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COMMUNICATION

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

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Sankararao Chappa,^a Rakesh N. Shinde^b and Ashok K. Pandey^{a*}

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A polymer membrane having asymmetric physical structure, dense at surfaces and fibrous interior, is developed to host the Ag, Au, Pd, Rh and Ru nanocatalysts that are formed by *in situ* reductions of the precursors with functional groups covalently attached with the membrane matrix. This membrane mimics an eggshell membrane in terms of reduction and stabilization of the nanocatalysts without involving external reagents. The nanocatalysts in this membrane exhibit high catalytic activity in both the inorganic and organic reductions.

A significant advancement in the redox reactions having technological and commercial importance can be achieved by employing the noble metal nanocatalysts (NCs) due to their larger surface area, higher dispersion, desired shapes for exposing reactive facets, under-coordinated surface sites, and quantum confinement effects.¹ However, the key issues involved in the utilization of nanoparticles (NPs) as the heterogeneous catalyst are their tendency to agglomerate (physical stability), chemical corrosion leading to deactivation of their surfaces (chemical stability), and difficulty in withdrawing them from the systems (recyclability and product contamination). There is a possibility to address these problems by immobilizing NCs on a solid support like carbon nanomaterials,² inorganic particles,³ superparamagnetic Fe₃O₄ particles,⁴ biopolymer matrices,⁵ synthetic polymer membranes,⁶ porous inorganic support,⁷ and resins/polymers.⁸ Among these, the NCs immobilized on the magnetic particles and films/membranes are easily retrievable from the processes.

The bio-materials are non-toxic, low cost, and may provide a control over shape and size distributions. Various biomaterials like vitamins, sugars, agriculture extracts and residues etc. can be used for the reduction as well as capping of the NPs.⁹ It has been shown that phenolic derivatives in the most of

biomaterials are responsible for the precursor ions reduction and sugars provides capping on the NPs.¹⁰ The polysaccharide biopolymers like chitosan are extensively used as a solid support for the NPs due their capability to reduce and stabilize the noble metal NPs.¹¹

The bacterial cells can also be utilized for the intracellular synthesis of the NPs, which release due to rupture of the cell wall.¹² Eggshell membrane has the glycoproteins consisting of amino and carboxylic groups that reduce and stabilize the noble metal NPs.¹³ The NPs in the eggshell membranes exhibit good catalytic activity due to the fibrous structure of eggshell membrane that provide a high accessibility to the NPs.¹³

In the present work, a synthetic polymer membrane has been prepared by grafting glycidyl methacrylate (GMA) along with a cross-linker in pores of a commercially available poly(propylene) membrane by the UV-initiator induced *in situ* graft-polymerization (see ESI† for details). The physical structure of the grafted membrane is asymmetric as shown in Fig.1. The final membrane has highly porous interior and dense surfaces that are quite different from the homogenous microporous membrane used for the grafting, see Fig.1.

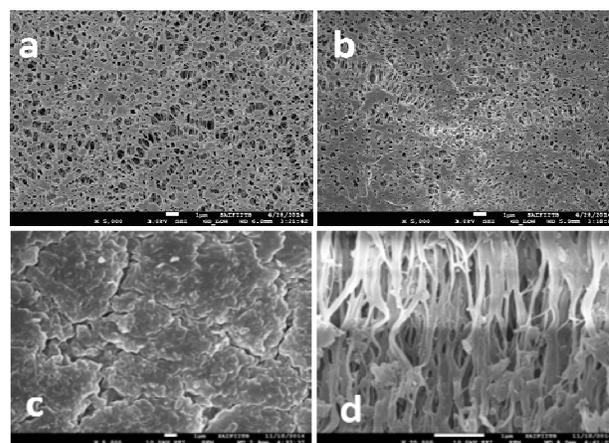
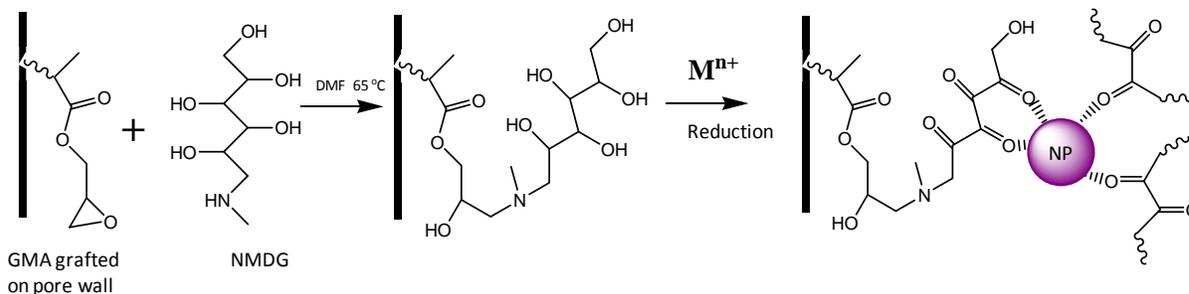


Fig.1. FE-SEM images showing surface (a) and cross-section (b) of host poly(propylene) membrane, and surface (c) and cross-section (d) of the same membrane after the grafting of GMA and subsequent treatment to attach *N*-methyl-*D*-glucamine (NMDG).

^aRadiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India; and Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India. Tel: +91-22-25594566; E-mail: ashokk@barc.gov.in.

^bDepartment of Physics, Savitribai Phule Pune University, Pune 411 007, India.

† Electronic Supplementary Information (ESI) available: [FE-SEM images, EDS, XRD, plots of reduction kinetics, and experimental details]. See DOI: 10.1039/x0xx00000x



Scheme 1. The chemical reaction involved in the anchoring of NMDG in a membrane that reduces noble metal precursor ions and stabilizes thus formed NPs.

The poly(propylene) host membrane provides a mechanical framework to soft microgel anchored in its pores. This membrane is similar to the hydrogel-filled membrane used for the applications like mass separations, sensing and analytical applications, catalysis, biomedical technologies etc.¹⁴ The interlinked microgels in pores of the membrane have connectivity that, in turn, provide a high accessibility to the functional groups. The physical structure of the pore-filled membrane synthesized in the present work is quite different from that of the homogenous pore-filled membranes reported in the literature.¹⁴ This is due to a reorganization of the 100 wt.% GMA-grafted membrane during drying that would shrink the polymer chains to form the dense surfaces and fibrous interior.

To anchor reducing functional groups in the membrane, the GMA grafted membranes have been reacted with *N*-methyl-*D*-glucamine (NMDG) using a procedure similar to that described for synthesis of the As(V)-selective membrane.¹⁵ The reducing properties of NMDG is not known. The overall process involved in the covalent attachment of NMDG groups in the membrane and its role in the reduction and stabilization of noble metal NPs are shown in Scheme 1.

The Ag, Au, Pd, Rh, and Ru NPs have been formed by just dipping the membrane samples in the 0.1 mol L⁻¹ solutions of AgNO₃, HAuCl₄, PdCl₂, RhCl₃ and RuCl₃, respectively, for 12 h at room temperature (see ESI[†]). It should be noted that loading of noble metals in the membrane occurs only by the reduction and deposition in the form of NPs. Thus, this process is similar to the electro-less deposition of metal. The image obtained by field emission scanning electron microscopy (FE-SEM) and elemental mappings by energy-dispersive spectroscopy (EDS) shown in Fig. 2 seem to suggest that the nitrogen (representing NMDG groups) and Rh NPs are uniformly distributed on the surface of membrane. It is seen from the FE-SEM images given in Fig. S1 (ESI[†]) that the noble metal NPs having different shapes and sizes are formed at the surfaces of the membrane depending upon the precursor ions. Thus, the self-reducing membrane developed in the present work is capable of reducing metal ions having redox potential $E^0 \geq 0.68$ V. It has been observed that Pt NPs are not formed using PtCl₆²⁻ precursor ions at room temperature. It is known that the formation of Pt NPs from PtCl₆²⁻ precursor ions using ethylene glycol or BH₄⁻ requires high temperature and pressure.¹⁶

The big sized Rh/Au/Ag NPs (> 50 nm) and small sized Pd/Ru NPs (10-15 nm) are formed at the surfaces of membrane equilibrated for the saturation loading. The Au cubes and prisms are formed at smooth surface and spherical Au NPs are formed at porous surface, see Fig. S1a (ESI[†]). The presence of Ru NPs has also been confirmed by energy dispersive X-ray fluorescence (EDXRF) analyses due to lower metal contents and small sized NPs loaded in the membrane samples, see Fig. S2 (ESI[†]). It is interesting to observe from the FE-SEM images of cross-sections of the membrane given in Fig. S3 (ESI[†]) that a negligible number of NPs are formed at the fibrous interior matrix. However, the FE-SEM image and elemental mapping clearly indicate Ag⁰ coating on the fibres at interior matrix of the membrane, see Figs. 3 & S3 (ESI[†]). The nitrogen mapping across the thickness of membrane indicates that NMDG is uniformly distributed at interior matrix of the membrane also.

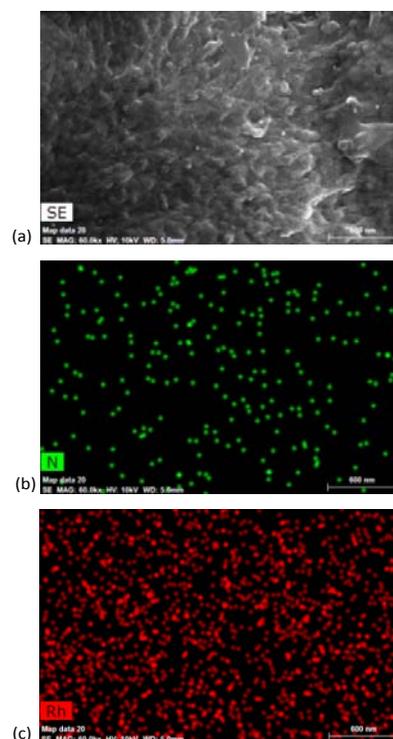


Fig. 2. The representative FE-SEM image of the surface of Rh NPs loaded membrane (a), and corresponding elemental mappings of nitrogen (b) and Rh (c) by EDS.

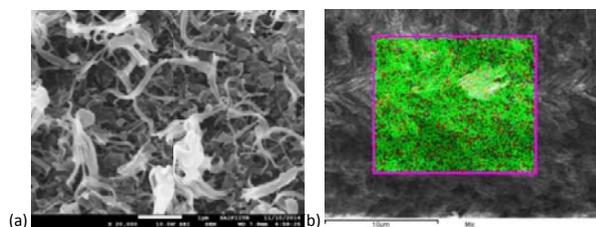


Fig. 3. FE-SEM image of the cross-section of Ag^0 loaded membrane sample (a), and corresponding elemental mapping of Ag (green) and nitrogen (red) (b) by EDS.

To explore a possibility of controlled loading of noble metal NPs, the membrane samples have been equilibrated with the well stirred $0.05 \text{ mol L}^{-1} \text{ AgNO}_3$ and PdCl_2 solutions as a function of time. The loading of Ag^0/Pd^0 in the membrane sample as a function of equilibration time is shown in Fig. 4. The amount of Ag^0/Pd^0 loaded in the membrane has been determined by leaching all the Ag^0/Pd^0 contents from the membrane samples in 10 mL of $3 \text{ mol L}^{-1} \text{ HNO}_3$, and subjecting these leach solutions to ICP-AES analyses. As can be seen from Fig. 4, the Ag loading attains 70 mg g^{-1} within 10 min , and slowly reaches to a saturation loading capacity 80 mg g^{-1} thereafter. It is evident from Fig. 4 that the rate of Pd^0 deposition is comparable to Ag^0 deposition in the membrane though the reduction of Pd^{2+} ions involves two electrons transfer. Also, the saturation loading of Pd^0 in the membrane is 120 mg g^{-1} that is higher than the Ag^0 saturation loading 80 mg g^{-1} in a same membrane. Thus, the reduction efficiency of NMDG-membrane increases with an increase in a redox potential of the precursor ions.

These preliminary results seem to suggest that the M^0 content and particles size can be controlled by equilibrating a membrane sample in the precursor ions solution for a predetermined time. The FE-SEM images given in Fig. 5 show that the Ag NPs sizes decrease from $\approx 75 \text{ nm}$ at the saturation loading to $\approx 15 \text{ nm}$ in the membrane equilibrated for 1 min in AgNO_3 solution. At some places, the clusters of Ag NPs have also been formed after 1 min equilibration, see Fig. 5a. The loading of metal content can also be reduced by controlling the grafting yield of reducing moiety NMDG in the membrane. This is based on a fact that the grafting yield is dependent upon the concentration of monomer in the solution used for grafting it in the membrane.¹⁵

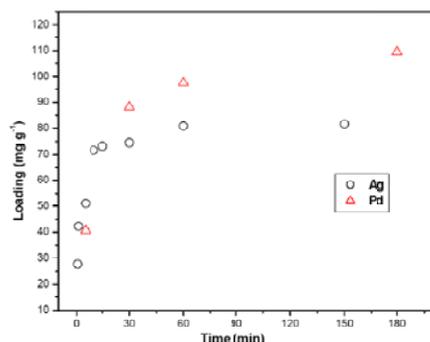


Fig. 4. Variations of Ag^0 and Pd^0 loadings in the membrane as a function of equilibration time in well stirred $0.05 \text{ mol L}^{-1} \text{ AgNO}_3$ and PdCl_2 solutions, respectively, at room temp.

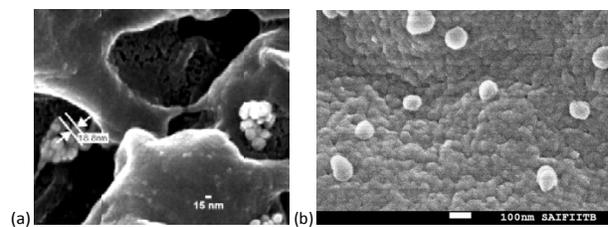


Fig. 5. FE-SEM images showing Ag NPs formed on surfaces of the membrane after 1 min (a) and 60 min (b) equilibrations in $0.05 \text{ mol L}^{-1} \text{ AgNO}_3$ solution.

The unchanged physical appearance, catalytic activity and XRD pattern of Ag NPs loaded membrane sample stored under ambient conditions for a time period of three months seems to suggest that the Ag NPs have a long shelf life in the membrane, see Fig. S4 (ESI[†]).

The catalytic properties of a Pd NPs loaded membrane have been studied in the reductions of U(VI) and Cr(VI) by formic acid at $45\text{--}50 \text{ }^\circ\text{C}$. The U(VI) reduction has several applications in the nuclear industries,¹⁷ and the Cr(VI) reduction is important for its remediation in a less toxic Cr(III) form.¹⁸ The choice of formic acid has been based on the good catalytic activity of Pd NPs in the oxidation of formic acid,¹⁹ and also U(IV) can be stabilized in formic acid. The formic acid has been used for reducing Cr(VI) to Cr(III).²⁰ In both cases, the reductions have been monitored by UV-Vis spectrophotometry as described in the experimental section. As can be seen from Fig. 6 & S5 (ESI[†]), both the reduction processes have proceeded efficiently in the presence of a Pd NPs embedded membrane (see ESI[†] for experimental details). The experiments under similar conditions using the blank NMDG-membrane show that the reduction of U(IV) or Cr(VI) does not occur in the absence of Pd NPs, see Fig. S6 (ESI[†]).

The conversion of U(VI) to U(IV) has been achieved within 20 min though there is a initial time lag in onset of the reduction process, see Fig. 6. U(IV) is stabilized in formic acid as its absorbance does not change even after two days. Thus, highly stable U(VI) could be reduced and stabilized to U(IV) just by formic acid at elevated temperature without need of addition of any reagents. The Pd NPs loaded membrane can be recycled.

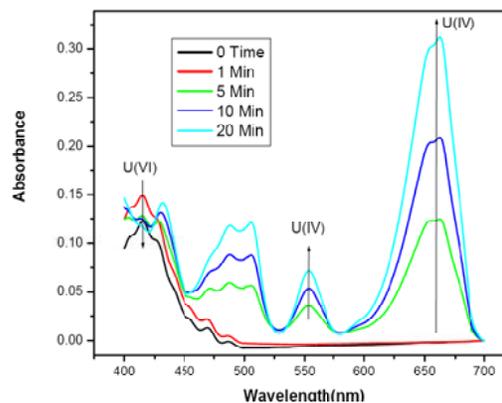


Fig. 6. Successive UV-Vis spectra showing reduction of U(VI) to U(IV) using formic acid at $50 \text{ }^\circ\text{C}$ as a function of time in the presence of a Pd NPs loaded membrane.

The coinage metal NPs are evaluated for their catalytic efficiencies in the model organic redox reactions involving reductions of *p*-nitrophenol (PNP) and methylene blue (mb) with BH_4^- ions.^{3,8,21} These organic redox reactions follow a pseudo-first-order kinetics in the presence of excess of NaBH_4 . In the present work, the BH_4^- reductions of PNP and MB have been studied using a Ag NPs loaded membrane as catalyst. The membrane developed in the present work is a neutral and, hence, both anionic (*p*-nitrophenolate) and cationic (MB) species would invade the membrane matrix easily.

It is seen from the growth of a product peak at 300 nm (*p*-aminophenol) in the UV-Vis spectrum of solution given in Fig. S7 (ESI[†]) that the membrane does not hold the reduced product *p*-aminophenol. As expected, both the reductions follow pseudo-first-order kinetics as shown in Figs. S7 & S8 (ESI[†]). It is interesting to observe that both the reductions are completed instantaneous (within a minute), and apparent reduction rate constants ($k_{\text{PNP}} = 0.1 \text{ s}^{-1}$, $k_{\text{mb}} = 1.5 \text{ s}^{-1}$) thus obtained are significantly higher as compared to that reported in the literature.²¹ There are several reasons that may be responsible for a higher redox catalytic activity of NPs in the membrane. These are: (i) high accessibility of NPs to the reactants, (ii) absence of capping that retard the catalytic activity,²² and (iii) nanoconfinement effects.²¹ It has been shown that silver citrate complexes readily undergo redox decomposition in the nanoscale confinement to form the Ag NPs.²³ It has also been reported that the catalytic behaviour of mesoporous materials is strongly influenced by the confinement effects.²⁴ These are related to geometrical constraints, reduced mixing of reactants and products, sorption reacting species on the pore-wall etc that may accelerate the redox kinetics.

In conclusions, the synthetic polymer membrane developed in the present work not only provides a green route for the syntheses of NPs in a solid matrix by simply dipping it in the precursor ions solution for a fixed period of time, but also enhances the redox catalytic activity of thus formed NPs in the inorganic and organic reactions. The membrane acts as a robust container of almost bare NPs without affecting their accessibility, and also NPs have a long shelf life. The same synthetic route can also be applied for synthesizing the self-reducing silica and Fe_3O_4 particles.

Notes and references

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- (a) T.-D. Nguyen, C.-T. Dinh, T.-O. Do, *Chem. Commun.*, 2015, **51**, 624; (b) Y. Li, W. Shen, *Chem. Soc. Rev.*, 2014, **43**, 1543; (c) N. Yan, Y. Yuan, P.J. Dyson, *Dalton Trans.*, 2013, **42**, 13294; (d) S. Zhang, L. Nguyen, Y. Zhu, S. Zhan, C.-K. Tsung, F. Tao, *Accounts Chem. Res.*, 2013, **46**, 1731; (e) M.A. Mahmoud, R. Narayanan, M.A. El-Sayed, *Accounts Chem. Res.*, 2013, **46**, 1795.
- (a) W. Yang, Y. Zhai, X. Yue, Y. Wang, J. Jia, *Chem. Commun.*, 2014, **50**, 11151; (b) D.S. Su, S. Perathoner, G. Centi, *Chem. Rev.*, 2013, **113**, 5782.
- (a) A. Corma, H. Garcia, *Chem. Soc. Rev.*, 2008, **37**, 2096; (b) W. Hu, B. Liu, Q. Wang, Y. Liu, Y. Liu, P. Jing, S. Yu, L. Liua, J. Zhang, *Chem. Commun.*, 2013, **49**, 7596.
- (a) M.B. Gawande, P.S. Branco, R.S. Varma, *Chem. Soc. Rev.*, 2013, **42**, 3371; (b) M.B. Gawande, A.K. Rathi, I.D. Nogueira, R.S. Varma, P.S. Branco, *Green Chem.*, 2013, **15**, 1895.
- R.B.N. Baig, M.N. Nadagouda, R.S. Varma, *Green Chem.*, 2014, **16**, 2122.
- (a) S. Troppmann, B. König, *Chem. Eur. J.*, 2014, **20**, 14570; (b) K. Soukup, P. Topka, V. Hejtmánek, D. Petráš, V. Valeš, O. Šolcová, *Catal. Today*, 2014, **236**, 3; (c) V.W. Faria, D.G.M. Oliveira, M.H.S. Kurz, F. F. Gonçalves, C.W. Scheeren, G.R. Rosa, *RSC Adv.*, 2014, **4**, 13446; (d) P. Ruiz, M. Muñoz, J. Macanás, D.N. Muraviev, *React. Funct. Polym.*, 2011, **71**, 916.
- (a) J. Liu, S. Ma, Q. Wei, L. Jia, B. Yu, D. Wang, F. Zhou, *Nanoscale*, 2013, **5**, 11894; (b) H.-L. Lin, N.-L. Sou, G.G. Huang, *RSC Adv.*, 2015, **5**, 19248.
- (a) Y. Lei, L. Wu, X. Zhang, H. Mei, Y. Gu, G. Li, *J. Mol. Catal. A: Chem.*, 2015, **398**, 164; (b) A. Alonso, A. Shafir, J. Macanás, A. Vallribera, M. Muñoz, D.N. Muraviev, *Catal. Today*, 2012, **193**, 200; (c) J. Kao, K. Thorkelsson, Peter Bai, Benjamin J. Rancatore, Ting Xu, *Chem. Soc. Rev.*, 2013, **42**, 2654; (d) B. Domènech, N. Vigués, J. Mas, M. Muñoz, D.N. Muraviev, J. Macanás, *Sol. Extract. Ion Exch.*, 2014, **32**, 301.
- (a) M.N. Nadagouda, R.S. Varma, *Green Chem.*, 2008, **10**, 859; (b) R. Eising, W.C. Elias, B.L. Albuquerque, S. Fort, J.B. Domingos, *Langmuir*, 2014, **30**, 6011; (c) J. Jung, S. Park, S. Hong, M.W. Ha, H.-g. Park, Y. Park, H.-J. Lee, Y. Park, *Carbohydr. Res.*, 2014, **386**, 57.
- S.A.O. Santos, R.J.B. Pinto, S.M. Rocha, P.A.A.P. Marques, C. P. Neto, A.J.D. Silvestre, C.S.R. Freire, *ChemSusChem*, 2014, **7**, 2704.
- A. Pestov, A. Nazirov, E. Modin, A. Mironenko, S. Bratskaya, *Carbohydr. Polym.*, 2015, **117**, 70.
- S.V. Gaidhani, R.K. Yeshvekar, U.U. Shedbalkar, J.H. Bellare, B. A. Chopade, *Process Biochem.*, 2014, **49**, 2313.
- (a) R. Mallampati, S. Valiyaveetil, *ACS Sustainable Chem. Eng.*, 2014, **2**, 855; (b) M. Liang, R. Su, W. Qi, Y. Zhang, R. Huang, Y. Yu, L. Wang, Z. He, *Ind. Eng. Chem. Res.*, 2014, **53**, 13635.
- (a) Q. Yang, N. Adrus, F. Tomicki, M. Ulbricht, *J. Mater. Chem.*, 2011, **21**, 2783; (b) A.K. Pandey, R.F. Childs, M. West, J.N.A. Lott, B.E. McCarry and J.M. Dickson, *J. Polymer Sci.: Part A*, **39**, 2001, 807, and references therein.
- R.N. Shinde, V. Chavan, R. Acharya, N.S. Rajurkar, A.K. Pandey, *J. Environ. Chem. Eng.*, 2014, **2**, 2221.
- A.L. Stepanov, A.N. Golubev, S.I. Nikitin, Y.N. Osin, *Rev. Adv. Mater. Sci.*, 2014, **38**, 160.
- (a) T. Toraiishi, T. Kimura, M. Arisaka, *Chem. Commun.*, 2007, 240; (b) A. Sahu, T. Vincent, J.G. Shah, P.K. Wattal, *J. Radioanal. Nucl. Chem.*, 2014, **300**, 163.
- M. Yadav, Q. Xu, *Chem. Commun.*, 2013, **49**, 3327.
- V. Mazumder, S. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 4588.
- (a) M. Zhu, C. Wang, D. Meng, G. Diao, *J. Mater. Chem. A*, 2013, **1**, 2118; (b) B. Baruah, G.J. Gabriel, M.J. Akbashev, M.E. Booher, *Langmuir*, 2013, **29**, 4225.
- S. Patra, A.K. Pandey, S.K. Sarkar, A. Goswami, *RSC Adv.*, 2014, **4**, 33366.
- Z. Niu, Y. Li, *Chem. Mater.*, 2014, **26**, 72.
- S. Patra, A.K. Pandey, D. Sen, S.V. Ramagiri, J.R. Bellare, S. Mazumder, A. Goswami, *Langmuir*, 2014, **30**, 2466.
- F. Goettmann, C. Sanchez, *J. Mater. Chem.*, 2007, **17**, 24.

Graphical Abstract

Highly stable metal nanocatalysts formed in self-reducing asymmetric polymer membrane exhibit good catalytic activity in inorganic and organic redox reactions.

