



# Silver nanoparticles stabilized in porous polymer support: A highly active catalytic nanoreactor



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## ARTICLE INFO

### Article history:

Received 13 March 2016

Received in revised form 22 June 2016

Accepted 3 July 2016

Available online 4 July 2016

### Keywords:

Silver nanoparticles

Catalysis

Para nitrophenol

Membrane

Nanoreactor

Nanoconfinement

## ABSTRACT

A catalytic nanoreactor with remarkable activity has been prepared by in-situ synthesis of colloidal silver nanoparticles of different sizes in a tailor made pore filled anion exchange membrane (AEM). Time resolved small angle X-ray scattering (SAXS) and field-emission scanning electron microscopy (FE-SEM) probe the evolution of size distribution of the nanoparticles during the course of synthesis. Borohydride reduction of *para*-nitrophenol to *para*-aminophenol has been used as a model reaction for catalysis throughout the study. Role of nanoparticle size vis-à-vis the role of nanoscale confinement on catalytic reaction has been investigated. It has been demonstrated that the overall catalytic performance of the silver nanoparticles is improved significantly in the nanoconfined environment as compared to that of the bare nanoparticles. The origin of such improved catalytic activity of spatially confined silver nanoparticles has been attributed to the effect of “nanoconfinement” that seems to accelerate the catalytic reduction. It has been shown that the catalytic rate constant is strongly dependent on the average occupancy of the *para*-nitrophenol molecule per pore when it is significantly less than one. This extraordinary effect may be attributed to the compartmentalization of the reactant molecules in nanoscale subvolumes, which essentially favours the forward reaction because of reduced molecular mixing of reactant with product.

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## 1. Introduction

Study of chemical reactions in spatial confinement at nanoscale has been a fascinating topic of research in recent years. Spatial confinement at nanoscale can be visualized as the division of a given volume into several small compartments of molecular dimensions by adiabatic walls. Upon spatial confinement, the reaction equilibrium switches to microcanonical ensemble situation from the classical canonical ensemble situation, as a reaction occurring in bulk solution. Though there is a lack of clear understanding, several explanations have been put forward in the literature regarding the nanoconfinement effect on chemical reaction equilibrium. These include surface effect, change of solvent structure in nanodomain, pore size selectivity, increased density inside pore due to higher pressure, reactant product reduced mixing, system-size dependent entropy variation etc [1–12]. Recently, we have shown that nanoconfinement in commercial ion-exchange membranes

and neutral XAD-4 beads significantly favours various types of redox reactions, which includes synthesis of inorganic nanoparticles under mild conditions [13,14]. Lorenz et al. have also reported the enhancement in electron transfer rate, during reduction of [Co(dipic)<sub>2</sub>]<sup>−</sup> (dipic = dipicolinato) complexes by ascorbic acid, in a nanoscale reverse micellar waterpool [15]. Many organic reactions, such as, borohydride reduction of esters, organic coupling reactions, degradation of phenol have been found to be facilitated in reverse micelles, and in organic supramolecules, having nanocavities [16–20]. It is of general interest to explore different types of reaction, driven by nanoconfinement. A few inorganic redox reactions have been reported so far under nanoconfinement conditions and there is a need for detail investigation on the effect of confinement on metal nanoparticle catalysed redox reactions.

Catalysis in nanoscale confinement has been an exotic research topic during last few years [21–34]. It has been shown that the solid catalytic nanoreactor, where the catalytic motif is confined in a nanoporous matrix, shows unique properties when catalyzing reactions under pseudohomogeneous conditions and exhibits more activity than just a solid supported catalyst [21]. These hybrid materials are popularly named as yolk-shell, core-shell, nanorat-

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tle, or ship-in-a-bottle nanoreactors, which consists of catalytic metal nanoparticles confined within nanoscale domains of organic or inorganic materials. Various kinds of catalytic reactions have been studied in nanoreactors, however the diffusion rate of the reactants through the encapsulating shells is an additional parameter involved. This problem may be overcome by preparing metal nanoparticle in thin porous ion-exchange polymer membranes. Ion-exchange membranes [35] (ion containing polymers) are well known for stabilizing various metal nanostructures because of their unique bi-continuous morphology in a combination of hydrophilic and hydrophobic nanodomains. Metal nanoparticles hosted in such matrices are good candidates as a catalytic nanoreactor for use in heterogeneous catalysis because of high thermal, chemical and mechanical stability and good contact of the reactants with the nanoparticle surfaces by the way of diffusion through hydrophilic channels. Also the membrane based catalyst can be easily separated from the reaction media after the completion of the reaction [36,37].

In this work, silver nanoparticles of varying sizes have been synthesized in the confined nanodomains of a pore filled tailor-made anion exchange membrane (AEM) by nanoconfinement driven redox decomposition of silver citrate complex. The method of nanoparticle synthesis has been described in our earlier publication [13]. The extent of silver loading ( $\text{mg cm}^{-2}$ ) in the membranes, required to determine the activity parameters of the catalyst, has been determined using  $^{110\text{m}}\text{Ag}$  radiotracer. Evolution of the size and shape of the nanoparticles during the course of reduction has been followed by small angle X-ray scattering (SAXS) experiment as well as field emission scanning electron microscopy (FE-SEM). The catalytic performance of the composite membrane has been evaluated using silver nanoparticles catalyzed borohydride ( $\text{BH}_4^-$ ) reduction of *para*-nitrophenol (PNP) as a model reaction [38–41]. Attempt has been made to discern the role of nanoconfinement vis-à-vis size effect of the nanoparticles on the catalytic activity. In order to investigate the nanoconfinement entropic effect on the reaction kinetics, PNP reduction rate has been determined with varying pore occupancy of PNP molecules. Plausible explanation for the origin of nanoconfinement effect on a redox reaction has been put forward in terms of significant decrease in the number of reactant-product mixed microstates in a confined nanospace.

## 2. Experimental section

### 2.1. Materials and reagents

The host polypropylene membrane (AccurelR PPIE) with  $0.1\ \mu\text{m}$  pore size was purchased from Membrana GmbH, Germany. The chemical reagents (3-acrylamido propyl) trimethyl ammonium chloride (APMC), (3-acryloxy propyl) trimethoxysilane (APTMS), ethylene glycol dimethacrylate (EDGM),  $\alpha$ - $\alpha'$ -dimethoxy- $\alpha$ -phenyl acetophenone (DMPA), silver nitrate, tri-sodium citrate, *para*-nitrophenol, and sodium borohydride were purchased from Sigma Aldrich.

### 2.2. Preparation of catalytic nanoreactor

The preparation of catalytic nanoreactor in the present work is a two step process, which includes the synthesis of nanoporous host anion exchange membrane (AEM) and the incorporation of silver nanoparticles within its matrix.

#### 2.2.1. Synthesis of anion exchange membrane (AEM)

The anion exchange membrane (AEM) was synthesized by pore filling of the commercially available porous polypropylene as a base membrane [42,47]. The monomers APMC and APTMS taken in 1:1 mol proportion were dissolved in dimethyl formamide (DMF)

solvent. The cross-linker EGDM (10 mol%) and UV-initiator DMPA (1 wt.%) were added in this polymerizing solution. The polypropylene membrane, cut into a  $5 \times 5\ \text{cm}^2$  piece, was soaked in such solution for overnight in order to fill the pores. After removing the excess of polymerizing solution, the membrane piece was exposed to UV light (365 nm) for 20 min to prepare the pore filled anion exchange membrane. Finally the pore-filled membrane was washed with hot DMF and water to remove any soluble components. The percentage of monomer grafting was found to be 100% by weight.

#### 2.2.2. Synthesis of silver nanoparticles of varying size in the AEM

The silver nanoparticles (AgNPs) were synthesized using redox decomposition of anionic silver-citrate complex in the confined nanospaces of the AEM, using the same protocol as described in our earlier publication [13]. Briefly silver citrate complex solution ( $\text{citrate}/\text{Ag}^+ \gg 1$ ) was prepared by dissolving 20 mg of  $\text{AgNO}_3$  salt in 20 ml of aqueous solution of tri-sodium citrate ( $0.2\ \text{mol L}^{-1}$ ). The AEM was dipped into this solution at  $75\ ^\circ\text{C}$  under stirring condition for 10, 20, 40 and 60 min respectively. AgNPs were formed in the confined nanospaces of the membrane. The median diameter of the nanoparticles were 17, 20, 30 and 61 nm, respectively, as determined by small angle X-ray scattering (SAXS) experiment.

### 2.3. Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS)

Field emission scanning electron microscopy (FE-SEM) was performed for the AEM hosted AgNPs. Prior to microscopy, the membranes were coated with gold to make them conducting. Also, the AEM was equilibrated with potassium iodide (KI) solution prior to EDS study in order to exchange the  $\text{Cl}^-$  ions of APMC with  $\text{I}^-$  ions.  $\text{I}^-$  was chosen because of its high Z value.

### 2.4. Small-angle X-ray scattering (SAXS) experiment

SAXS experiments were performed by a laboratory based SAXS instrument using  $\text{CuK}\alpha$  as probing radiation. Radial averaging of the raw experimental data was performed in order to obtain the scattering intensity ( $I(q)$ ) with respect to a wave vector transfer ( $q = 4\pi \sin(\theta)/\lambda$ , where  $\lambda$  represents the wavelength and  $2\theta$  represents the scattering angle) range  $\sim 0.1\ \text{nm}^{-1}$  to  $2.5\ \text{nm}^{-1}$ . The scattering contribution of the pristine AEM was subtracted from each scattering curve of the silver nanoparticles loaded AEM (Ag@AEM). In order to estimate the structural parameters, polydisperse spherical particle model was considered and the model was fitted to the background subtracted scattering profiles. Indeed the choice of the scattering model was supported by field emission scanning electron microscopy (FE-SEM) data.

The scattering intensity  $I_{\text{NP}}(q)$  is represented as

$$I_{\text{NP}}(q) = \left( \int_0^{\infty} P_{\text{NP}}(q, R) R^6 D_{\text{NP}}(R) dR \right) \quad (1)$$

where the term  $P_{\text{NP}}(q, R)$  represents the form factor of the nanoparticle. For spherical nanoparticle of radius R,

$$P_{\text{NP}}(q, R) = 9 \frac{(\sin(qR) - qR \cos(qR))^2}{(qR)^6} \quad (2)$$

$D_{\text{NP}}(R)$  represents the size distribution of the nanoparticles, i.e.,  $D_{\text{NP}}(R)dR$  indicates the probability of having size between R to

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