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Self-reducing asymmetric polymer membrane for in situ formation and containment of noble metal nanocatalysts

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Fig. S1. FE-SEM images showing (a) Au NPs, (b) Ag NPs, (c) Pd NPs, and (d) Ru NPs formed at the surfaces of membrane samples equilibrated with 0.1 mol L^{-1} $HAuCl_4$/$AgNO_3$/$PdCl_2$ /$RuCl_3$ solutions for overnight.

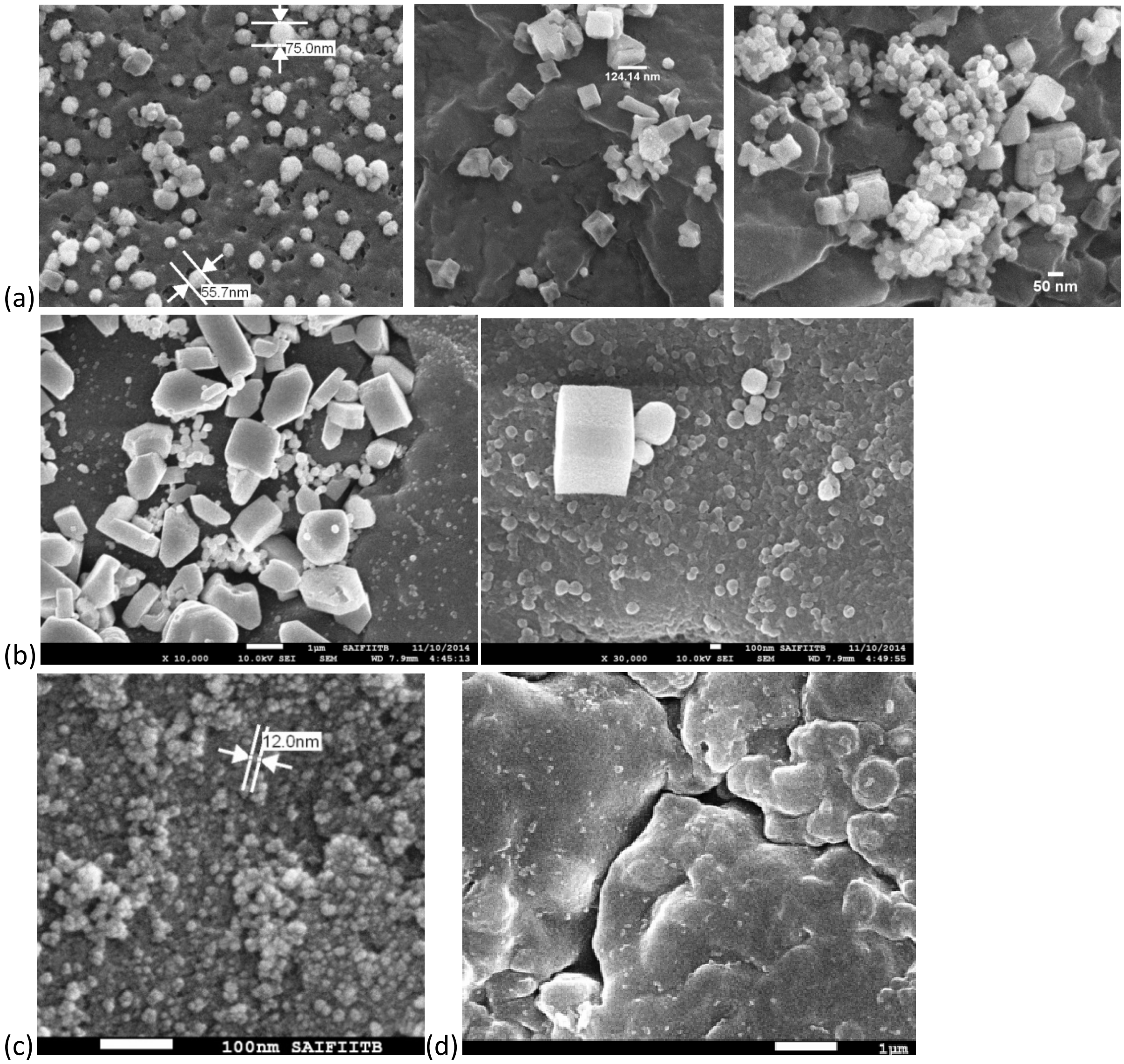
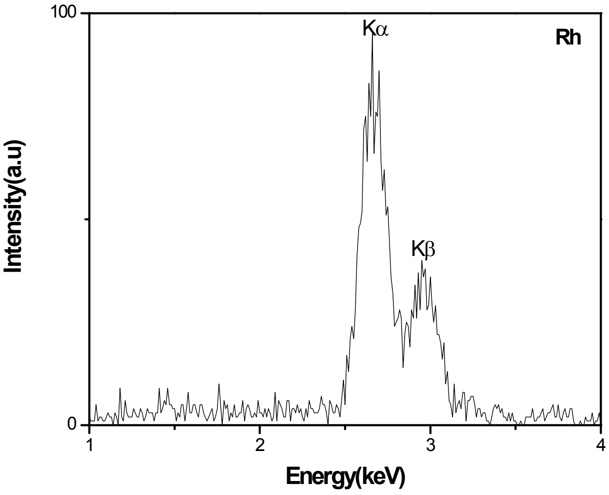
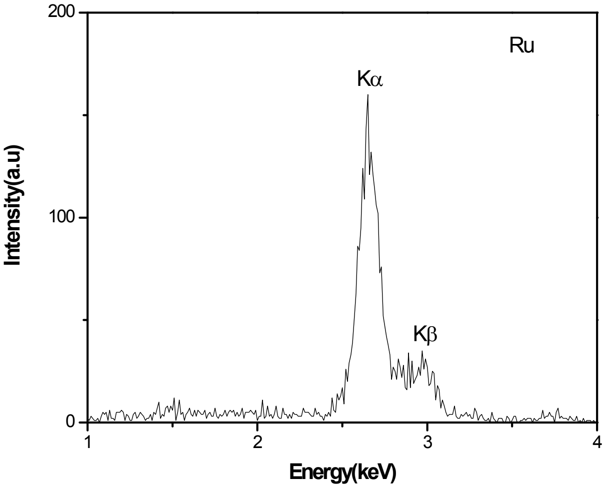


Fig. S2. EDXRF spectra of Rh NPs loaded membrane (a) and Ru NPs loaded membrane(b).



(a)



(b)

Fig. S3. FE-SEM images of the cross-sections of Au^0 (a) and Ag^0 (b) loaded membrane samples, and elemental mappings of nitrogen (c) and Ag (d) in 15x15 µm area across of the thickness of Ag NPs loaded membrane.

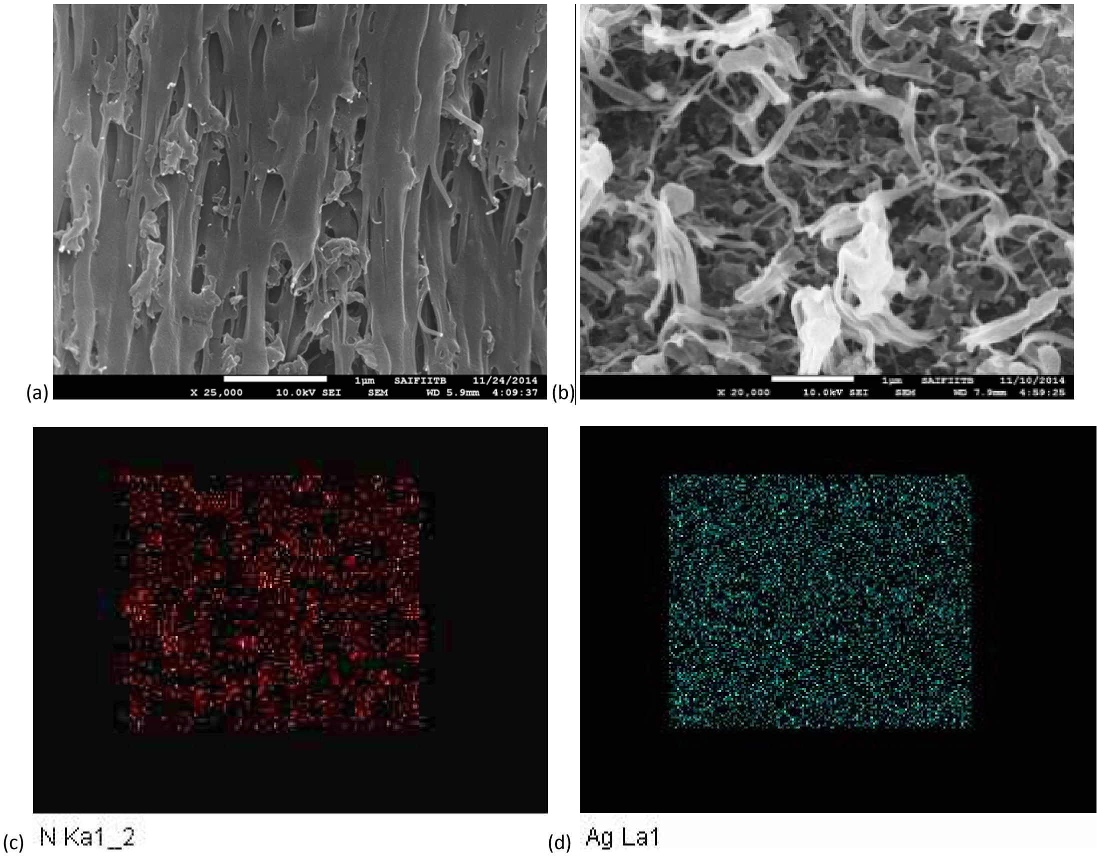


Fig. S4. XRD pattern of Ag NPs loaded membrane sample stored for three month under ambient conditions.

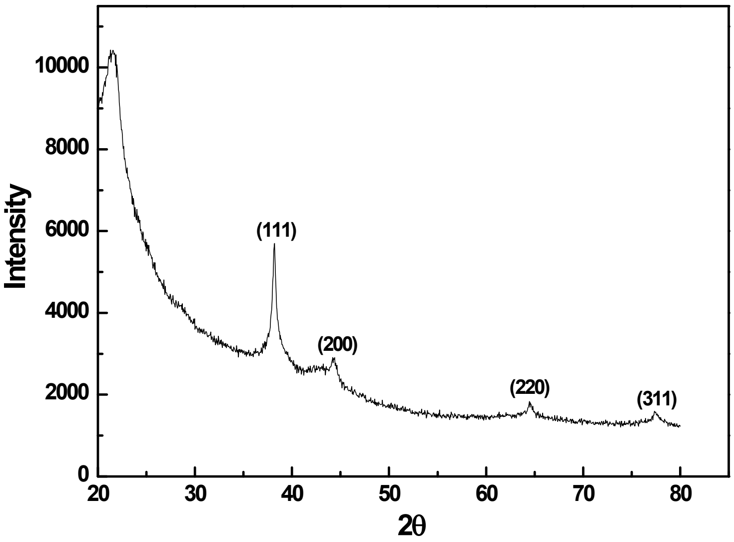
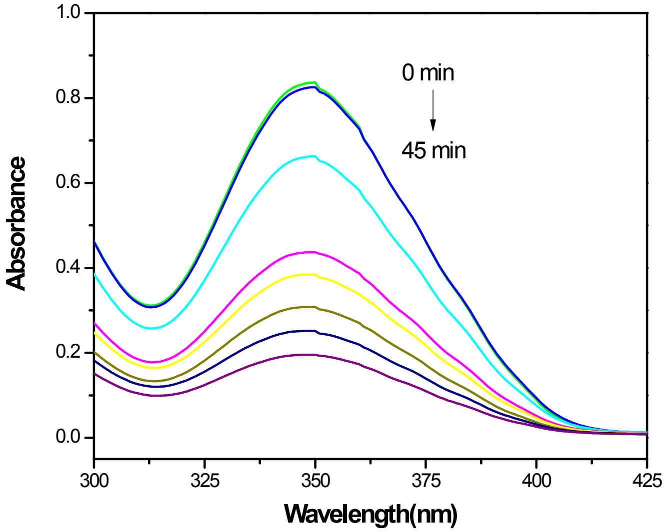
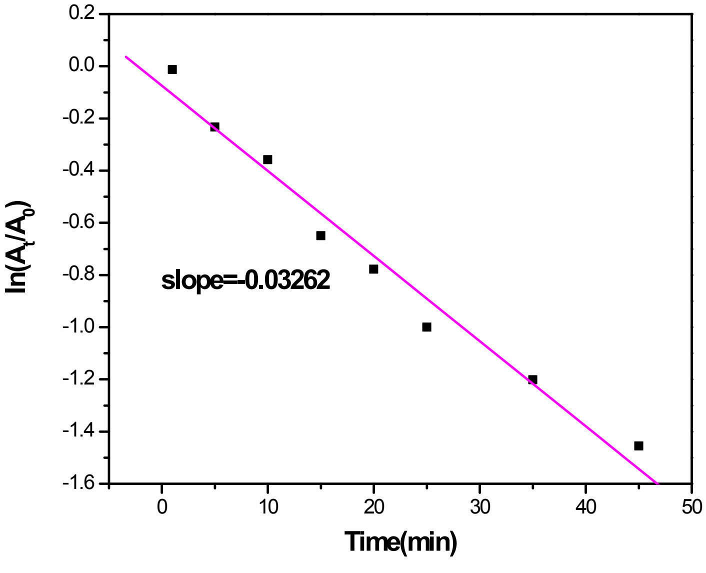


Fig. S5. (a) Successive UV-Vis spectra showing reduction of Cr(VI) to Cr(III) with formic acid at 45 ^{0}C as a function of time in the presence of Pd NPs loaded membrane, and (b) variation of logarithm of A_t/A_o as a function of reduction time. A_t and A_o represent absorbance of 350 nm (corresponding to concentration of Cr(VI)) at time t and initial, respectively.

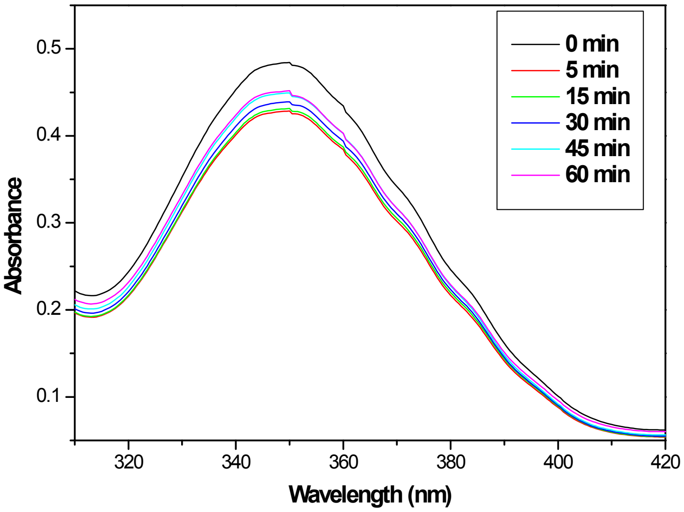


(a)

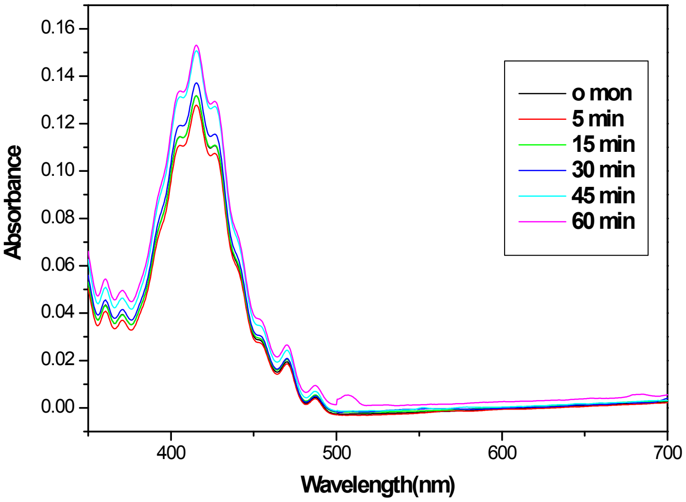


(b)

Fig. S6. UV-Vis spectra showing the absence of significant reductions of Cr(VI) (a) and U(VI) (b) with formic acid at 45 and 50 ^{0}C, respectively, as a function of time in the presence of NMDG-membrane sample without Pd NPs.

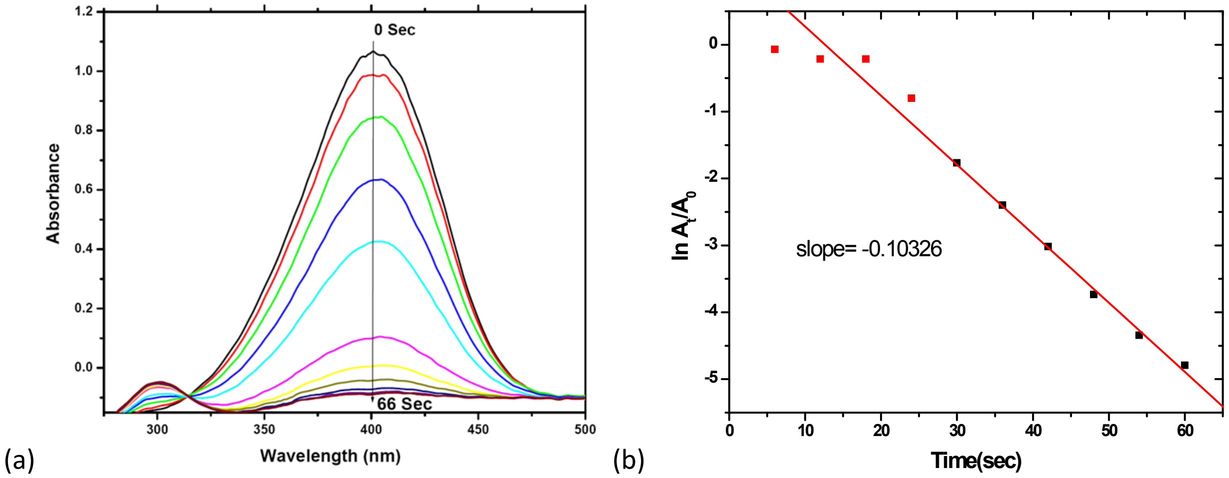


(a)



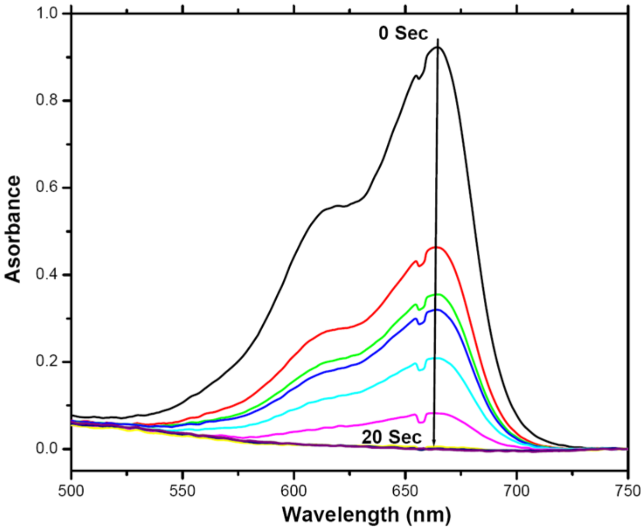
(b)

Fig. S7. (a) Successive UV-Vis spectra showing the reduction of *p*-nitrophenol to *p*-aminophenol with BH_4^- ions at room temperature as a function of time in the presence of Ag NPs loaded membrane, and (b) variation of logarithm of A_t/A_o as a function of reduction time. A_t and A_o represent absorbance of 400 nm (corresponding to concentration of p-nitrophenolate ions) at time t and initial, respectively.

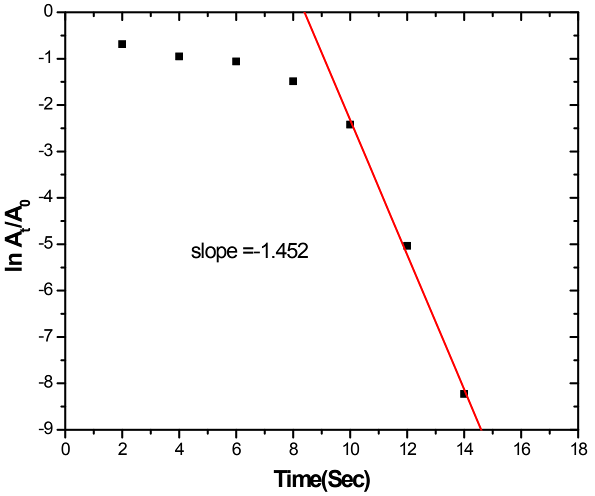


(a) (b)

Fig. S8. (a) Successive UV-Vis spectra showing reduction of methylene blue with BH_4^- ions at room temperature as a function of time in the presence of Ag NPs loaded membrane, and (b) variation of logarithm of A_t/A_o as a function of reduction time. A_t and A_o represent absorbance of 665 nm (corresponding to concentration of methylene blue) at time t and initial, respectively.



(a)



(b)

Experimental Section

Synthesis of self-reducing membrane

Glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDM), α,α'-dimethoxy-α-phenyl-acetophenone (DMPA) and *N*-methyl-*D*-glutamine (NMDG) were obtained from Sigma-Aldrich. Methanol and *N*-*N'*-dimethyl formamide (DMF) were obtained from Merck (Mumbai, India). The microporous poly(propylene) (PP) membranes (Accurel^R PP 1E) having 0.1 µm pore-size and 90 µm thicknes were procured Membrana GmbH, Germany. The grafting was done in a multilamps photoreactor from Heber Scientific, Chennai, India (model no. HML-SW-MWLW-888).

For grafting GMA, the polymerizing solution was prepared by dissolving 1.5 g of GMA in 2 mL of DMF solvent, and adding 5 mol% of crosslinker (EGDM) and 2 wt% of UV-initiator (DMPA) to this. Thus formed polymerizing solution was sonicated for 20 min for homogenization. The PP membranes samples having 5×5cm^2 areas were soaked in the polymerizing solutions for overnight, and then excess of solution adhering to surfaces of the host substrates were removed gently. The polymerizing solution filled membranes were sandwiched between two Garware polyester sheets and exposed to 365 nm UV light in a multilamps photoreactor for a period of 20 min. After exposure to UV-light, the membrane samples were first washed thoroughly with DMF and then with water to remove un-polymerized components from the membranes. The membrane samples were washed till constant weights were obtained. The grafting yield obtained from the increase in weight of the grafted membrane with respect to pristine membrane was found to be 100 wt %. The GMA-grafted membrane samples were reacted with a 1 (w/v%) solution of NMDG in DMF at 60^{0}C maintained by a water bath for 4 h to anchor NMDG by opening epoxy ring of GMA. After chemical treatment, the membrane samples were washed with methanol and water, and dried at 45 ºC under vacuum condition.

Formation of noble metal NPs in self-reducing membrane

The noble metal salts $AgNO_3$, $PdCl_2$, $RuCl_3$, $RhCl_3$ and $H_2PtCl_6.xH_2O$ from S.D. Fine Chem. Ltd., India, $HAuCl_4$ from Pravat Chemicals, India was used. These metal salts were dissolved in de-ionized water whose pH was adjusted to 2 by dil HCl or HNO_3 (for $AgNO_3$). The final concentration of the salt in solution was kept to 0.1 mol L^{-1}. The NMDG anchored membrane samples (2x2 cm^2) were equilibrated with 10 mL of noble salt solution for 12 h at room temperature without stirring. For loading Ag^0 in the membrane as a function of time, the weighted NMDG-grafted membrane samples (2x1 cm^2) were equilibrated in the 0.05 mol L^{-1} $AgNO_3$ solutions for a predetermined time with constant stirring at room temperature. The membrane samples were thoroughly washed with de-ionized water, and immersed in the 10 mL of 3 mol L^{-1} HNO_3 solutions to leach out Ag loaded in the membrane samples. The nearly complete leaching of Ag was confirmed by EDXRF analysis of the membrane sample. The leach solutions were subjected to ICP-AES analyses for determining the Ag content.

Reduction of methylene blue and *p*-nitrophenol

The reductions of *p*-nitrophenol (PNP) and methylene blue (MB) with BH_4^- were carried out in a standard quartz cell with a path length of 1 cm containing appropriate concentrations of reactants in aqueous solution and a 2x1 cm^2 Ag NPs embedded membrane catalyst. The solution was stirred gently using micro-bar magnetic stirrer. The cuvette was placed in a portable UV-VIS spectrophotometer (K-MAC Technology, South Korea) kept on a magnetic stirrer, and the successive UV-VIS absorption spectra were recorded to monitor the reaction kinetics. In reaction involving PNP, the reaction solution consisted of 0.1 mL of 2 mmol L^{-1} PNP and 2 mL water, and 100 μL of freshly prepared 0.2 mmol L^{-1} $NaBH_4$ was added to it. The Ag-membrane was immersed in cuvette avoiding light beam path. The reduction of 4-nitrophenolate anions was monitored by measuring the absorbance at 400 nm as a function of reduction time. Similar experiments were carried out with BH_4^- reduction of MB. The reaction solution contained 0.5 mL of 0.2 mmol L^{-1} MB, 2 mL water, and 500 μL of freshly prepared 0.2 mmol L^{-1} $NaBH_4$. The progress of reduction was monitored by measuring the absorbance at 665 nm (λ_{max} of MB). The absorbance values at 665 nm (MB) and 400 nm (PNP), were used to obtain apparent reduction rate constant (k) using following equation.

$$\ln\left(\frac{A_t}{A_0}\right) = -kt$$

where A_0 and A_t are absorbance at time 0 and t, respectively.

Reduction of U(VI) and Cr(VI) ions

The reduction of U(VI) to U(IV) was carried out in formic acid using the Pd NPs embedded membrane. The reduction process was studied by recording UV-Vis spectra of the aliquots taken from the solution as a function of time. The absorbance corresponding to U(VI) (400 nm) and U(IV) (490,550 and 650 nm) were monitored by UV–vis spectrophotometer model V 53 from JASCO (Tokyo, Japan). The solution used for U(VI) reduction were made by mixing 7 mL of 0.1 mol L^{-1} $UO_2(NO_3)_2$ and 7 mL of 1 mol L^{-1} HCOOH in a 25 mL beaker. The temperature of this solution was kept as 50^oC using water bath, and a Pd loaded (1x2 cm^2) membrane was immersed in this solution. The solution was stirred with magnetic stirrer with constant 300 rpm. At regular time intervals, 1mL of reaction mixture was taken in a cuvette and diluted to 3 mL by Millipore water to record the UV-Vis spectrum.

Similar experiment was carried out to study reduction of Cr(VI) to Cr(III). In this case reaction solution consisted of 5 mL of 7 mmol L^{-1} Cr(VI) solution and 5 mL of 70 mmol L^{-1} formic acid. The temperature of this solution was maintained at 45^0C. The Pd-loaded membrane sample was used as a catalyst. The decrease in absorbance at 350 nm corresponding to Cr(VI) was monitored by taking out 0.5 mL of aliquot in a cuvette and diluted it to 3 mL for measuring the aborbance.