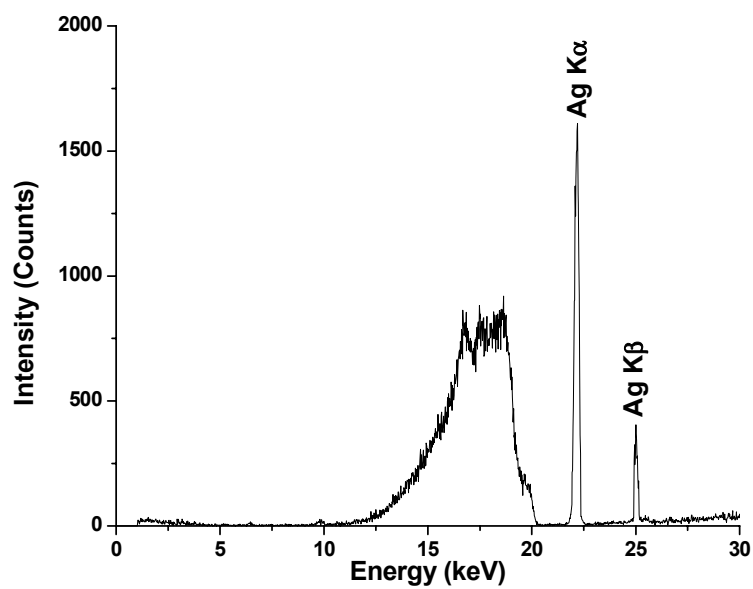


**Table S1.** Radiotracer studies of formation of metal nanoparticles during galvanic reactions of ions with Ag nanoparticles in the matrix of Nafion-117 membrane.

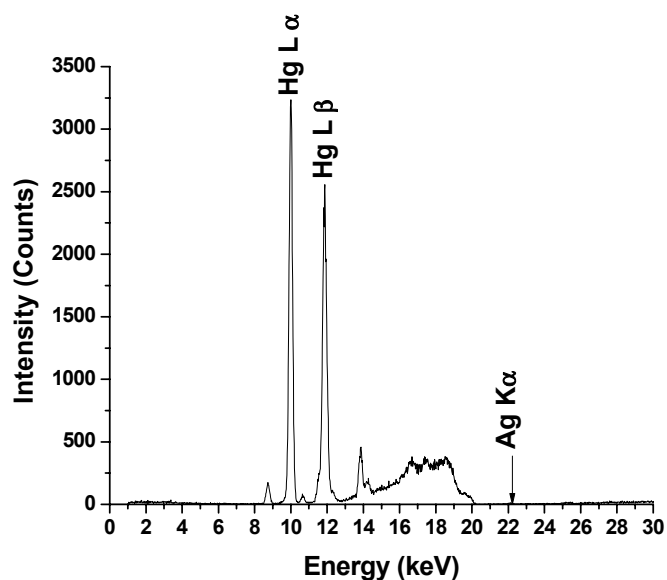
Ion undergoing galvanic reaction	Method of formation of Ag nps in the membrane sample*	Equilibration time in salt solution (0.01 mol L <sup>-1</sup> )	Radioactivity of <sup>110m</sup> Ag present as Ag nps before galvanic reaction in membrane		Replacement of Ag <sup>0</sup> from membrane (%)
			Before (count min <sup>-1</sup> )	After (count min <sup>-1</sup> )	
Hg <sup>2+</sup>	BH <sub>4</sub> <sup>-</sup> reduction	5 min	62191±249	496±22	99±2
Hg <sup>2+</sup>	Formamide reduction at 65 °C	5 min	24377±156	636±25	97±4
AuCl <sub>4</sub> <sup>-</sup>	BH <sub>4</sub> <sup>-</sup> reduction	4 h	59400±243	2746±52	95±2
AuCl <sub>4</sub> <sup>-</sup>	Formamide reduction at 65 °C	overnight	22387±149	6575±81	70±1

\* BH<sub>4</sub><sup>-</sup> reduction produces 15±4 nm Ag nps positioned near surface of the membrane, Formamide reduction at 65 °C produces 9±2 nm Ag nps uniformly spread in the membrane matrix

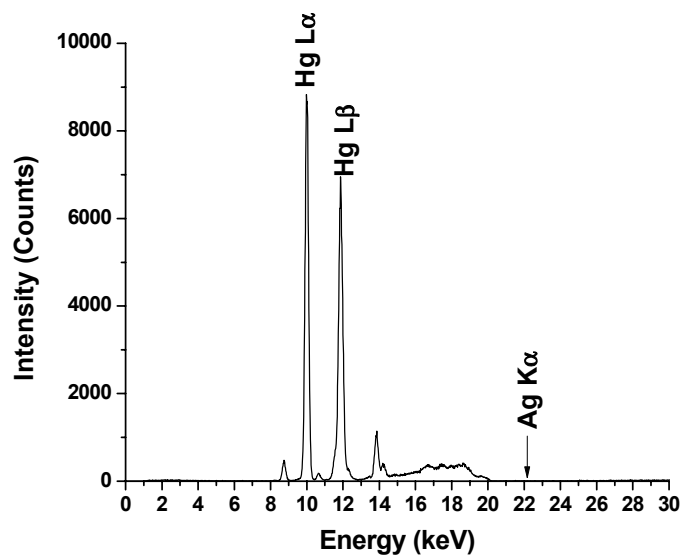
**Fig. S1a** Energy Dispersive X-ray Fluorescence (EDXRF) spectra of the Ag nps embedded membrane samples before subjecting to galvanic reaction.



**Fig. S1b** Energy Dispersive X-ray Fluorescence (EDXRF) spectra of the Ag nps embedded membrane samples treated with aqueous solution containing  $\text{Hg}^{2+}$  ions. Spectra shown in “a” and “b” are obtained from the membrane samples in which Ag nps were formed by the reduction with formamide (at 65 °C) and  $\text{BH}_4^-$  ions, respectively, and subsequently equilibrated with the solution containing excess of  $\text{Hg}^{2+}$  ions.

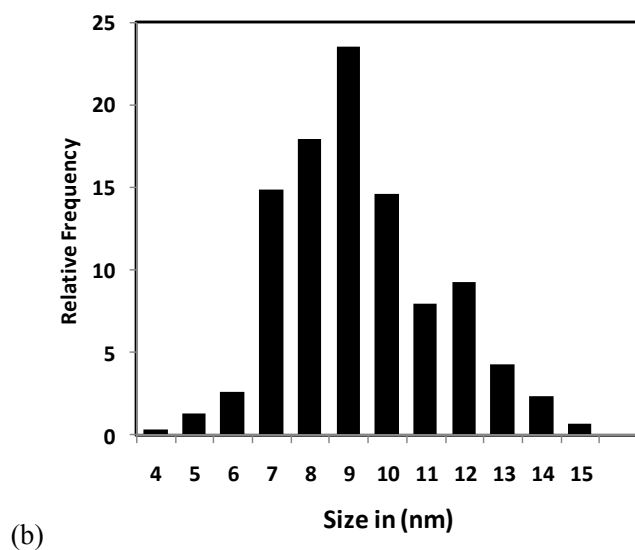
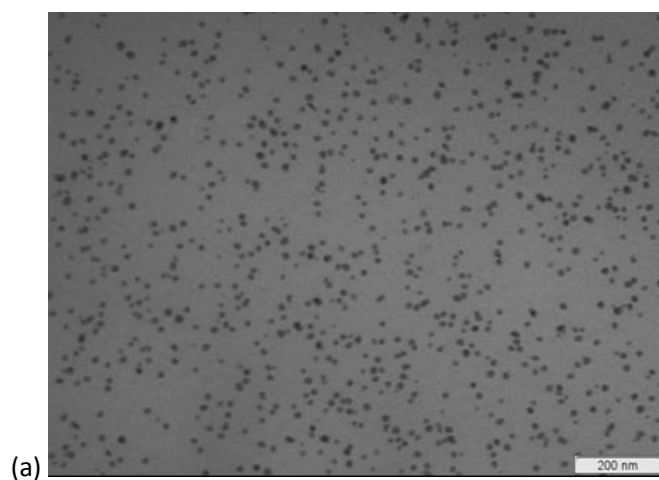


(a)

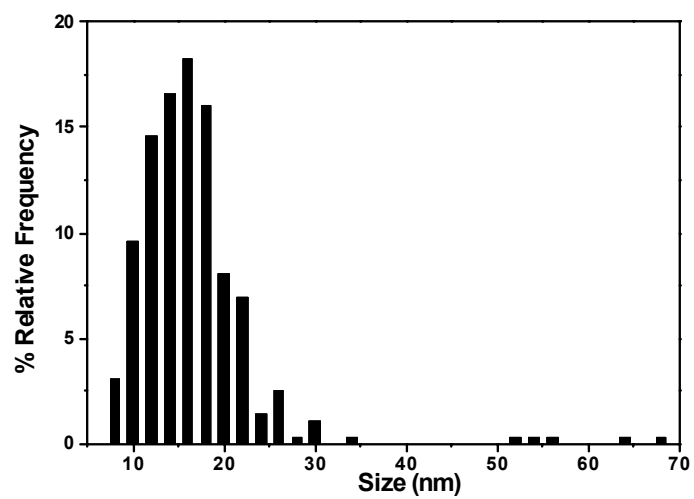
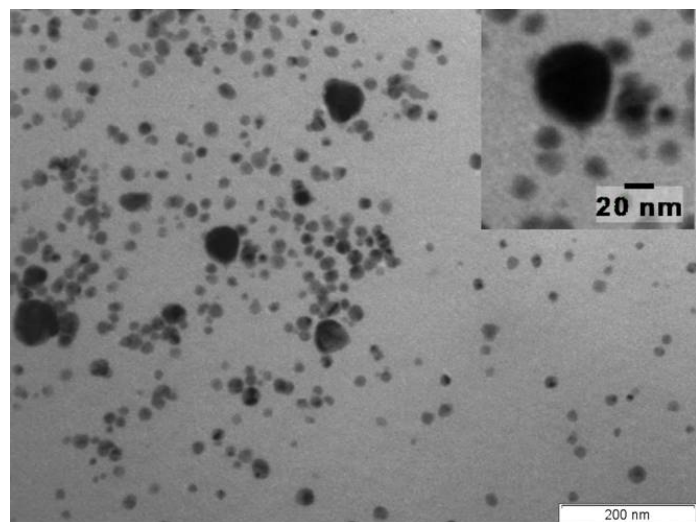


(b)

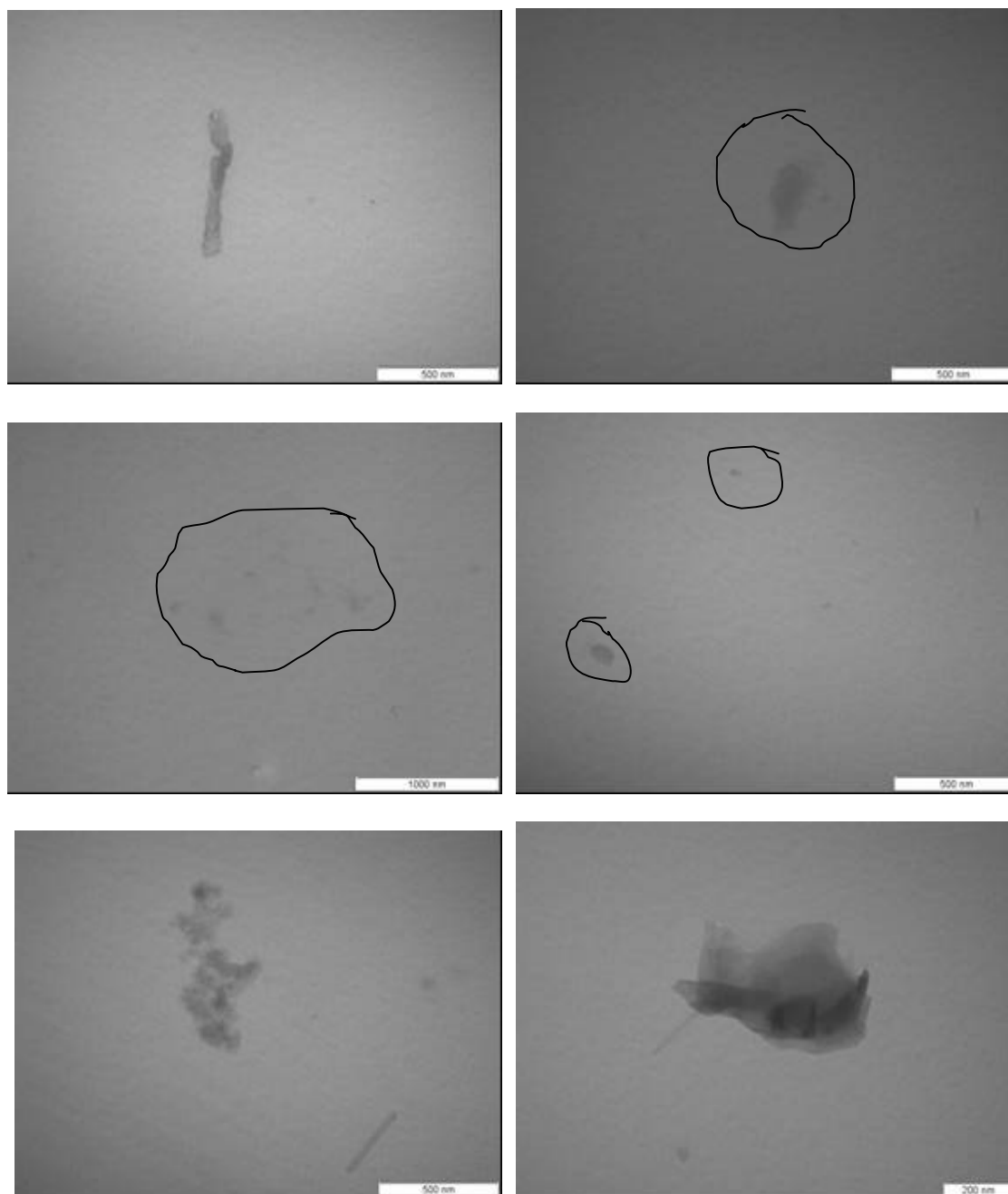
**Fig S2a** TEM image of the across sections of the membrane sample showing distribution of Ag nps formed by reduction of  $\text{Ag}^+$  ions with formamide at 65 °C in the membrane matrix. The size dispersion is shown in histogram in Fig.b.



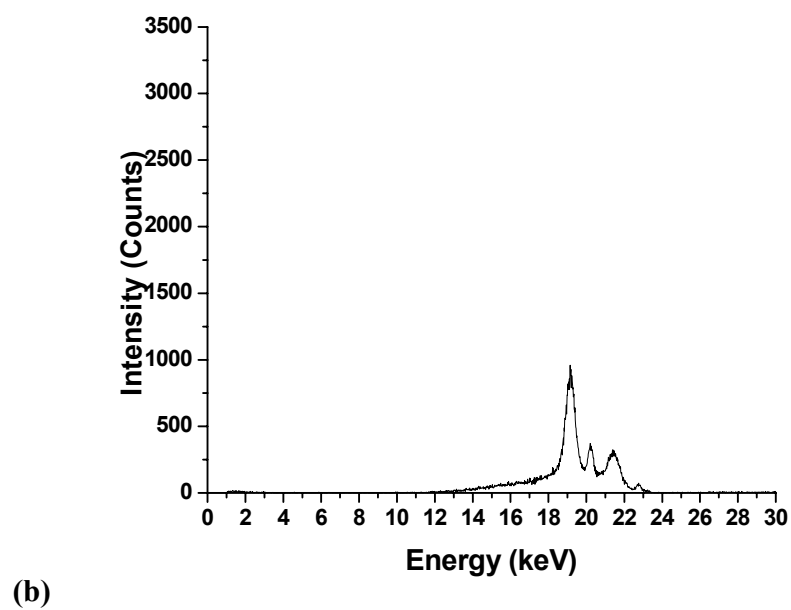
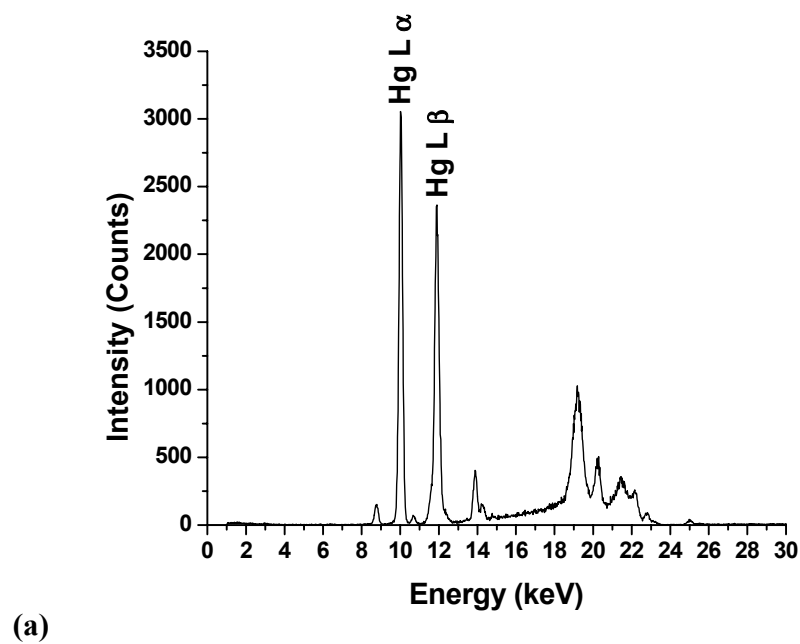
**Fig. S2b** TEM images of the across sections of the membrane samples subjected to quantitative galvanic replacement of Ag nanoparticles with  $\text{Hg}^{2+}$  ions.



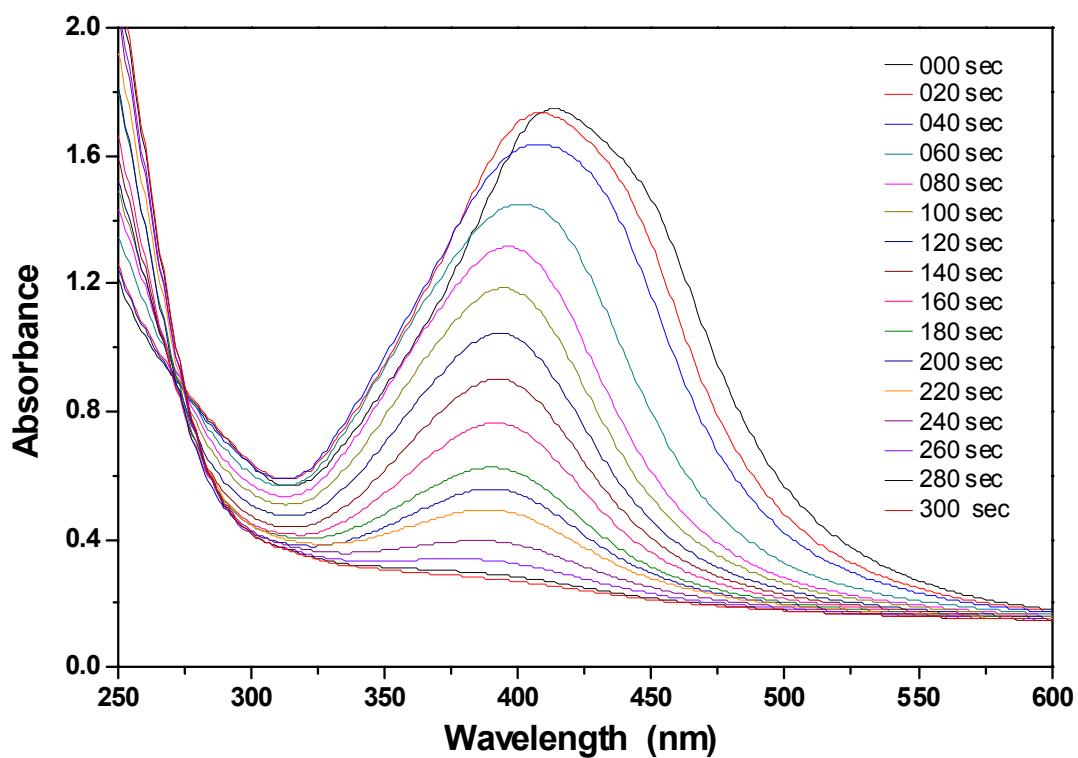
**Fig. S2c** TEM images of the across sections of the membrane samples subjected to quantitative galvanic replacement of Ag nanoparticles with  $\text{Hg}^{2+}$  ions.



**Fig. S3** Energy Dispersive X-ray Fluorescence (EDXRF) spectra of the  $\text{Hg}^0$  loaded membrane samples before (a) and after (b) equilibration with  $0.5 \text{ mol L}^{-1} \text{ HNO}_3$  at room temperature for overnight without stirring.  $\text{Hg}^0$  was loaded in the membrane sample by galvanic reaction of Ag nanoparticles with excess of  $\text{Hg}^{2+}$  ions.

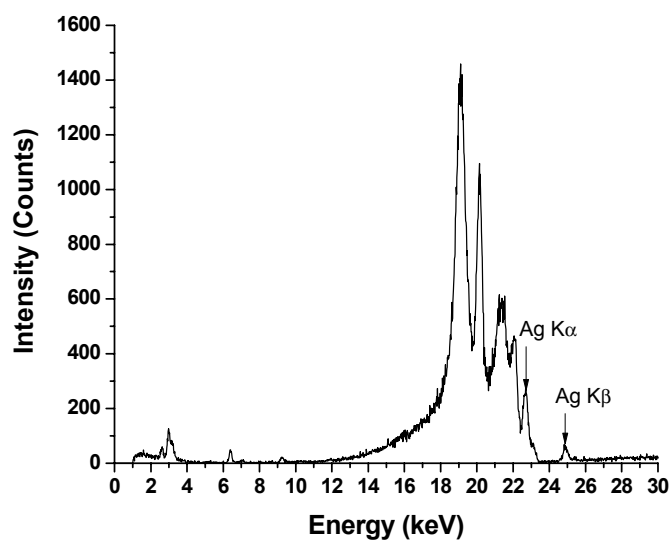


**Fig. S4** UV-Vis spectra of the membrane sample (Ag embedded) as a function of equilibration time  $t$  sec in the well-stirred equilibrating solution containing excess of  $\text{Hg}^{2+}$  ions.

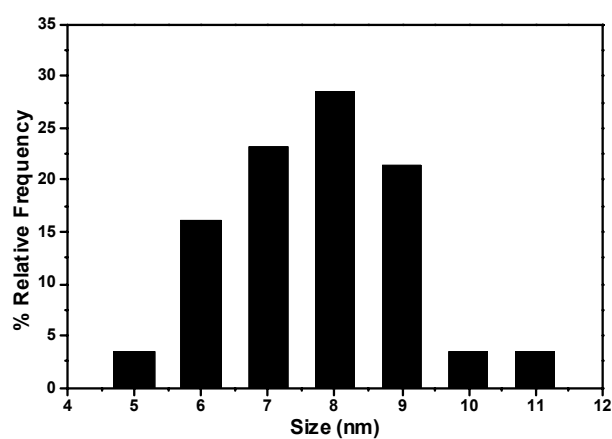
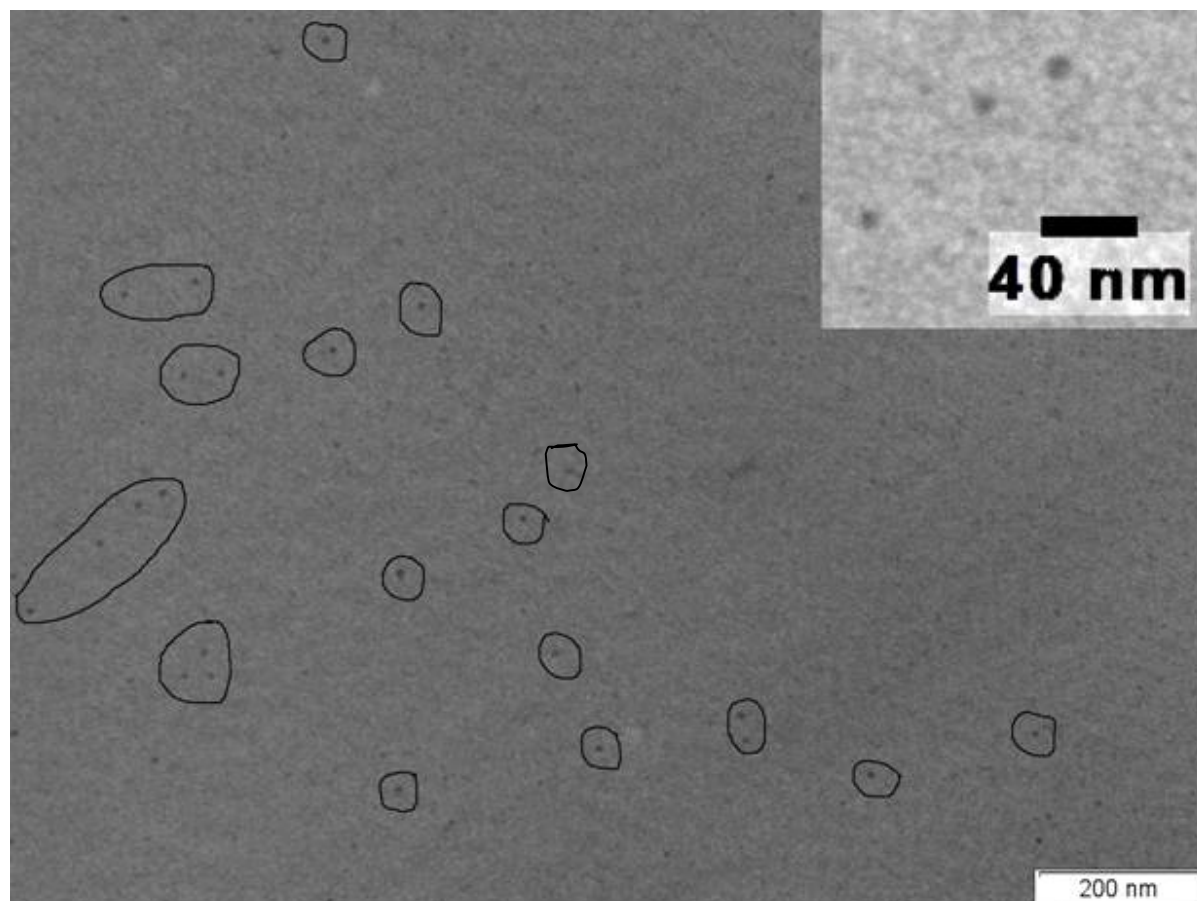




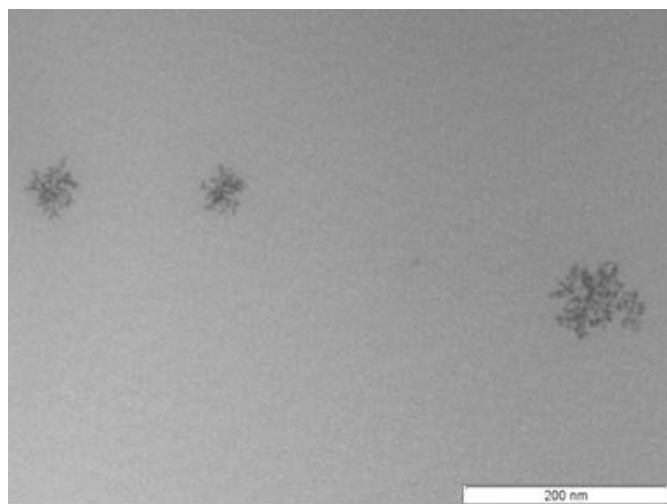
**Fig. S5** EDXRF Spectra of the Ag nps embedded membrane samples treated with aqueous solution containing excess of  $\text{Rh}^{3+}$  ions. The absence of Ag peaks in the spectrum confirms nearly complete oxidation of Ag with  $\text{Rh}^{3+}$  ions. The major peaks seen in these spectra correspond to Rh nps as well as from excitation source.



**Fig. S6** TEM image of the across sections of the membrane samples in which Ag nps were formed by reduction with formamide (at 65 °C) and subsequently treated with aqueous solution containing Rh<sup>3+</sup> ions. The radiotracer and EDXRF analyses of these membrane samples showed complete replacement of Ag with Rh. Some Rh nps are encircled for easy identification.



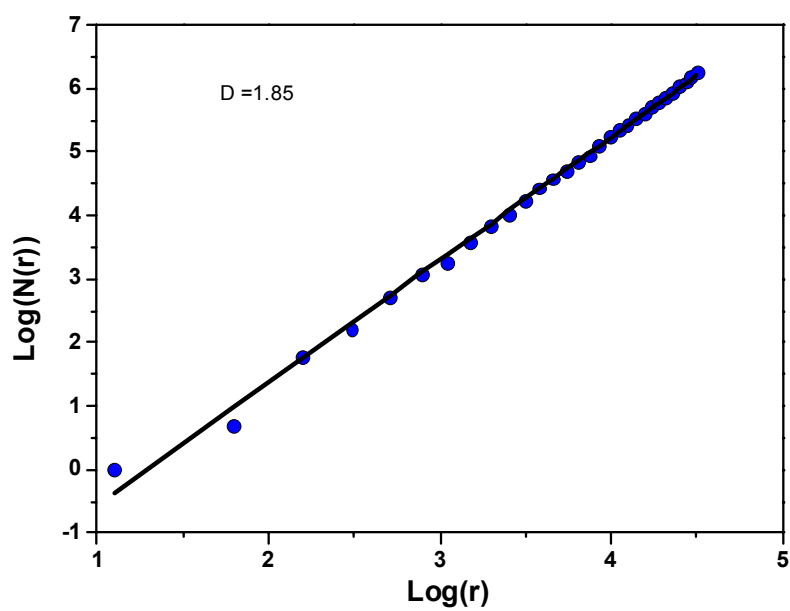
**Fig. S7** TEM image of the across sections of the membrane samples in which Rh were formed by direct reduction of  $\text{Rh}^{3+}$  ions with formamide (at 65 °C).



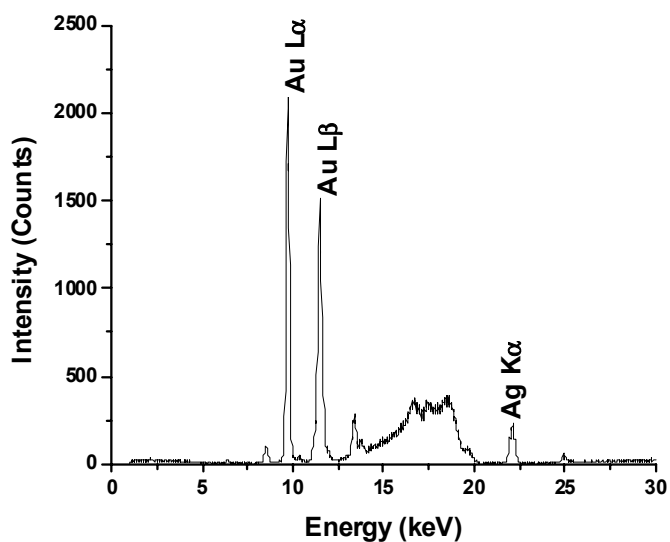
**Fig. S8** The fractal dimension of the two dimensional cluster has been calculated by the power

law relationship between no. of particles and radius,  $N(r) \propto r^D$  where  $r$  is the radius of the

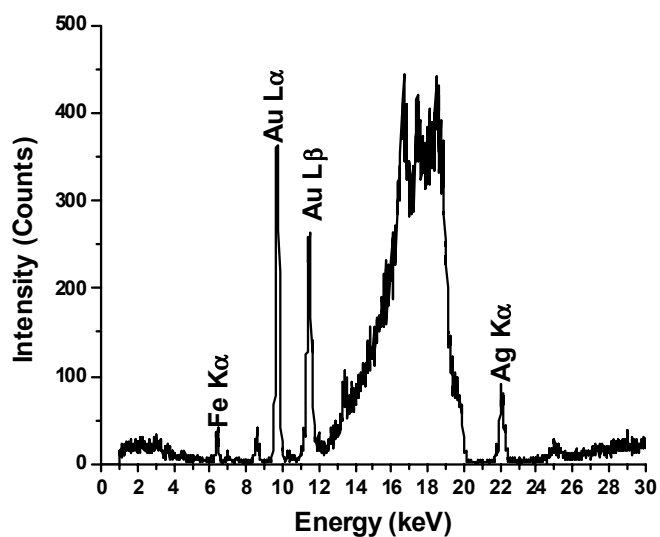
searching circle assuming the centre of mass of the cluster as the origin. The fractal dimension of cluster has been estimated 1.85.



**Fig. S9** EDXRF Spectra of the Ag nps embedded membrane samples treated with aqueous solution containing excess of  $\text{AuCl}_4^-$  anions for 3 h with constant stirring. The spectra “a” and “b” are of the membrane samples in which Ag nps were formed by reduction with sodium borohydride and formamide, respectively.

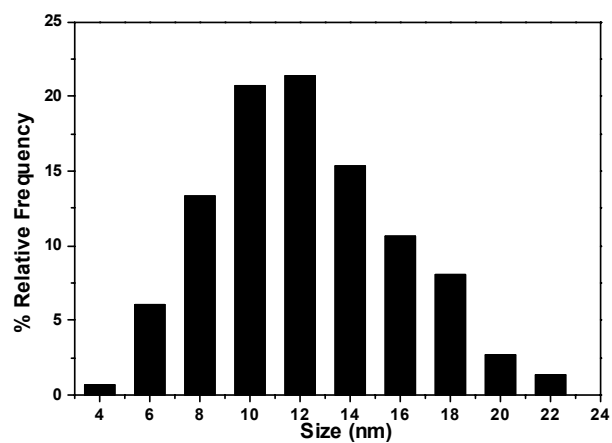
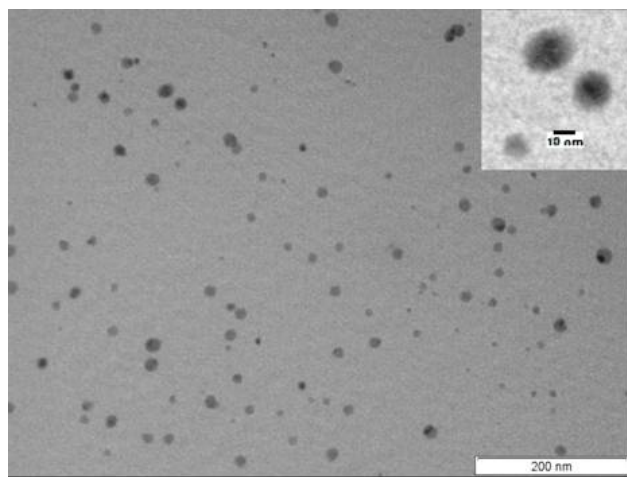


(a)

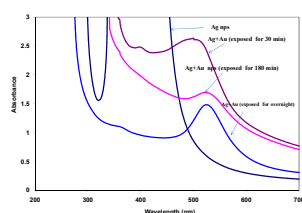


(b)

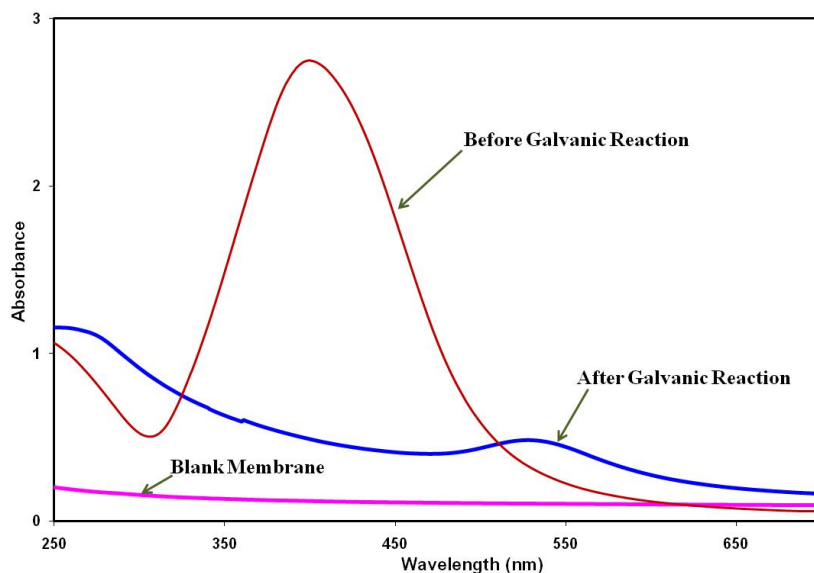
**Fig. S10** TEM images of the across sections of the membrane samples after galvanic reaction of  $\text{AuCl}_4^-$  ions with Ag nps. Ag nps in the membrane samples were formed by reduction with formamide (at 65 °C)



**Fig. S11** UV-Vis absorbance spectra of the membrane samples showing surface plasmon absorption bands of Ag nps (before galvanic reaction), Ag+Au nps (during galvanic reaction), and after galvanic reaction. Ag nps in the membrane samples were prepared by reduction of  $\text{Ag}^+$  ions loaded membrane samples with formamide at  $65^\circ\text{C}$  for 30 min. The Ag nps embedded membrane samples were equilibrated with  $0.01\text{ mol L}^{-1}$   $\text{HAuCl}_4$  solution with constant stirring for 30 min, 180 min, and overnight. Ag and Au contents in these membrane samples were obtained by EDXRF analyses. Fig. a and b were obtained by using membrane samples higher and lower amounts of Ag.



(a)



(b)

## Experimental Section

**Materials and Reagents.** AR grade chemicals and deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q USA) were used in the present study. Nafion-117 ion-exchange membrane with an equivalent weight of 1100 and thickness of 178 μm (Ion Power Inc.) was used after conditioning as described elsewhere.<sup>11</sup> Radiotracer <sup>110m</sup>Ag was obtained from the Board of Radiation and Isotope Technology, Mumbai, India. The γ-activity of <sup>110m</sup>Ag in the membrane was monitored by a well-type NaI(Tl) detector connected to a multi-channel analyzer.

**Preparation of Ag Nanoparticles.** The conditioned membrane samples (2×2 cm) were equilibrated with 25 mL of 0.25 mol L<sup>-1</sup> of AgNO<sub>3</sub> solution to convert it in Ag<sup>+</sup> form. The Ag<sup>+</sup>-loaded membrane samples were reduced by equilibration for a 30 min with 15 mL of formamide at 65 °C temperature with a constant stirring. In case of BH<sub>4</sub><sup>-</sup> reduction, the amount of Ag<sup>+</sup> ions was kept 15% of ion-exchange sites by equilibrating fully Ag<sup>+</sup> ions loaded membrane samples in the well-stirred 0.25 mol L<sup>-1</sup> NaNO<sub>3</sub> for 45 s as described in our earlier work.<sup>10</sup> The fully Ag<sup>+</sup> ions loaded Nafion membrane sample was found to produce Ag metallization at surface of the membrane on reduction with BH<sub>4</sub><sup>-</sup> ions. After this, the membrane samples were subjected to reduction in well stirred 0.2 mol L<sup>-1</sup> NaBH<sub>4</sub> solution at room temperature for 30 min. After reduction, the membrane samples were thoroughly washed with water and equilibrated with NaNO<sub>3</sub> (0.25 mol L<sup>-1</sup>) to remove unreduced Ag<sup>+</sup> ions from ion-exchange sites of the membrane sample. Radiotracer tagged Ag nps were prepared in the similar fashion except that the membrane samples were loaded with Ag<sup>+</sup> ions containing known radioactivity of <sup>110m</sup>Ag radiotracer. These radiotracer loaded membrane samples were reduced with NaBH<sub>4</sub> and formamide as described above.

**Galvanic reaction of Ag nanoparticles embedded membrane.** For galvanic reactions experiments, the 10 mL aqueous solutions containing Hg<sup>2+</sup> (0.01 mol L<sup>-1</sup> HgNO<sub>3</sub>), Rh<sup>3+</sup> (0.01 mol L<sup>-1</sup> RhCl<sub>3</sub>), and AuCl<sub>4</sub><sup>-</sup> (0.01 mol L<sup>-1</sup> HAuCl<sub>4</sub>) ions were used. The membrane samples (2×2 cm) containing Ag nps were equilibrated in aqueous salt solution for known period of time with a constant stirring. The membrane samples equilibrated with chloride salt solution was washed with ammonia or 0.5 mol L<sup>-1</sup> NaCl to remove AgCl deposited on surface of the membrane samples.

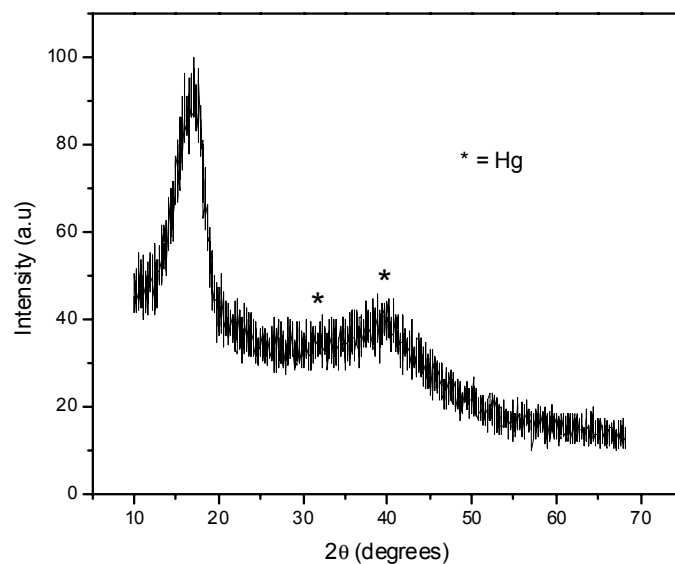
**Characterization.** UV-Vis spectra of Ag nps embedded membrane samples were recorded using UV-Vis spectrophotometer (V-530, JASCO, Japan). The absorbance measurements were



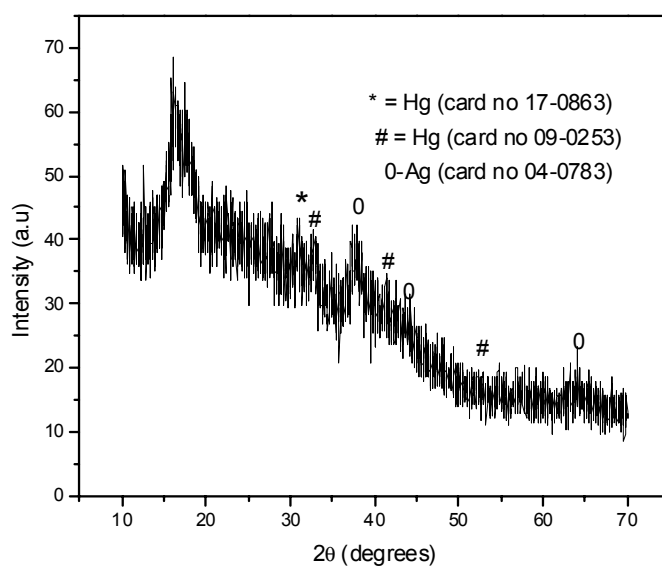
carried out by mounting the sample (1 x 2 cm) on to the inside wall of a (1 x 1 x 3 cm) quartz cell and placing it in a spectrophotometer to record spectrum with respect to air. For TEM analyses, Samples were embedded in spurr medium and cured at 70°C for 10hrs to make a hard block and sectioned in Leica ultracut[UCT] of 70 nm, these sections were taken on 200 mesh fomvar coated copper grids. The grids were examined in an FEI Technai G2 CryoTEM in IIT Bombay [Central Facility at SAIF], Mumbai at 120 KeV without any staining or post-treatment.

The amount of Ag nps embedded the membrane samples (2 x 2 cm pieces) were measured by equilibrating them for 24 h with 0.1 mol L<sup>-1</sup> AgNO<sub>3</sub> stock solution containing known activity of <sup>110m</sup>Ag radiotracer. After equilibration, the membrane samples were thoroughly washed with de-ionized water to remove equilibrating solution clinging to the surface of the samples. These samples were reduced as described above. The membrane samples were equilibrated with 0.25 mol L<sup>-1</sup> NaNO<sub>3</sub> to remove Ag<sup>+</sup> ions tagged with the radiotracer. This ensured that <sup>110m</sup>Ag radioactivity in the samples represent only content of Ag nps and not Ag<sup>+</sup> ions, if any. Filter paper standards were prepared by taking pieces of filter paper of the same dimensions (2 x 2 cm) as the membrane samples and adding known a volume (50, 100 and 200 μL) of the radiolabeled 0.1 mol L<sup>-1</sup> AgNO<sub>3</sub> stock solution. AgNO<sub>3</sub> stock solution used for preparing standard samples was same solution used for equilibrating the membrane samples. Each standard was prepared in duplicate. The soaked filter papers were dried at room temperature and counted in a well type NaI(Tl) detector in a similar counting geometry as the membrane samples. The amount of Ag in the membrane sample was obtained by comparing the γ-activity of <sup>110m</sup>Ag in membrane samples with the filter paper standards. X-ray diffraction (XRD) measurements were carried in the range of 2θ (10-70°) on the thin films of polymer for phase identification and crystallite size estimation, using monochromatized Cu-Kα (Kα<sub>1</sub> = 1.5406 Å and Kα<sub>2</sub> = 1.5444 Å) radiation by Philips X-ray diffractometer Model PW 1710, Netherlands. Silicon was used as an external standard for correction due to instrumental broadening. The broadening of the diffraction peak width of Bragg reflection plane was analyzed to estimate the size of nps embedded in the membrane using Debye-Scherrer equation (Klug, H.P., Alexander, L.E. (1959) *X-ray Diffraction Procedures*, John Wiley and Sons: New York).

**Fig.** X-ray diffraction patterns of Ag nps embedded membrane samples after galvanic with  $\text{Hg}^{2+}$  ions. (a) XRD patterns of the membrane sample after complete galvanic replacement with Hg, and (b) and after 50% galvanic replacement with Hg.



(a)



(b)

**Table S2** Comparison of XRD pattern and Crystallite size of thin film samples

Sample No	Expected composition	XRD Result	PCPDF Card No	Remark
NP1	Hg	Hump present at position of Hg	(card no 17-0863)	Crystallite size cannot be calculated
NP2	Hg+Ag	Very weak Hg (2 phases) Ag peak present	(card no 17-0863) (card no 09-0253) (card no 04-0783)	Crystallite size 6nm (Ag)
NP3	Hg+Ag	Ag peak present	(card no 04-0783)	11nm (Ag)
NP4	Rh	Broad hump present at Rh position	-----	Crystallite size cannot be calculated -
NP5	Au+Ag (Negligible)	Au present	(card no - 04-0784)	9 nm (Au)
NP6	Au+Ag (Negligible)	Au present	(card no - 04-0784)	11 nm (Au)

Au (card no - 04-0784), Hg (card no 17-0863), Hg (card no 09-0253), Ag (card no 04-0783)

