel to the formation of pores, which is much more convenient as there is no need for post-modification of the existing pores. More importantly, the tertiary amines in the PDMAEMA chains distributed in the surface and pore walls provide bonding sites for the subsequent immobilization of AuNPs on the membranes.

3.2 Morphology of AuNP-immobilized BCP membranes

The prepared BCP membranes were used as porous supports to immobilize AuNPs for building continuous flow reactors. Since the interaction between tertiary amine groups of the PDMAEMA chains and the pre-synthesized AuNPs is weak, not enough to anchor the AuNPs robustly, the in situ reduction of the Au precursors was chosen to load the AuNPs on the membranes, as shown in Scheme 1b. When the nanoporous BCP membranes were soaked in the aqueous solution of HAuCl₄, the weak polyelectrolyte PDMAEMA chains containing tertiary amine groups on the surface and pore walls of the membranes would be protonated, forming positively charged ammonium sites. Consequently, the negatively charged Au precursor ions ([AuCl₄]⁻) could be strongly anchored on the membrane through the electrostatic interaction. Although there have been reports utilizing amine containing polymers to reduce Au(III) ions to Au(0) with no requirement of an external reducing agent, it usually takes a long time to form AuNPs at room temperature. Therefore, NaBH₄ was employed to facilitate the reduction process in this work. Generally, after sufficient contact with the Au precursors for 12 h, the membranes were removed from the HAuCl₄ solution and then immersed in the NaBH₄ solution (1 mg mL⁻¹). With the assistance of NaBH₄, the reduction proceeded very fast at room temperature as the color change of membranes was observed immediately by the naked eye once they were exposed to the solution of NaBH₄.

The pristine BCP membrane presented a white appearance (inset in Fig. 1a), while the color of the membranes after anchoring with AuNPs varied from pink to dark purple (insets in Fig. 3a–d) with the increased concentrations of HAuCl₄ solutions because of the surface plasmon resonance of AuNPs. The as-prepared AuNP-immobilized BCP membranes all presented a relatively uniform color, indicating the homogeneous distribution of the AuNPs in the membranes.

We examined the surface morphologies of the AuNP-immobilized BCP membranes prepared with different HAuCl₄ concentrations (Fig. 3). The surface of the membranes after AuNP immobilization became coarser compared with the membrane before immobilization (Fig. 1). Coverage of homogeneous AuNPs over the pore walls of the membranes was observed. For the membrane prepared with the 0.5 mg mL⁻¹ HAuCl₄ solution, AuNPs anchored on them were sparse (Fig. 3a). However, with increased HAuCl₄ concentrations, coverage of the AuNPs on the membranes became denser (Fig. 3b–d). Semi-quantitative EDX analysis was employed to examine the contents of Au on the membranes (Fig. 4). With the 0.5 mg mL⁻¹ HAuCl₄ solution, the membrane was found to have an Au content of 1.34 wt%. As the concentration was increased to 1.25, 2.5 and 5.0 mg mL⁻¹, the Au contents of the corresponding membranes reached 1.45 wt%, 1.70 wt% and 2.01 wt%, respectively, which are consistent with SEM observations. Thus, it is clear that the Au content on the membranes can be flexibly tuned by changing the concentration of the HAuCl₄ solutions. In order to characterize the anchored AuNPs in detail, the AuNP-immobilized BCP layers were exfoliated and dissolved by soaking the membranes in dichloromethane, and then the dispersions of the AuNPs were utilized for TEM observations. The particle sizes of the AuNPs were measured from the TEM images, and the statistical results are shown in Fig. 5. The average diameters of the AuNPs were 9.4,
11.0, 11.4 and 13.5 nm, respectively, implying a slight size growth with the increase of HAuCl₄ concentration. In addition, the membranes retained their porous structures after anchoring the AuNPs, and no obvious pore blocking was observed from SEM images although the pores seemed to become narrower when high HAuCl₄ concentrations were used (Fig. 3d), probably because of the denser coverage of the AuNPs. The nanoporous structure is essential for the subsequent continuous flow catalytic reactions because it not only guarantees the fluent permeation of liquids but also provides tortuous channels for sufficient contact of the reactants with the AuNPs anchored on the pore walls of the membranes.

3.3 Continuous catalytic performances of AuNP-immobilized BCP membranes

The reduction reaction of 4-NP to 4-aminophenol (4-AP) (the former is a relatively toxic pollutant in the environment, while the latter is an important pharmaceutical intermediate) was employed to evaluate the catalytic performance of AuNP-immobilized BCP membranes with the presence of NaBH₄ at room temperature. Unlike other AuNP nanocomposites, for example Au-polymer hybrid microgels, which need to be mixed with the reactant solution, the solution containing 4-NP and NaBH₄ simply flows through the AuNP-immobilized BCP membranes to conduct the reduction reaction in this work, thus, there is no requirement to separate catalysts from solutions after the reaction. The original solution of 4-NP (10 ppm) and NaBH₄ (500 ppm) presented a yellow color and had an absorption peak at 400 nm (Fig. 6a). After flowing through the AuNP-immobilized BCP membrane prepared with the 5.0 mg mL⁻¹ HAuCl₄ solution at a rate of 0.3 mL min⁻¹, the permeated solution became colorless and the characteristic peak of 4-NP disappeared completely. Simultaneously, the absorption peak of 4-AP at about 300 nm was increased notably. The conversion efficiency of 4-NP to 4-AP was determined to be 100%. In contrast, when the same solution of 4-NP and NaBH₄ was filtered through the BCP membrane without anchoring the AuNPs, the peak of 4-NP did not...
demonstrated a much higher reaction efficiency as the flow rate increased to 3.0 mL min\(^{-1}\). The membranes prepared with the HAuCl\(_4\) solution of 5.0 mg mL\(^{-1}\), the 100% conversion efficiency of 4-NP to 4-AP at 0.3 mL min\(^{-1}\) gradually fell to 83% as the flow rate increased to 3.0 mL min\(^{-1}\) due to the decreased retention time of the reactant solutions in the catalytic membranes. Meanwhile, the AuNP-immobilized BCP membranes prepared with higher HAuCl\(_4\) concentrations demonstrated a much higher reaction efficiency at all feed rates than those prepared with lower concentrations. For example, when the flow rate was kept at 0.5 mL min\(^{-1}\), the conversion efficiency of the membranes was 76%, 83%, 86% and 97%, respectively, as the HAuCl\(_4\) concentration was increased from 0.5 to 5.0 mg mL\(^{-1}\). This result should be attributed to the increased Au contents in the membranes prepared with increased HAuCl\(_4\) concentrations as evidenced by the EDX analysis. Considering the relatively high reaction efficiency of the AuNP-immobilized BCP membranes prepared with the 5.0 mg mL\(^{-1}\) HAuCl\(_4\) solution, we investigated their catalytic performance at elevated concentrations of the reactant solution. As the concentration of 4-NP solution was increased from 10 ppm to 20, 30, 40 and 50 ppm, the conversion efficiency of 4-NP to 4-AP at a flow rate of 0.5 mL min\(^{-1}\) decreased from 97% to 92%, 81%, 70% and 50%, respectively (Fig. 6d). This can be easily explained by the fact that the chances of the reactants in a higher concentration solution being in contact with the anchored AuNPs on the surface of the membranes were decreased, thus leading to lower conversion efficiencies. The recyclability and catalytic stability of the AuNP-immobilized BCP membrane for flow catalytic reduction of 4-NP to 4-AP were investigated. The membrane prepared with 5.0 mg mL\(^{-1}\) HAuCl\(_4\) was reused for 8 cycles, and a conversion efficiency of 4-NP to 4-AP higher than 90% can be achieved at a flow rate of 0.5 mL min\(^{-1}\) (Fig. 5S1†), indicating the excellent recyclability of the AuNP-immobilized BCP membrane. Moreover, the catalytic reaction was continuously conducted for 6 h at a flow rate of 0.5 mL min\(^{-1}\), and the conversion efficiency can be maintained above 88%.

Synthetic organic dyes used in the textile industry are the common pollutants in wastewater, and their release into the environment would cause damage of ecological systems and threaten human health. AuNPs have been used as the catalyst for the efficient degradation of organic dyes in water.\textsuperscript{15,36} Herein, the prepared AuNP-immobilized BCP membranes in this work are expected to have good ability to degrade organic dyes. Rhodamine B (RhB) and methyl orange (MO) were utilized to evaluate the catalytic ability of the membranes fabricated from the 5.0 mg mL\(^{-1}\) HAuCl\(_4\) solution. First, the solution containing RhB (10 ppm) and NaBH\(_4\) (500 ppm) was filtered through the AuNP-free BCP membrane. No absorption or degradation of RhB was observed according to the UV-vis absorption spectroscopy of the solution before and after filtration (Fig. 5S6†). When the AuNP-immobilized BCP membrane was employed, the characteristic peak of RhB at 555 nm diminished significantly (Fig. 7a), along with the fading of the color of the RhB solution. This result indicates that the effective degradation of RhB was essentially caused by the catalytic effect of AuNPs anchored on the membrane. In addition, the presence of NaBH\(_4\) was necessary for the degradation of RhB as no weakening of the RhB characteristic peak was observed without the assistance of NaBH\(_4\) (Fig. 5S7).\textsuperscript{†} The degradation efficiency of RhB was determined to be 91% at the flow rate of 0.5 mL min\(^{-1}\). For the continuous flow catalytic degradation of MO, a similar procedure was conducted. The color of the MO solution changed from yellow to nearly colorless after flowing through the AuNP-immobilized BCP membrane, indicating the effective catalytic degradation of MO, and the degradation efficiency of MO was measured to be 88% based on the decreased absorbance of MO at 463 nm (Fig. 7b). Similarly, no absorption occurred between MO and the BCP membrane, and the reducing agent of NaBH\(_4\) was necessary during the catalytic degradation process (Fig. 5S6b and 5S7).\textsuperscript{†}

4. Conclusions

In this work, we have demonstrated a facile approach for the preparation of AuNP-immobilized BCP membranes as efficient reactors for the continuous flow catalytic reactions. The BCP of PDMAEMA-b-PS was coated on the PVDF substrates to form composite membranes followed by soaking in ethanol to cavitate the BCP layers based on the mechanism of selective swelling induced pore generation. Interestingly, the PDMAEMA chains, which contain tertiary amines that could provide bonding sites for the immobilization of AuNPs, migrated to the surface and pore walls of membranes during the selective swelling process. AuNPs were loaded on the BCP membranes by \textit{in situ} reduction of Au precursors, and the content of Au in
the membranes can be tuned by changing the concentration of the HAuCl₄ solutions used. Thus-produced AuNP-immobilized BCP membranes exhibited excellent catalytic performance in the continuous flow catalytic reduction of 4-NP and degradation of organic dyes. The catalytic efficiency of 4-NP to 4-AP can reach as high as 100% when the AuNP-immobilized BCP membrane prepared with the 5.0 mg mL⁻¹ HAuCl₄ solution was employed at a flow rate of 0.3 mL min⁻¹. Moreover, decoloration of water polluted by organic dyes including RhB and MO by this membrane was also proved. This work provides a new platform for the design and synthesis of functionalizable nanoporous polymeric supports which are highly demanded in flow-through catalytic production of value-added chemicals and wastewater treatment.

Conflicts of interest
There are no conflicts to declare.

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Notes and references