

Functional Block-Copolymer Template-Mediated Electrocatalytic Nanoparticle Assembly For Fuel Cells.

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ABSTRACT

The usefulness of nanosized metallic particles in new energy generation devices and their superior electrochemical activity and utilization efficiency have prompted researchers to synthesize particles on various novel supports. The tunability in the size and its distribution of nanoparticles via bottom up tools opens up new avenues in electronic and catalytic applications. The nano tool we report here, are molecules of simple chemical structure which, as a result of functionalization, can build up a variety of self-organized superstructure for potential applications. This work explores methods to prepare nanoparticles of platinum (PT) and its alloys on a conductive carbon nanotube support capable of promoting both proton and electron transport.

Keywords: functional block copolymers, nanoparticles, self-assembly, fuel cell, electrocatalyst

1 INTRODUCTION

Realization of full potential of nanoparticles (NPs) has been so far limited due to the difficulty in their synthesis that exhibit poor control over size, monodispersity and uniform dispersion. Control of nanostructure and ordered assemblies of metallic particles is crucial in futuristic applications that are size driven.¹⁻⁵ It is well known that Pt and its alloys have a broad application in fuel cell catalysis.⁶⁻⁸ In recent years much research has been devoted on the synthesis of Pt in nanometer scale, as higher surface activity and utilization efficiency could be realized when the size of particles decreases. Recently, much of the research has been focused on the depositing particles on various novel carbon supports. Pt and its alloys are traditionally prepared by the reduction of metallic precursors impregnated on the carbon support. Catalyst prepared via electroless plating, solid state reaction offered better dispersion of NP over the supporting material.⁹⁻¹¹ Though varying size of nanocatalytic materials could be realized by employing various procedures, however it is realized that precise control over the size can be achieved by stabilizing the nanoparticles using suitable stabilizers. But conventional strategies involving ligands, stabilizers, and surfactants for creating NP often yield less ordered structures. Meanwhile block copolymer (BCP) as a bottom

up tool exhibits inherent capabilities of self-assembly that ultimately make up well ordered nanostructures that are periodic on a nanometric scale.¹²⁻¹⁴ In recent past, there have been reports on various BCP molecules and their unique self-organization that have been used as a template to create and organize NP. Control over the size and shape of the metal colloids can be achieved by growing the desired colloids within domains of suitable shape and size.¹⁵

Recently, we have reported the directed synthesis of Pt nanoparticle and its attachment on the MWCNT, using sodium borohydride as a reducing agent and functionalized block copolymer styrene-b-ethylenebutylene-b-styrene (f-SEBS), as stabilizer in solution.^{16,17} The f-SEBS is carefully chosen because of their unique self organization characteristics in suitable solvent. Furthermore, the ionic groups selectively attached onto the PS domains acts as a reservoir for trapping various metallic ions. In this report we discuss the self-organization, synthesis and electrochemical activity of the Pt nanoparticles and its alloys. The synthesized catalyst particles are found to be electrochemically active for methanol oxidation reaction.

2 EXPERIMENTAL

2.1 Materials and preparation

Materials: All the chemicals used were of analytical grade. PtCl₄, AuCl₃.3H₂O, RuCl₃.3H₂O, Co(NO₃)₂ and reducing agent NaBH₄ were purchased from Aldrich. Tetrahydrofuran (THF), methanol, Sulfuric acid (all from Merck) was used as received. Multiwalled carbon nanotube MWCNT were procured from NanoLab Inc., MA, USA. Nafion 5% solution was obtained from Aldrich and was used as received. Acid-bearing f-BCP from the styrene-b-ethylenebutylene-b-styrene block copolymers was prepared by selective sulfonation/phosphonation of the styrene segment.^{18,19}

Synthesis of Pt Colloids in THF: Metallation of BCP domains was performed by mixing metal salts such as PtCl₄ (Ru, Co, Fe, Au salts) as precursors. The metal salt containing micelle solutions were reduced with sodium borohydride, (1.5 x the amount of metal in methanol to assure complete reduction) thus resulting in Pt, Pt-alloy metallic colloid. All the above metallation reactions were performed in liquid phase.

Loading of Pt Colloids on MWCNTs: The as-purchased MWCNTs were functionalized using a sonochemical oxidation technique before loading Pt nanoparticles on them. The sonochemical treatment introduced a high density of polar groups as a result the treated tube exhibits a pronounced tendency to disperse in THF. The nanotube suspension was then mixed with the synthesized metallic colloid sols. The resulting heterogeneous catalyst mixture was allowed to stir for overnight. Once the catalytic particles are stabilized, the quantitative removal of the surfactants was achieved by annealing the catalysts at 500°C, followed by washing with alcohol.

2.2 Characterization

FTIR, Dynamic light scattering, fluorescence spectroscopy, Uv-Vis absorbance and TEM-EDX microscopic analysis of the metallic colloids were performed on a Nicolet infrared spectrometer, Malvern Instruments Zetasizer Nano ZS, Varian spectrophotometer and a Philips 200 EX instrument operated at an accelerating voltage of 120 Kv respectively. The samples for TEM studies were prepared by placing a drop of the solutions on carbon-coated copper grids followed by drying.

Voltammetric techniques were used to study the synthesized catalysts. Cyclic voltammetry (CV) was conducted in 0.5 M H₂SO₄ to evaluate the electrochemical activity in the hydrogen adsorption/desorption regions and was used to investigate methanol electro oxidation in 0.5M H₂SO₄ solution containing 1.0 M methanol. The experiments were performed at room temperature using an Electrochemical Workstation (Solartron analytical, Hampshire, England). Glassy carbon disk (3mm in diameter) was polished to a mirror finish with alumina pastes before each measurement and served as the substrate for the catalysts. An aliquot of the catalyst dispersed in water was pipetted onto the glassy carbon substrate followed by a thin layer of nafion, which acted as both a binder and the electrolyte. The thin film electrode was then put in the electrochemical cell (BASi) for measurement. Potentials of the working electrode were measured against an Ag/AgCl reference electrode, and a platinum wire was used as the counter electrode.

3 RESULTS AND DISCUSSION

Fig 1 shows the morphology of thin film of typical f_SEBS (phosphonated SEBS) in THF. Thin films of the polymer were spin-cast at 3500 rpm from 0.1wt% solution in THF on silicon wafer substrate and dried under vacuum at room temperature. In the AFM images PS and EB segments appear darker and lighter respectively, and as such, the morphology reveals high degree of order in the air substrate interface. It is evident that loading of metallic particles onto the PS domains would result in the formation of highly dispersed nanoparticles. Loading is made possible due to the presence of ionic groups attached selectively onto the PS domains.

TEM image (Figure 2) shows the distribution of NP (only Pt is shown) in the resultant colloidal sols. The findings of TEM are consistent with our previous results showing f_SEBS as a nanoreactor.^{16,17} The formation of metallic nanoparticles of narrow size distribution is achieved due to the combination of low solute concentration used, presence of f_BCP as stabilizer; and the use of strong reducing agent, NaBH₄ that results faster nucleation to create small primary particles. The effect of stabilization of NP can be explained by the unique role of f_SEBS and the electrostatic attraction between metallic precursors and acid groups. Both low solute concentration and presence of polymeric monolayer adhered onto the growth surfaces ensures large diffusion distance between the primary particles; and restricts the diffusion of the growth species from the surrounding solution to the growth surfaces. Therefore, the diffusion process is deemed to be the rate limiting step, resulting in the formation of uniform size nanoparticles.^{20,21} The presence of strong reducing agent also ensures fast reaction rate and favor the formation of small nanoparticles. TEM studies also confirmed the success of the attachment of metallic nanoparticles onto MWCNT (not shown). Well-dispersed nanoparticles decorate the walls and ends of the nanotubes quite uniformly. Since the nanoparticles are attached through a well-defined interaction involving the sites on the nanotube walls decorated by polar groups. It is also noted that the interaction between the nanoparticles and nanotubes is quite strong, because sonication and thorough washing does not remove them. EDX analysis (as seen in Figure 3) confirms the presence of Pt in the respective colloids.

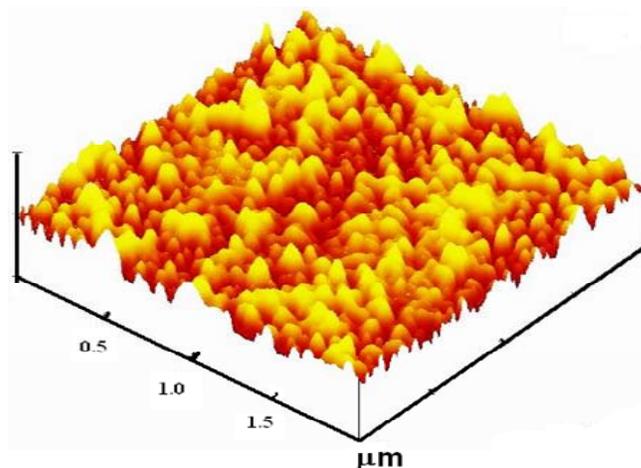


Figure 1: 3D AFM image of a thin film of phosphonated SEBS onto a silicon substrate. Increased PS domain size results from the presence of the ionic groups (-PO₃H)

Figure 4 shows the voltammograms of the treated Pt catalyst in 0.5 M H₂SO₄ solution. The catalyst synthesized as such (prior to removal of stabilizer) shows no characteristic features in the hydrogen and oxygen

adsorption-desorption regions and, suggests the complete blockage of the active sites of the Pt particles. For the catalyst that is subjected to annealing at 500°C, a well defined hydrogen adsorption-desorption features are observed, which in turn prove the high surface area of the catalyst. This has indicated that the f_BCP molecules completely eliminated from the surface of the Pt particles and all platinum were deposited on MWCNT. For all the synthesized catalyst (not shown here) a well defined hydrogen adsorption-desorption peaks are observed in the potential region -0.22 to 0.04 V, demonstrating the higher surface area of the catalyst [22]. The broad and featureless H-desorption peak observed for the catalyst in the potential region -0.22 to 0.04 V indicates the presence of Pt (111) sites [22]. This observation is consistent with the literature data and explains the fact that the nanostructure of platinum is composed of low coordination-number single crystals. Generally, owing to the problem of severe aggregation of the particles the particles would not result in well defined profiles, due to the limited amounts of Pt (111) and Pt (100) faces [23]. In the cathodic sweep the monolayer (PtOx) reduction peak (a) of the monolayer oxide formed during anodic sweep(b) is clearly observed in the potential region of 0.5 V. The efficiency of the catalyst also exhibits no significant sign of degradation after several potential cycling periods.

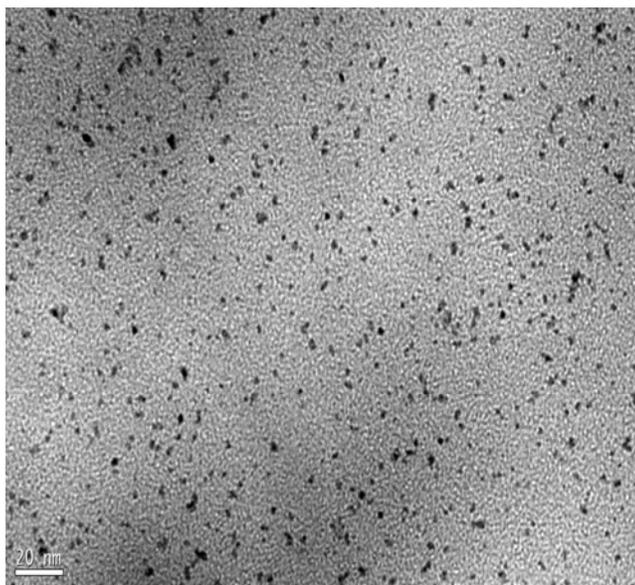


Figure 2: TEM image showing the dispersion of Pt NP onto the fn.SEBS

The cyclic voltammograms of Pt/Au/CNT in 0.5 M H₂SO₄ + 1M CH₃OH solution are presented in Figure 5, which indicates that the catalysts are highly active for methanol oxidation. Onset potential for methanol oxidation occurs at (0.08 - 0.22V) for the synthesized catalyst, which is relatively more negative than the reported catalyst. The

lower onset potential indicates clear evidence for superior electrocatalytic activity for methanol oxidation. This may be attributed to the easier formation of Pt-OH species on the catalyst. These Pt-OH species can facilitate oxidation of methanol adsorbents on the adjacent sites. On the forward potential sweep, the current increases slowly at lower

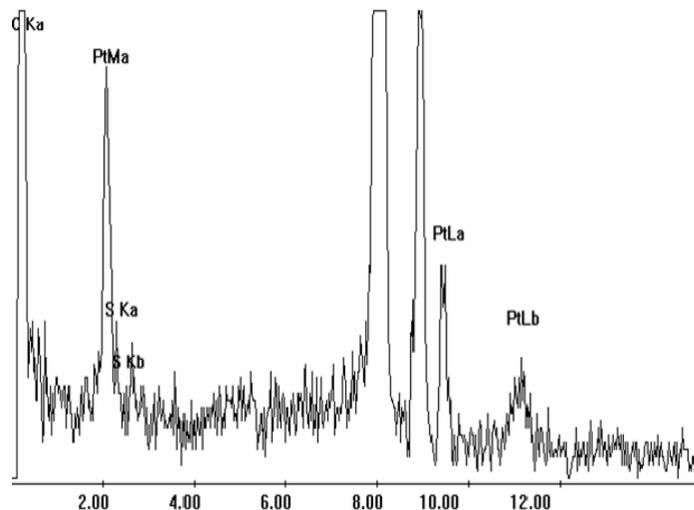


Figure 3: EDX confirms the presence of Pt in the synthesized colloids absence of chloride peak indicates the complete reduction of platinum precursor

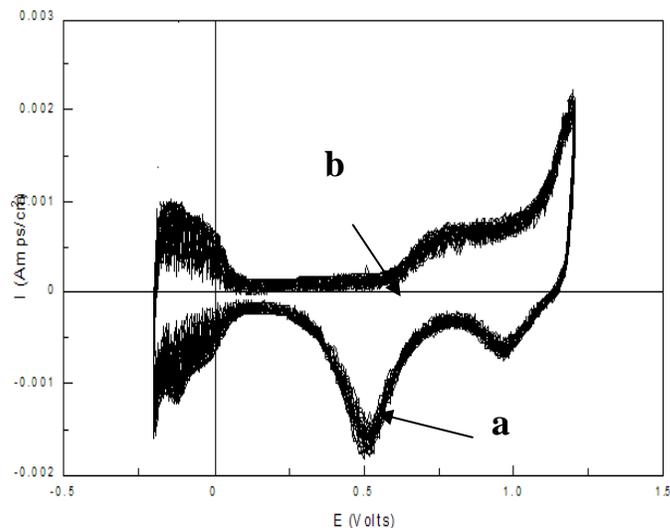


Figure 4: Cyclic voltammograms of PtAu/CNT catalysts in N₂-saturated 0.5 M H₂SO₄ at the scan rate of 50mVs⁻¹

potentials and then quickly increases at the potentials higher than 0.3 V with oxidation occurring at about 0.65 V. The slow increase in currents at lower potential on the forward sweep results from the adsorption of poisonous intermediates (COads) on platinum surfaces formed from the oxidation of small organic molecules. The quick

increase in currents at higher potentials on the forward sweep results from the partial oxidation of surface platinum to give Pt(OH)_{ads}, which aids in the transformation of intermediates to carbon dioxide^[22,24]. The predominance of the Pt(110) crystallite phase on the catalyst (as identified from the hydrogen adsorption/desorption profiles) and the higher electrochemical surface area and high electronic conductivity of SWCNT are decisive factors in enhancing the methanol oxidation reaction

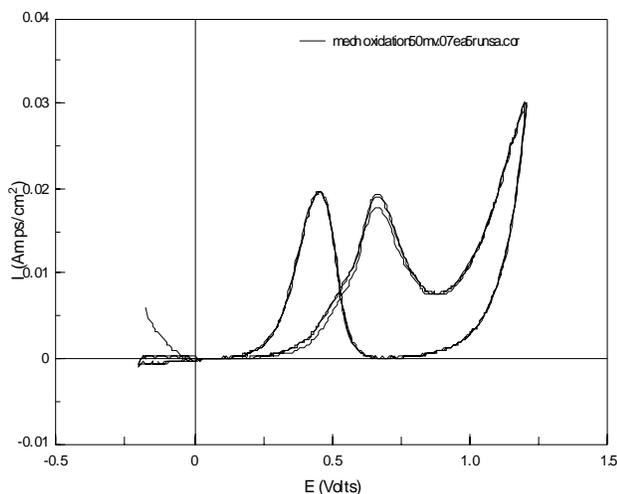


Figure 5: Cyclic voltammograms of PtAu/CNT catalysts in N₂-saturated 0.5 M H₂SO₄ + 1 M CH₃OH at the scan rate of 50mVs⁻¹

4 CONCLUSION

The platinum and its alloy nanoparticles supported on MWCNT are synthesized successfully using f₁-SEBS as a stabilizer in the solvent THF-MeOH. The morphological properties of these catalysts are evaluated by the TEM and it is found that catalyst has well-separated smaller particles (2-3 nm). The cyclic voltammetric response reveals that the catalysts are electrocatalytically active and very effective in the methanol oxidation.

5 ACKNOWLEDGMENT

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