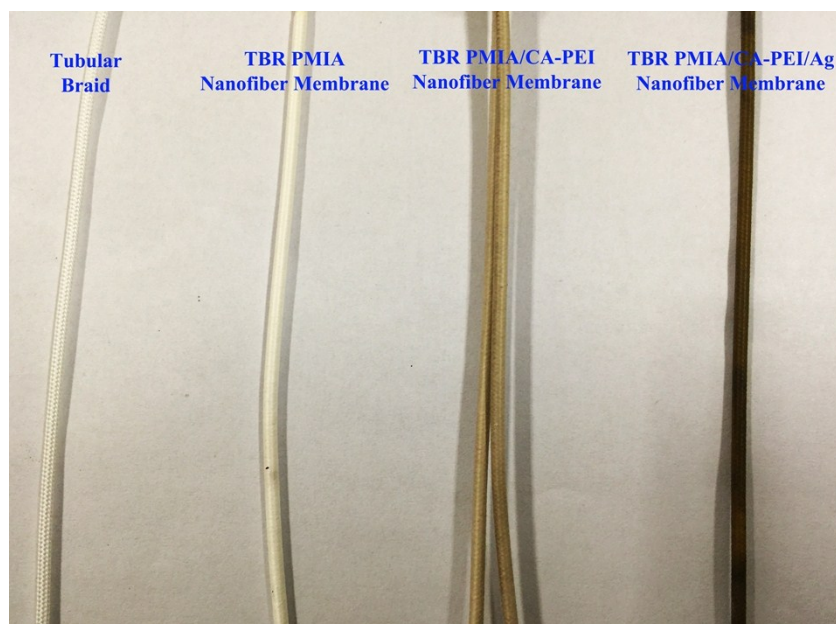


## Supporting Information

# Fabrication of Tubular Braid Reinforced PMIA Nanofiber Membrane with Mussel-Inspired Ag Nanoparticles and its Superior Performance for the Reduction of 4-nitrophenol

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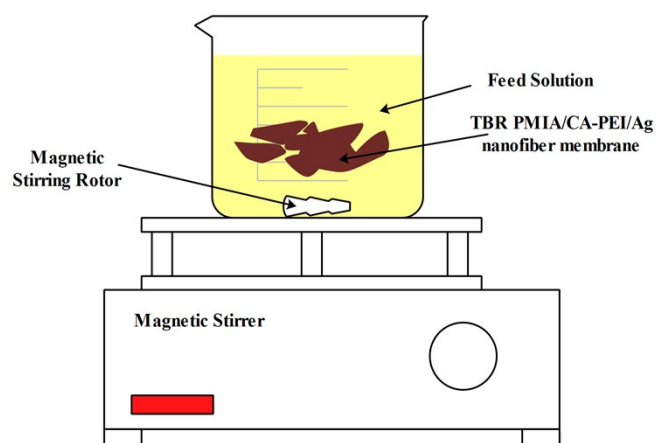
*State Key Laboratory of Separation Membranes and Membrane Processes, National Center for International Joint Research on Separation Membranes, School of Material Science and Engineering, Tianjin Polytechnic University, No. 399 Binshui West Road, Tianjin, 300387 PR China*



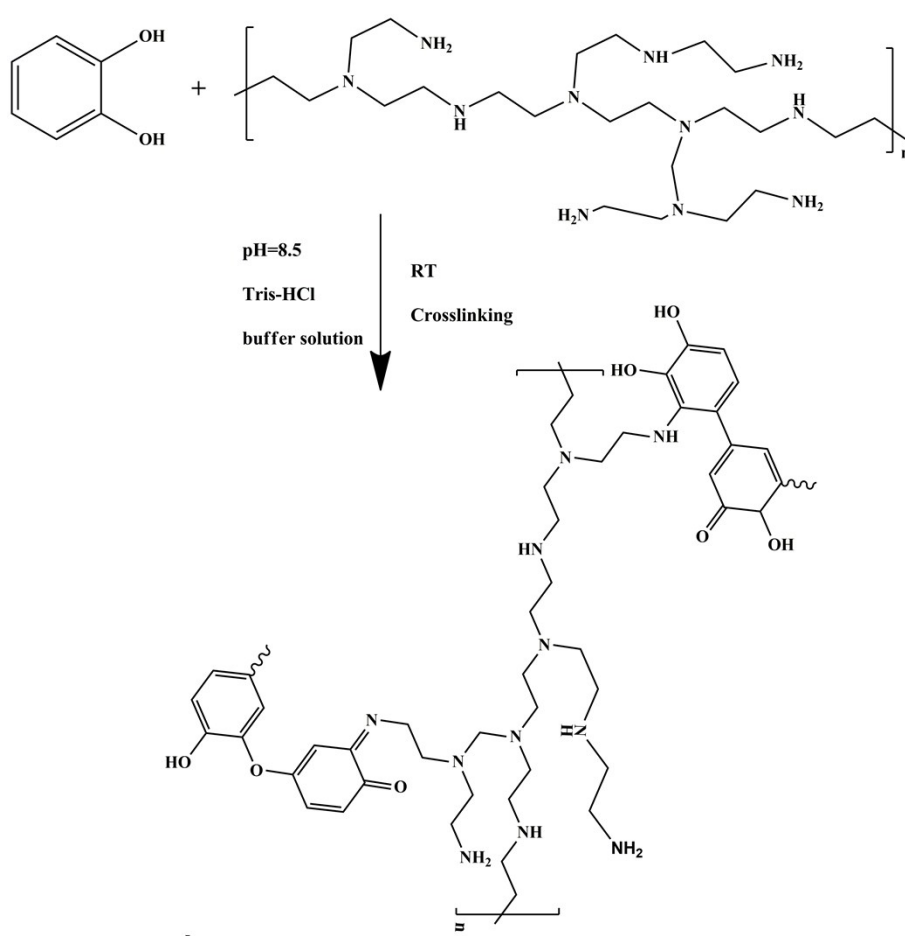
**Figure S1.** The digital photograph of tubular braid and various TBR nanofiber membrane.

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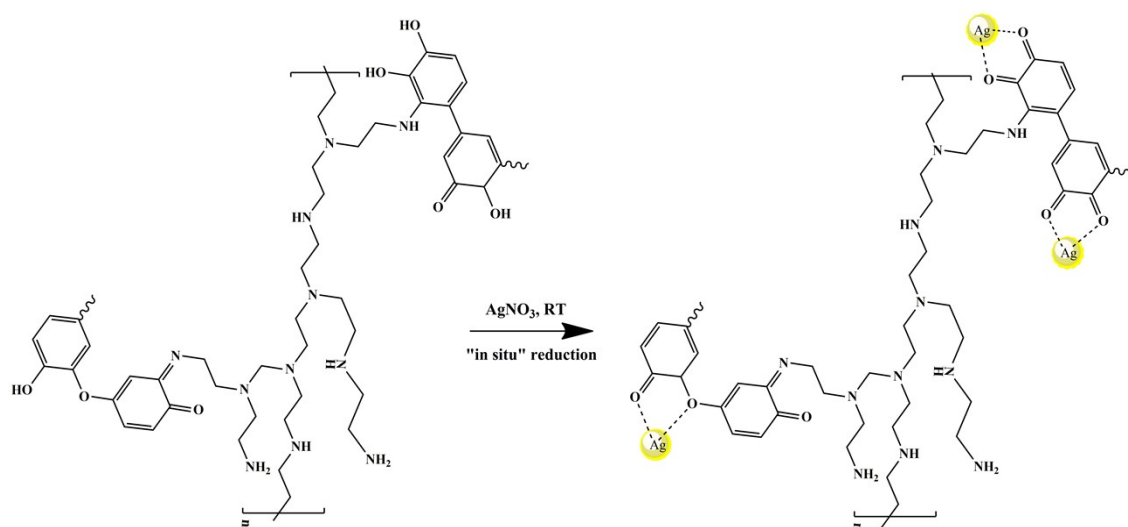
**Figure S2.** The schematic diagram of static catalysis process.



**Figure S3.** The schematic illustration for the possible polymerization mechanism of CA and PEI.<sup>1-</sup>

In the process of surface modification, CA could be oxidized to a quinoid form by the dissolved oxygen in Tris-HCl buffer solution (10mM, pH=8.5). The o-quinone

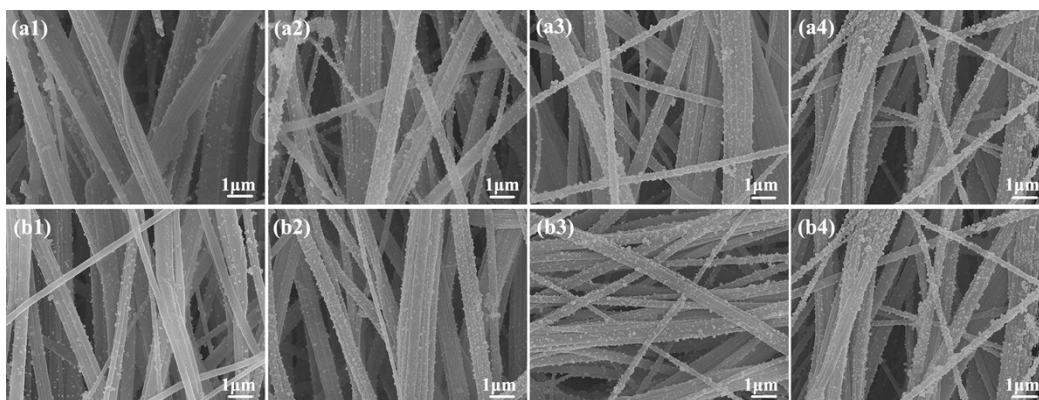
could react with CA via quinone-phenol dismutation, or with primary amine groups derive from PEI via Michael addition and Schiff base reaction. The reactions gradually formed CA-PEI aggregates (Figure S3) in the solution and then deposited onto the nanofibers surface.<sup>1-4</sup> This process was similar to that of dopamine self-polymerization for the surface modification of various materials.<sup>5</sup>



**Figure S4.** The schematic illustration for the “in situ” reduction of Ag nanoparticles.

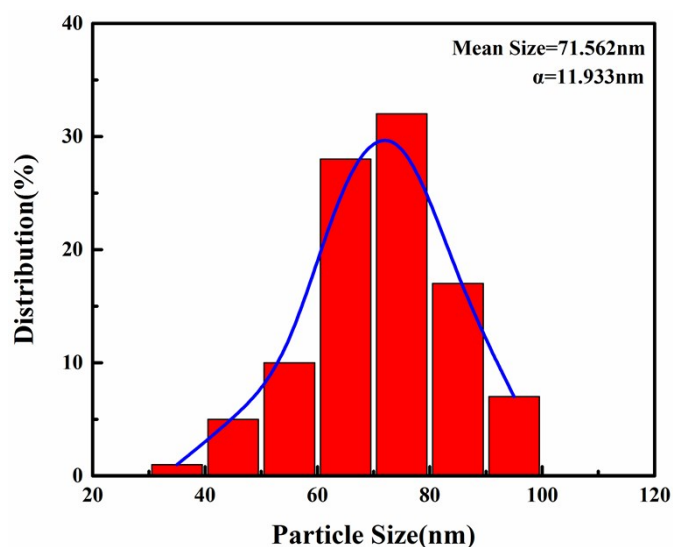
After surface modification, the nanofibers were immersed in the fresh prepared  $\text{AgNO}_3$  solution. In particular, the catechol group in CA-PEI aggregates which was similar to the catechol group of polydopamine had superior binding properties toward metallic ions. It could act as strong reducing agents for metal ions for the production of metal nanoparticles.<sup>6</sup> Therefore, the CA-PEI aggregates could play a role as an effective reducing agent to reduce metal precursor to metal nanoparticles due to the spontaneous oxidation to quinone of the catechol group.<sup>7-9</sup> As TBR PMIA/CA-PEI nanofiber membrane immersed in the fresh prepared  $\text{AgNO}_3$  solution, the Ag precursor ( $\text{Ag}^+$  ions) in the solution was adsorbed onto the CA-PEI layer and then reduced to Ag NPs in situ by the catechol groups of CA-PEI layer while the catechol

group was oxidized to corresponding quinone simultaneously.<sup>10-14</sup> This process was shown in Figure S4.

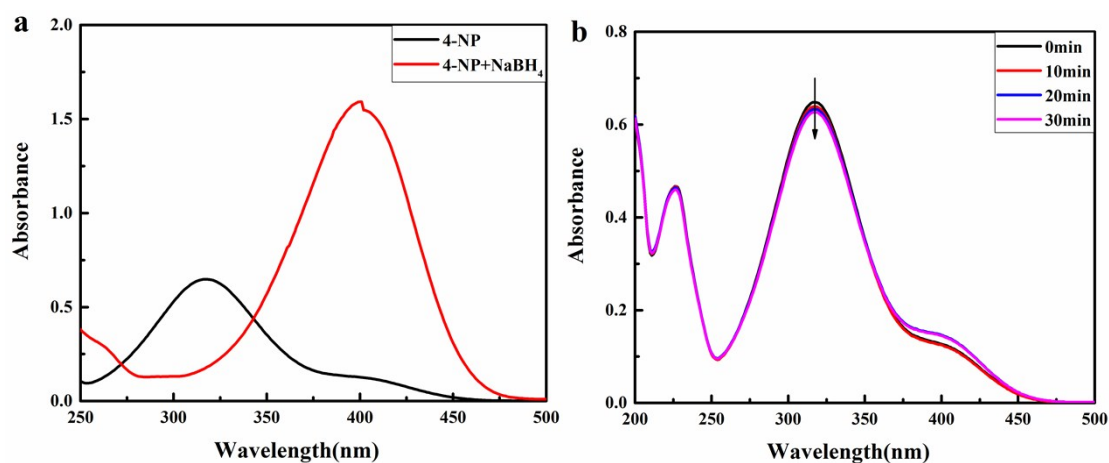


**Figure S5.** The effects of AgNO<sub>3</sub> concentration (a, immersion time: 24 h) and immersion time (b, AgNO<sub>3</sub> concentration: 10g/L) on the Ag nanoparticle size and its distribution: (a1) 1 g/L, (a2) 3g/L, (a3) 5g/L, (a4) 10 g/L; (b1) 1 h, (b2) 4 h, (b3) 12 h, (b4) 24h.

The effects of AgNO<sub>3</sub> concentration and immersion time on Ag nanoparticle size and its distribution were investigated. The results was shown in Figure S5. As shown in Figure S5, the AgNO<sub>3</sub> concentration and immersion time had no significant impact on Ag nanoparticle size, while the density of Ag nanoparticle increased as the AgNO<sub>3</sub> concentration and immersion time increased. This was consistent with the results of previous study.<sup>15-17</sup>



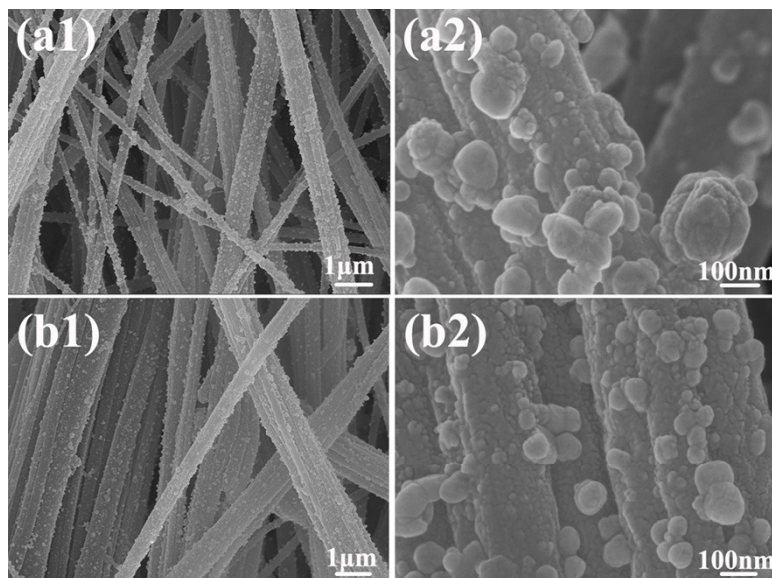
**Figure S6.** The particle size and its distribution of Ag nanoparticles.



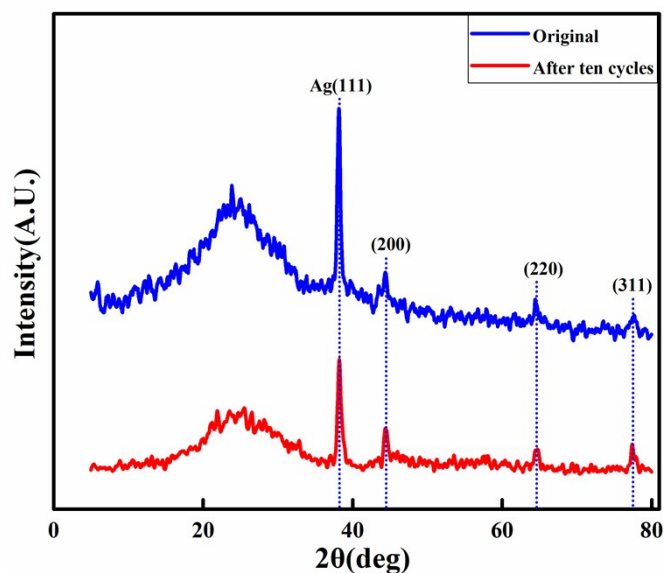
**Figure S7.** (a) The UV-Vis spectra of 4-NP and 4-NP with NaBH<sub>4</sub>; (b) UV-Vis spectra of 4-NP solution treated by TBR PMIA/CA-PEI/Ag nanofiber membrane without NaBH<sub>4</sub>.

As shown in Figure S7(a), the 4-NP aqueous solution exhibited an adsorption peak at 317 nm, while the adsorption peak of 4-NP aqueous solution with NaBH<sub>4</sub> shifted from 317 to 400 nm due to the formation of 4-nitrophenolate anions under alkaline conditions after adding NaBH<sub>4</sub>. Figure S7(b) showed the UV-Vis spectra of 4-NP solution treated by TBR PMIA/CA-PEI/Ag nanofiber membrane without NaBH<sub>4</sub> versus time. It could be seen that the UV-Vis spectra of the 4-NP solution barely changed after running for 30 min. Since this catalytic reaction would not be

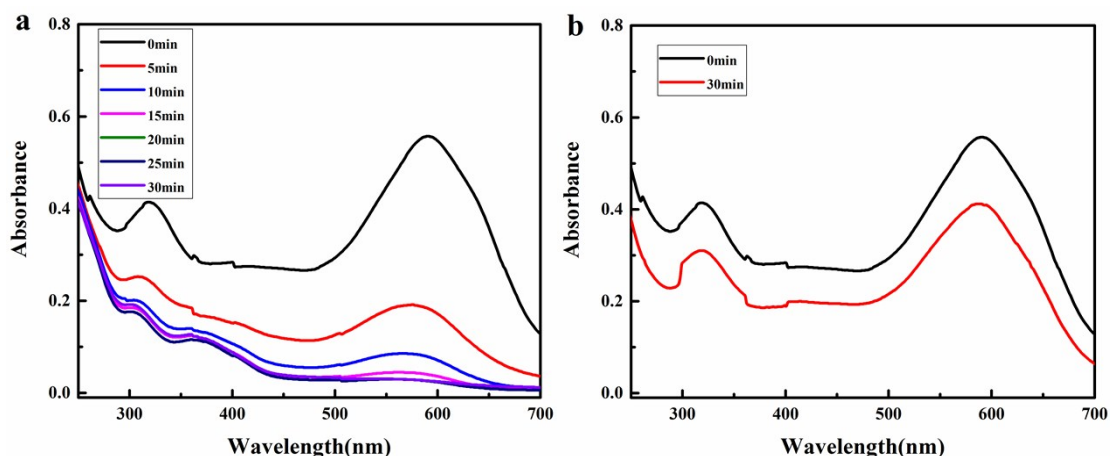
occurred without  $\text{NaBH}_4$  as reductant. This meant there was no reduction in the concentration of 4-NP in feed solution. It was certainly that the 4-NP in feed solution did not absorbed by TBR PMIA/CA-PEI/Ag nanofiber membrane.



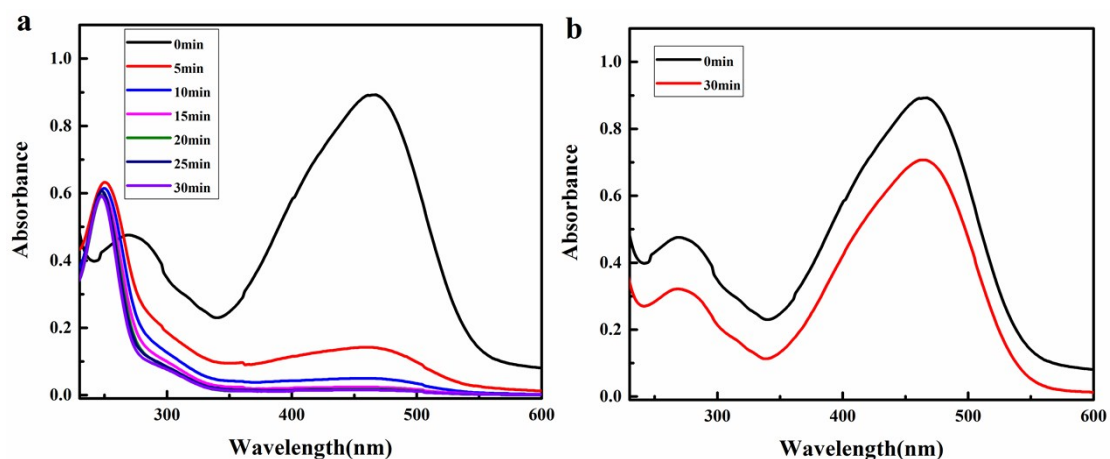
**Figure S8.** SEM images of TBR PMIA/CA-PEI/Ag nanofiber membrane: (a) original, (b) after ten cycles; (1)  $\times 10$  K, (2)  $\times 100$  K.



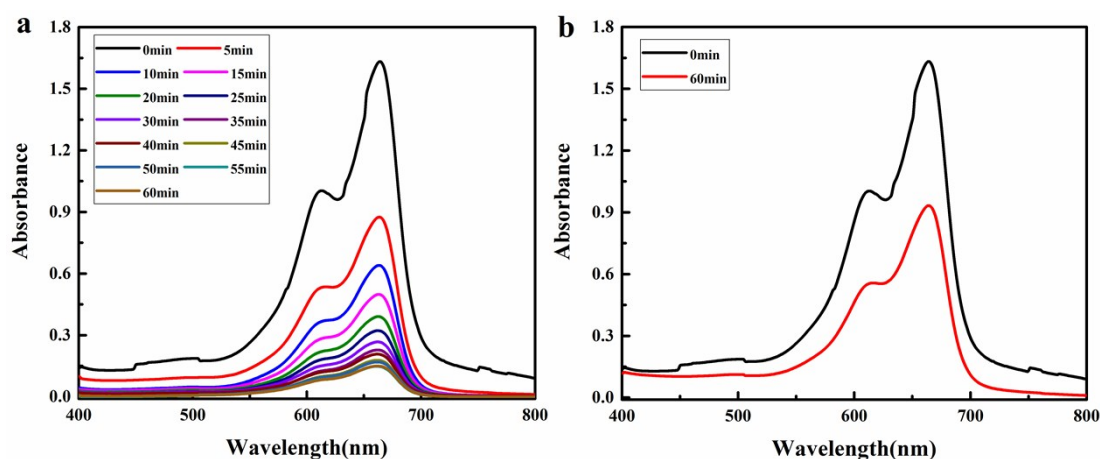
**Figure S9.** The XRD patterns of TBR PMIA/CA-PEI/Ag nanofiber membrane before and after ten cycles.



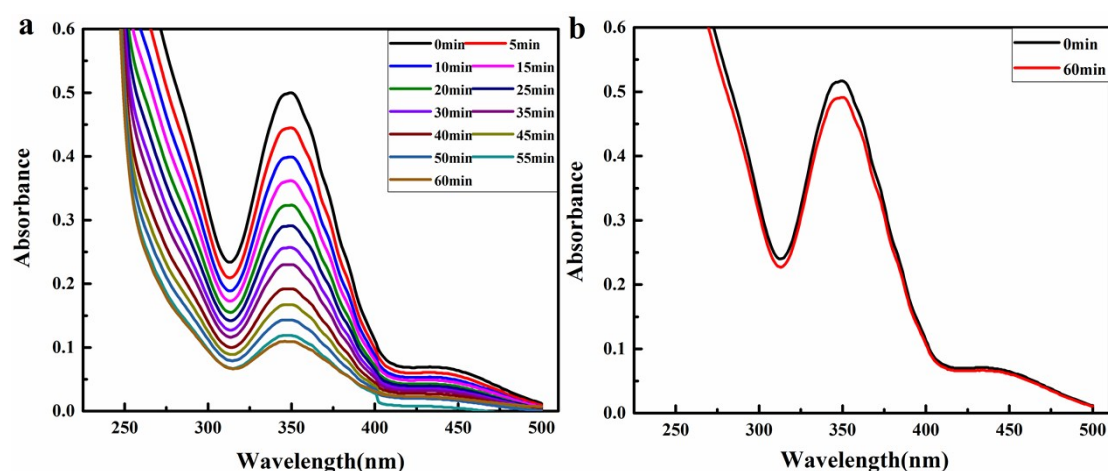
**Figure S10.** UV–visible absorption spectra of degradation of direct blue 15 by  $\text{NaBH}_4$  in the presence of TBR PMIA/CA-PEI/Ag nanofiber membrane: (a) dynamic catalysis process (b) static catalysis process (feed solution: 500 ml, 2g/L  $\text{NaBH}_4$  and 30 mg/L direct blue15 aqueous solution; operating conditions: 0.05 MPa, 25 °C).



**Figure S11.** UV–visible absorption spectra of degradation of methyl orange (MO) by  $\text{NaBH}_4$  in the presence of TBR PMIA/CA-PEI/Ag nanofiber membrane: (a) dynamic catalysis process (b) static catalysis process (feed solution: 500 ml, 2g/L  $\text{NaBH}_4$  and 15 mg/L MO aqueous solution; operating conditions: 0.05 MPa, 25 °C).



**Figure S12.** UV–visible absorption spectra of degradation of methylene blue (MB) by  $\text{NaBH}_4$  in the presence of TBR PMIA/CA-PEI/Ag nanofiber membrane: (a) dynamic catalysis process (b) static catalysis process (feed solution: 500 ml, 2g/L  $\text{NaBH}_4$  and 10 mg/L MB aqueous solution; operating conditions: 0.05 MPa, 25 °C).



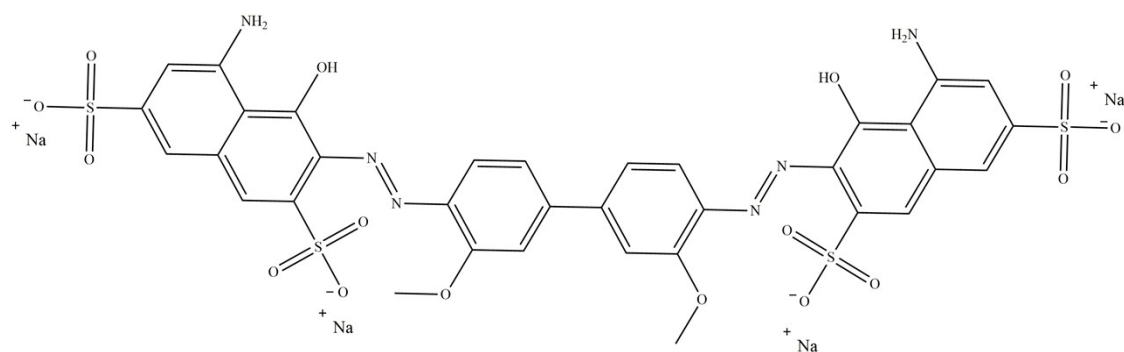
**Figure S13.** UV–visible absorption spectra of reduction of hexavalent chromium by  $\text{HCOOH}$  in the presence of TBR PMIA/CA-PEI/Ag nanofiber membrane: (a) dynamic catalysis process (b) static catalysis process (feed solution: 500 ml, 10ml/L  $\text{HCOOH}$  and 50 mg/L  $\text{K}_2\text{Cr}_2\text{O}_7$  aqueous solution; operating conditions: 0.05 MPa, 25 °C).

**Table S1.** The conversion of dyes and hexavalent chromium in the presence of TBR PMIA/CA-PEI/Ag nanofiber membrane.

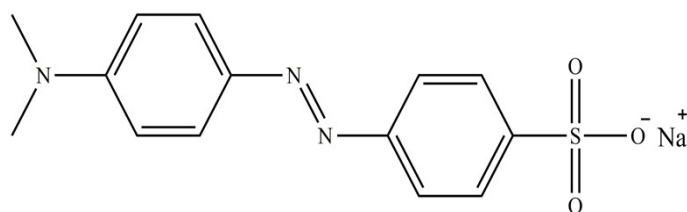
| The conversion in the presence of nanofiber membrane |                          |
|------------------------------------------------------|--------------------------|
| Dynamic catalysis process                            | Static catalysis process |

|                     |        |       |
|---------------------|--------|-------|
| direct blue 15      | 94.43% | 26%   |
| methyl orange (MO)  | 98.3%  | 20.8% |
| methylene blue (MB) | 90.8%  | 42.9% |
| hexavalent chromium | 80%    | 4%    |

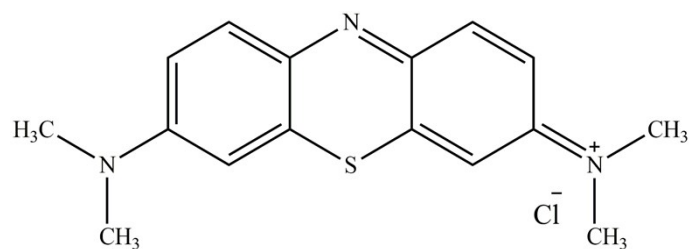
In order to further evaluate the catalytic properties of TBR PMIA/CA-PEI/Ag nanofiber membrane, the degradation of dyes and reduction of hexavalent chromium were carried out. The results were shown in Figure S10-S13. The chemical structure of the dyes was illustrated in Figure S14-S16. The conversions of dyes and hexavalent chromium in the presence of TBR PMIA/CA-PEI/Ag nanofiber membrane were shown in Table S1. These results further demonstrated the superior catalytic property of the TBR PMIA/CA-PEI/Ag nanofiber membrane via dynamic catalysis process than static catalysis process.



**Figure S14.** The chemical structure of direct blue 15.



**Figure S15.** The chemical structure of methyl orange (MO).



**Figure S16.** The chemical structures of methylene blue (MB).

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