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Combining catalysis and separation on a PVDF/Ag composite membrane allows timely separation of products during reaction process

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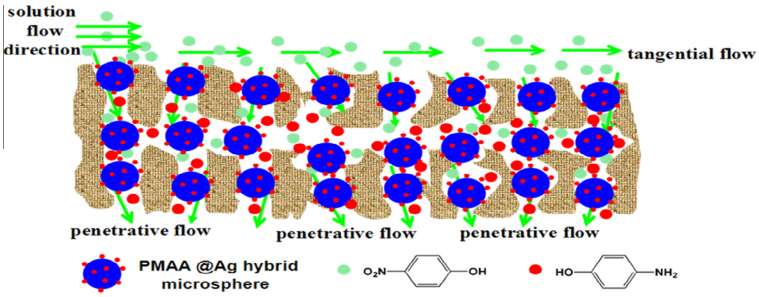
HIGHLIGHTS

- Microspheres decorated by Ag nanoparticles were immobilized in membrane pores.
- A cross-flow model of membrane was applied in catalysis for the first time.
- Rapid catalytic reaction was obtained under cross-flow operation.
- Reaction and separation were simultaneously realized by one-step operation.
- Catalysis operation was convenient, economical and environmentally-friendly.

GRAPHICAL ABSTRACT



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ABSTRACT

The faced key issues for a catalytic reaction are improving catalytic reactivity, and decreasing the operating costs of separating products and catalysts from the treated system. These drawbacks are simultaneously overcomed for the first time by constructing a novel structured poly (vinylidene fluoride) (PVDF)/Ag hybrid membrane with microspheres decorated by Ag nanoparticles (NPs) in membrane pores, which is prepared by immersion precipitation phase inversion of the *N*,*N*-dimethylformamide solution containing poly (methacrylic acid) (PMAA) microspheres loaded by Ag nanoparticles and PVDF in aqueous solution. The as-formed hybrid membranes are used for the catalytic reduction of 4-nitrophenol under a cross-flow model. Results indicate this membrane prevents the agglomeration of Ag nanoparticles, improves the stability of Ag nanoparticles, having the advantages of a fast catalytic rate, a high efficiency and a long service life. Furthermore, using this membrane avoids the additional steps for separating metal NPs catalysts from reaction system. More importantly, products, for the first time, can be timely separated from the treated solution during the catalytic reaction process, which is ascribed to Ag NPs only in membrane pores.

Abbreviations: NPs, nanoparticles; MAA, methacrylic acid; AIBN, azodiisobutyronitrile; PVDF, poly (vinylidene fluoride); EDX, energy dispersive X-ray spectrograph; ε, porosity; W_w, weight of wet membrane; l, thickness of membrane; Q, volume of pure water penetrating through the membrane; ΔP, working pressure; C_t, concentration of *p*-nitrophenol at the reaction time t; k_s, surface area-based rate constant; ρ_m, mass concentration of the nanoparticles; R, ideal gas constant; A_0, pre-exponential factor; V_{pores}, volume of the pores in the membrane; V_{mem}, volume of the membrane including porous and nonporous regions; PMAA, poly (methacrylic acid); DMF, dimethyl formamide; EGDMA, ethyleneglycol dimethacrylate; FESEM, field-emission scanning electron microscope; ATR-FTIR, attenuated total reflectance fourier transform infrared spectroscopy spectra; ICP-AES, inductively coupled plasma atomic emission spectroscopy; W_d, weight of dried membrane; η, water viscosity; A, effective membrane surface area; C_0, initial concentration; k_{app}, apparent first-order rate constant; a_s, specific surface area of the nanoparticles; E_a, apparent activation energy; T, Kelvin temperature; S, surface area of the Ag nanoparticles in a litre of solution; t_{res}, residence time in the membrane; F, solution flux through the membrane.

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1. Introduction

Noble metal (e.g., Pt, Rh, Au, Pd, Ag and so on.) NPs have higher catalytic activity than their corresponding bulk materials, and thus have attracted growing attention in their potential applications for many chemical reactions [1–4]. Utilization of noble metal NPs instead of their corresponding bulk materials as catalysts can improve treatment efficiency and simultaneously reduce the consumption of the limited natural resources [5]. However, the powder or colloid forms of the metal NPs tend to agglomerate and then form larger particles, leading to a large reduction of their catalytic activity [6,7]. A great effort has been tried to overcome this limit in the past few years. For example, to prevent the agglomeration, the metal NPs are coated by porous shell materials [8,9] or are immobilized on various supported materials such as silica nanosphere [10], halloysite nanotube [11], polymer [12] and graphene [13]. Although the development on this topic is very encouraging, preparation of such materials needs strict conditions, are complicated and costly [8–13]. What is worse, use and reuse of noble metal NPs are difficult and inconvenient [8–13]. These issues must be addressed before pushing noble metal NPs into practical catalytic application.

The difficulties for use and reuse are mainly due to the wrap of the noble metal NPs by the supported materials and the inconvenient separation of noble metal NPs from the treated solution [8–14]. To solve these problems, researchers suggest porous membranes to support noble metal NPs [15–18]. The open structure, large pore channels and easy operation model of the porous membranes are very favorable for the catalytic application of noble metal NPs. First, the internal open pore structures provide a possibility that allows a high loading of the nanocatalyst [15–18]. More importantly, it can attain a highly efficient utilization of available active sites as well as an easy accessibility to the nanocatalysts immobilized inside the membrane matrix under a proper operation condition [15–18]. Finally, metal NPs, which are stabilized by a polymeric membrane, are very convenient for reuse [15–18]. Up to now, two strategies have been reported for the introducing noble metal NPs into membrane matrix. One is self-assembly method by layer-by-layer adsorption of polyelectrolytes and metal NPs on the surfaces of the porous membranes [15–17]. Another one is first chemical modification of a membrane by complexing ligands or functional groups and then reduction of the metal ion nanoparticle precursors retained in the complexing ligands or functional groups [18,19]. Both solutions have been successfully developed to introduce noble metal NPs into membrane matrix [15–19], which are very effective in stabilization and reuse of noble metal NPs. But since noble metal NPs are on the surfaces or the near surface layers of the polymeric membranes, products produced from the membrane surface always coexist with reactants and can not be separated from reaction system during reaction process [15–19]. An ideal option that might actually solve the problem is immobilization of the noble metal NPs in membrane pores. In such a case, reaction is desired to only take place in membrane pores when reactants in feed solution flow through the membrane under a cross flow model. Thus, the membrane is expected to make reactants of the penetrative flow be completely changed into products, which is then collected. To adapt to this situation, it is imperative for researchers to develop an easy and powerful method to construct a membrane with only membrane pore rather than membrane surface containing noble metal NPs. To our best knowledge, no similar reports are shown.

In the present study, we for the first time show the preparation and catalytic behavior of a novel PVDF hybrid membrane containing cross-linked PMAA microspheres coated by Ag NPs in the membrane pores. To begin with, distillation precipitation polymerization was utilized to synthesize cross-linked PMAA microspheres [20], on the surface of which Ag NPs were subsequently deposited via in situ reduction method. Then, an immersion precipitation phase inversion method made a blend of PVDF powders and PMAA microspheres coated with Ag NPs form hybrid membranes, with the PMAA microsperes coated by the Ag NPs in the membrane pores [21]. Finally, cross flow model was used to examine in detail the catalytic properties of the hybrid membranes under various experimental conditions such as loading content of Ag, applied pressure and temperature.

2. Experimental

2.1. Materials

Methacrylic acid (MAA) monomer, dimethyl formamide (DMF), acetonitrile, and sodium borohydride ($NaBH_4$) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Azodiisobutyronitrile (AIBN) and silver nitrate ($AgNO_3$) were obtained from Tianjin Yingda Rare Chemical Reagents Factory. Ethyleneglycol dimethacrylate (EGDMA) was obtained from J&K Scientific. Polyvinylidene fluoride (PVDF) powder ($M_w = 3.52 \times 10^5$ g/mol, $M_w/M_n = 2.3$, Solef 1010) was got from Solvay in Belgium. Absolute ethyl alcohol was obtained from Tianjin Bodi Chemical Engineering Limited Corporation. 4-Nitrophenol was purchased from Tianjin Guangfu Fine Chemical Engineering Institute. Sodium hydroxide (NaOH) was purchased from Tianjin Fengchuan Chemical Reagent Co., Ltd. All the chemical reagents and chemicals are analytical grade and used as received.

2.2. Synthesis of PMAA microsphere

PMAA microsphere denoted as MS00 was synthesized by distillation- precipitation polymerization with AIBN as initiator and EGDMA as cross-linking agent [20]. MAA (2.0 g), EGDMA (2.1 g), and AIBN (0.08 g) were dissolved in 160 mL acetonitrile in a dried 250 mL round-bottom flask, equipped with a fractionating column, a Liebig condenser, a receiver and a stirrer. The flask was submerged in a water bath, and rapidly heated from room temperature to the boiling state within 5 min. The acetonitrile was then distilled off from the reaction system. After an about 5 min distillation, the reaction solution became white and then stayed for 1.5 h. The obtained sample was centrifuged, washed with the absolute ethyl alcohol and deionized water for three times respectively, and then dried in a vacuum oven at room temperature till a constant weight.

2.3. Preparation of PMAA microsphere/Ag NPs hybrid

PMAA microspheres coated by Ag NPs with various diameters were in situ formed by reduction of silver nitrate with $NaBH_4$ as a reductant. PMAA microspheres (1.7 g) were firstly suspended in 100 mL of deionized water in a 250 mL beaker with a stirrer. Then $AgNO_3$ with different mass ratios of PMAA microsphere/$AgNO_3$ ($m_{PMAA}/m_{AgNO3} = 1134/1$, 760/1, 507/1) was added to the suspension under dark conditions. After the mixture was stirred at room temperature for 24 h, 0.05 g of $NaBH_4$ was rapidly added to the suspension, leading to Ag NPs formation on PMAA microspheres. The obtained samples were separated by ultracentrifugation and subsequently washed with deionized water for three times, and then dried in a vacuum oven at room temperature till a constant weight. Finally, three kinds of PMAA microsphere/Ag NPs hybrids ($m_{PMAA}/m_{Ag} = 1786/1$, 1197/1, 798/1; Ag content measured by inductively coupled plasma atomic emission spectroscopy) were obtained and denoted as MS10, MS20 and MS30, respectively.