

Electrocatalyst on Insulating Support?: Hollow Silica Spheres Loaded with Pt Nanoparticles for Methanol Oxidation

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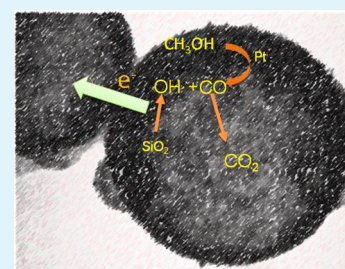
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S Supporting Information

ABSTRACT: Electrocatalytic oxidation of methanol on silica hollow spheres, loaded with platinum nanoparticles (Pt-SiO₂-HS), is reported. The functionalized hollow silica spheres were prepared by the surfactant (lauryl ester of tyrosine) template-assisted synthesis. These spheres were loaded with platinum nanoparticles by γ -radiolysis. Energy-dispersive X-ray analysis (EDAX) and X-ray photoelectron spectroscopy (XPS) analyses confirmed presence of Si and Pt in the composite. High-resolution transmission electron microscopy showed the formation of uniformly deposited Pt nanoparticles over the hollow spheres with a predominant Pt(111) lattice plane on the surface. In spite of the poor conducting nature of the silica support, the oxidation potential and current density per unit mass for methanol oxidation were noted to be ca. 0.72 V vs NHE and 270 mA mg⁻¹, respectively, which are among the best values reported in its class. The composite did not show any sign of a degradation even after repeated use. In fact, the anodic current was found to increase under constant polarization, which is attributed to a facile reaction between adsorbed CO with a surface hydroxyl group present on the silica support. These results are in favor of Pt-SiO₂-HS as a promising electrocatalyst material in the direct methanol fuel cell (DMFC) applications.

KEYWORDS: electrocatalysis, methanol oxidation, Pt nanoparticle, silica hollow spheres, γ -radiolysis, direct methanol fuel cell



INTRODUCTION

Over the past couple of decades, direct methanol fuel cells (DMFCs) have received considerable attention in energy research due to the possibility of using fuel (methanol) directly, without having a prior step of high-temperature reforming.^{1–3} Electro-oxidation of methanol at a reasonable rate in acidic medium is best conceivable on a Pt-based anode. Detailed investigation of oxidation of CO on a Pt surface revealed that adsorbed carbon monoxide (CO_{ad}) reacts with surface hydroxyl groups (–OH_{ad}) via the Langmuir–Hinshelwood mechanism.^{3,4} As the reaction proceeds, most of the surface gets blocked by CO_{ad}; less sites are available to form –OH_{ad}, and eventually the reaction ceases. One of the strategies to surmount this challenge is to introduce the cocatalyst or a support which will continuously provide hydroxyl groups for the reaction and will reduce the impact of poisoning. Recent studies indicate that incorporation of cocatalysts⁵ such as Au,⁶ Rh,⁷ Fe,⁸ Cu,⁹ Ru,^{10,11} or support such as CeO₂,^{12,13} MgO,¹⁴ carbon nanotubes,¹⁵ and diamond¹⁶ helps to improve the performance of Pt-based catalysts. Among them, the metal oxides seem to be the more attractive choice as they spontaneously form surface hydroxyl groups, albeit most of them in an alkaline medium. On the contrary, DMFCs operate in acidic medium. This requirement is partly associated with the better stability and proton conductivity of the Nafion membrane in acidic pH. Among various oxide supports, SiO₂

is a unique oxide that forms hydroxyl species even in the acidic pH.¹⁷ Therefore, it would be interesting to test the silica-supported Pt catalyst for the electro-oxidation of methanol. Pt metal, coated on colloidal SiO₂, has been tested for cathode material in the oxygen reduction reaction (ORR), pertaining to the PEM fuel cell applications.¹⁸ The Pt SiO₂ catalyst has also been tested for ethanol oxidation reaction.¹⁹ Silica has also been used as a filler in a Nafion membrane for DMFCs as it is known to impart structural stability to the membrane.²⁰ Besides the nature of materials, its morphology also has a significant impact on the catalysts' performance. For example, an enhanced electrocatalytic activity has been reported in the case of Pt deposited on hollow support such as mesoporous hollow carbon spheres²¹ and hollow Pt spheres.^{22,23} It has been attributed to the confinement of the reactants in the sphere cavity which helps in optimum collisions and causes catalytic enhancement.²⁴ So, with this background, it would be of immense interest to investigate the electrocatalytic activity of Pt catalyst loaded on hollow silica spheres, for the methanol oxidation. To the best of our knowledge, this kind of investigation has not been reported so far. One of the reasons could be its inherent insulating nature which would forbid the

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current flow toward the collector electrode. This problem has been addressed previously by loading Pt/mesoporous silica on the carbon support.²⁵ In the present investigation, we demonstrate that this limitation can be overcome by loading Pt on the functionalized hollow SiO₂ surface that forms a connecting path to carry the electrons toward the collector electrode.

In our previous studies, we have reported anchoring of silver nanoparticles on a functionalized silica hollow sphere by the electrophoretic method.²⁶ Here, in this work, we have deposited Pt nanoparticles on the amino acid functionalized hollow silica spheres by *in situ* reduction of Pt salt via the γ -radiolysis method. Here, the reduction takes place without any external reducing agents due to which the catalyst is free from possible surface contaminations.¹⁵ Moreover, this method could be scalable to the gram scale, without affecting the final composition. These Pt nanoparticles (Pt NPs) loaded over the hollow silica sphere (Pt-SiO₂-HS) have been tested for the electro-oxidation of methanol. For the measurements, the sample was drop-casted on a Au-disc electrode. The choice of gold as a collector electrode is based on: (1) bulk gold is not known to catalyze methanol oxidation and (2) amino functionalization of the spheres helps in anchoring the gold surface. The results suggest that SiO₂ HS not only minimizes the impact of CO poisoning but also imparts a structural and chemical stability to the catalyst in the acidic media, which is manifested in its outstanding performance for the methanol oxidation. These results are in favor of Pt-SiO₂-HS as a promising electrocatalyst material in the DMFC applications.

EXPERIMENTAL SECTION

Materials. Tetraethylorthosilicate (TEOS), aminopropyltriethoxysilane (APTES), commercial Pt catalyst (E-TEK, 40% Pt loading), and potassium chloroplatinate were purchased from Sigma-Aldrich. Lauryl ester of L-tyrosine (LET) was prepared as described by Baskar and co-workers.²⁷ All the reagents were of analytical grade and used as received, without further purification.

Synthesis of the SiO₂ Hollow Sphere (SiO₂-HS). The detailed synthesis procedure for the preparation of hollow SiO₂ spheres along with its mechanism of formation is described in our previous report.²⁶ In brief, 20.0 mg of LET was dispersed in 20 mL of water followed by heating the mixture at 40 °C for 5 min to ensure complete dissolution of LET. After cooling, it was subjected to vortex, and TEOS (0.25 mL) followed by APTES (30 μ L) were added in the vortexing mode. The cloudy suspension at the air/water interface was recovered by drying at 40 °C.

Preparation of Pt-SiO₂-HS by γ -Radiolysis. Reduction of Pt by γ -radiolysis was carried out by the procedure reported previously by us.¹⁵ For that, 6.0 mg of SiO₂ hollow spheres (prepared in the first step) was dispersed in 10 mL of 0.25 mM K₂PtCl₆. The resultant dispersion was transferred in a 15 mL cylindrical glass cuvette having a silicon septum. Into it, 0.1 mL of 2-propanol was added, and the dispersion was degassed with nitrogen gas and exposed to γ -irradiation, using a Co⁶⁰ source. For the optimum results, the total dose of 1.6 kGy (dose rate of 300 Gy h⁻¹) was applied. The resultant product was centrifuged, washed, and dried in vacuum. The morphological and material characterizations of the products were carried out by using field emission scanning electron microscopy (FESEM model Nova NanoSEM 450) and EDAX analysis (Bruker XFlash 6130), TEM (Zeiss Libra 120), and HRTEM (FEI Technai). The surface characterization of the product was accomplished using X-ray photoelectron spectroscopy (ESCA-3000 VG Scientific Ltd., England, Al_{K α} target 1486.6 eV, 150 W).

Voltammetric Measurements. Voltammetric measurements were performed with the help of a potentiostat/galvanostat (Autolab PGSTAT100 Metrohm, Netherlands) in a conventional three-

electrode system, having a Pt rod and Hg/HgO/saturated Ca(OH)₂ ($E^\circ = 0.0998$ V vs NHE) as counter and reference electrodes, respectively. Hg/HgO/Ca(OH)₂ (sat.) was chosen as the reference electrode instead of the more commonly used Ag/AgCl electrode, to avoid the possible poisoning of Pt catalysts by adsorption of Cl⁻ ions.²⁸ In order to minimize the junction potential, a K₂SO₄ (saturated) salt bridge was employed.²⁹ All measurements were performed in N₂ atmosphere and at room temperature. The working electrode was prepared by drop-casting an aqueous dispersion of Pt-SiO₂-HS (0.658 g mL⁻¹) on a pre-cleaned commercial Au electrode. It was vacuum-dried in a desiccator and used for the measurements. Prior to the sample loading, the Au electrode was polished (with 0.5 μ m alumina) and rinsed with a copious amount of Millipore water. The reproducibility and cleanliness of the Au electrode were verified by a recording cyclic voltammogram (CV) in 0.5 M H₂SO₄.

RESULT AND DISCUSSION

The synthesis of Pt-SiO₂-HS was accomplished by γ -radiolysis of a mixture of potassium chloroplatinate, dispersion of SiO₂-HS, and propanol. The radiolysis of water produces hydroxyl and hydrogen radicals which get scavenged by propanol and form hydrated electrons. These electrons subsequently reduce the Pt ions for which the SiO₂ surface provides a nucleation center. The amino groups present on the sphere help to anchor Pt NPs on the silica surface.^{23,26}

The surface morphology and composition of Pt-SiO₂-HS were determined by scanning electron microscopy as shown in Figure 1(a). A spherical SiO₂ structure of average size in the range ca. 2–3 μ m and decorated with Pt NPs (small white spots on big spheres) is legible in the picture. EDAX-based element mapping for the Pt loading has been carried out on an individual Pt-SiO₂-HS and shown as the Figure 1(a) inset. The continuous network of Pt nanoparticles is legible on the sphere. Further analysis of the data yields the presence of Si and Pt as the major elements in the sample with ca. 8.0 atomic weight % of Pt (Supporting Information, Figure S1). This value is close to 7.4%, used as the stoichiometry of the starting reagents. A trace of chlorine is observed in the EDAX spectrum, and its presence is associated with potassium chloroplatinate used during the radiolysis.

To gain further insight into the morphology, high-resolution transmission electron microscopy (HRTEM) was performed on the samples. Figure 1(b) shows a typical bright-field image of Pt-SiO₂-HS. For the comparison, the micrograph was also recorded on the sample prior to the Pt loading, i.e., on SiO₂-HS (Figure 1(b) inset). A dark contrast over otherwise relatively transparent spheres is interpreted as deposition of Pt over the spheres. From the particle size analysis, the size of the sphere is noted to be ca. 2 μ m with a wall thickness ca. 10–20 nm, over which Pt NPs are deposited to form a continuous network. The average diameter of the nanoparticle is determined in the range ca. 3–5 nm. Figure 1(c) shows the lattice fringes recorded on one such sphere. The interplanar spacing of ca. 0.22 nm noted in the image agrees well with the (111) lattice plane of Pt.

The presence of Pt on the SiO₂ surface is further evidenced by X-ray photoelectron spectroscopy (XPS). Figure 2(a) shows XPS recorded in the Pt 4f region and its corresponding fitting into four deconvoluted peaks. The larger peaks at 70.0 and 73.0 eV are assigned to the zero oxidation state of Pt. The two small peaks at 71.5 and 75.5 eV are matched Pt(IV) oxidation state and are related either to the presence of a small amount of PtO₂ on the surface or to the formation of a Pt–O bond with the silica surface. Similarly, the XPS signal associated with Si⁴⁺ (2p) (Figure 2(b)) observed at 103.2 eV is associated with SiO₂.

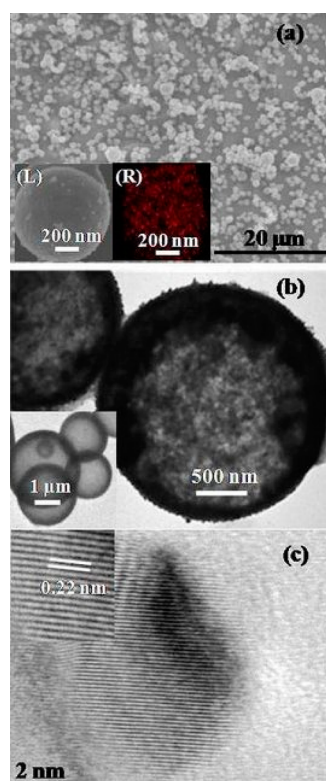


Figure 1. (a) Typical SEM image for Pt-SiO₂-HS. Left side inset (L) shows a magnified portion of one such sphere indicating deposition of Pt on the spheres. Right side inset (R) shows elemental mapping of Pt over the identical sphere. The red dots represent the presence of Pt. (b) Bright-field TEM image recorded on Pt-SiO₂ hollow-sphere composite. The dark contrast on the sphere is attributed to the deposition of Pt. The inset shows the TEM image of spheres, prior to Pt deposition. (c) The lattice fringes for Pt, recorded over one such sphere.

For the electrochemical characterization of Pt associated with Pt-SiO₂-HS, the cyclic voltammogram was obtained on the sample drop casted on the indium tin oxide (ITO) substrate (refer to Figure S2, Supporting Information) in 0.5 M H₂SO₄. The Au electrode was avoided as it gives a characteristic response in H₂SO₄, which overlaps with the Pt response. The overall profile of CV matched well with the one known for the polycrystalline Pt electrode, and it further confirms the presence of the electroactive Pt on the SiO₂ surface. From the hydrogen desorption peak (marked as * in Figure S2, Supporting Information) the electrochemical surface area was estimated to be 8.6 m² g⁻¹, and it is close to the value 11.4 m² g⁻¹, estimated by the BET (chemisorption) method.

Electrochemical oxidation of methanol on the Pt-SiO₂-HS was studied by cyclic voltammetry. Figure 3(c) shows a typical CV recorded on Pt-SiO₂-HS drop-casted on a Au electrode in 1.0 M methanol/0.5 M H₂SO₄. The controlled measurements on SiO₂ spheres without Pt (Figure 3(a), black dotted curve) did not yield any measurable current under identical conditions. Two anodic peaks, one at +0.72 V in the forward scan and +0.51 V in the reverse scan, are noted for Pt-SiO₂-HS. The peak in the forward scan is attributed to the oxidation of methanol to CO as a major product. In the reverse scan, most of them get further oxidized to CO₂.⁴ The experiment performed on the Pt-ETEK commercial catalyst under the identical condition is shown as Figure 3(b). It gave

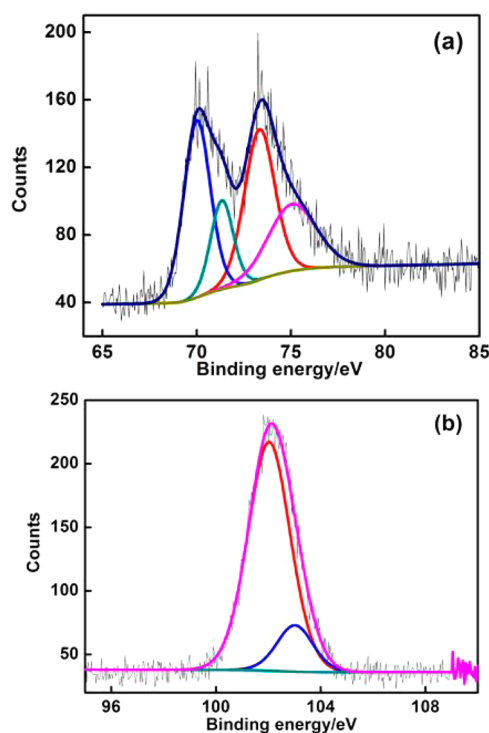


Figure 2. XPS recorded on a Pt-SiO₂-hollow sphere sample. (a) The spectral analysis in the Pt 4f region. Thin black line is the experimental data. Blue and red plots are fitting in the Pt(0) oxidation state. Green and purple plots are fitting in the Pt(IV) oxidation state. The thick black line is the best fit to the experimental data from the deconvolution analysis. (b) XPS in the Si(IV) region and corresponding fitting.

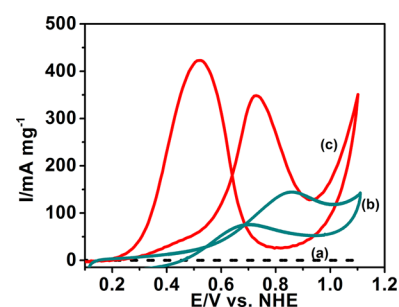


Figure 3. Cyclic voltammograms recorded in 1 M methanol and 0.5 M H₂SO₄ on (a) SiO₂-HS (without Pt) (black dotted curve) drop-casted on the Au electrode. (b) Commercial ETEK catalyst (60 μL dispersion ca. 0.39 μg) (blue curve) and (c) Pt-SiO₂-HS (0.39 μg Pt loading) drop-casted on the Au electrode (red curve). The scan rates were 100 mV s⁻¹.

corresponding peaks at +0.85 and +0.69 V, respectively. The shift toward less positive potentials by 0.13 and 0.18 V, for Pt-SiO₂-HS, compared to Pt ETEK, suggests facile oxidation of methanol on Pt-SiO₂-HS. Figure 4 summarizes the critical parameters for electrooxidation of methanol on Pt-SiO₂-HS and Pt-ETEK and their comparison with other reported similar systems,^{15,21–23,30,31} from which comparatively less overpotential value for Pt-SiO₂-HS is noted. This observation is attributed to the edges between Pt NPs and SiO₂ which plausibly provide favorable sites for the adsorption of methanol and stabilization of the activated complex. A continuous network of discrete Pt nanoparticles on SiO₂ (refer to Figure

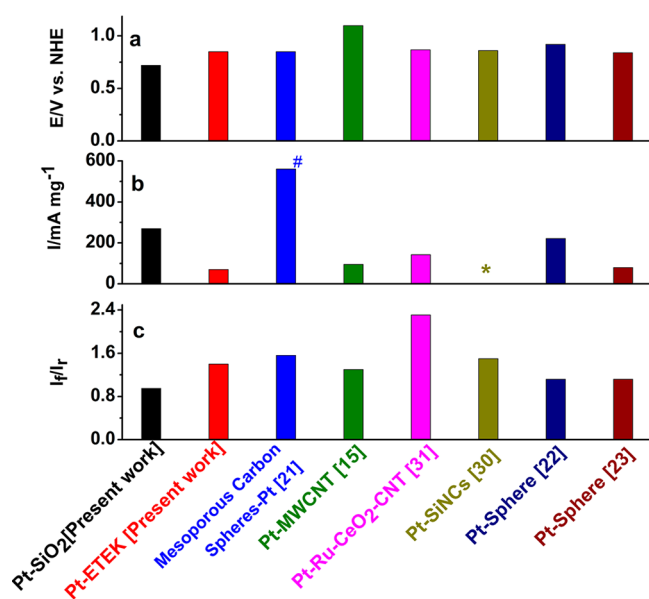


Figure 4. Comparison of the important electrochemical parameters for the methanol oxidation reaction. (a) Oxidation potential, (b) mass current density, and (c) I_f/I_r ratio. The data for Pt-SiO₂-HS samples and Pt-ETEK are compared with those reported for the similar systems, viz., Pt-mesoporous carbon spheres,²¹ Pt spheres,^{22,23} Pt/MWCNTs,¹⁵ Pt/Ru-CeO₂-CNT,³¹ and Pt/Si nanocones.³⁰ (*) indicates no information available. (#) indicates the value was deduced from the graph in ref 21.

1) provides a large number of such sites which eventually shift the potential toward the lower values.

Another important parameter to judge the electrocatalytic performance is current density per unit mass of Pt loading called mass current density. In the case of Pt-SiO₂-HS, this value turns out to be ca. 270 mA mg⁻¹ which is significantly high compared to the reported systems, except for Pt mesoporous carbon spheres²¹ (refer to Figure 4). So, higher mass current density is attributed to the hollow spherical support similar to that of Pt-mesoporous carbon spheres. This observation has been interpreted on the basis of entrapping of reactants in the sphere cavity which leads to optimum collision frequency for the electrocatalytic enhancement.²⁴ Moreover, abundant hydroxyl groups present in the case of SiO₂ even in acidic pH further increase the rate of second-order reaction between adsorbed CO and -OH which may lead to further enhancement. In spite of structural similarity between Pt-SiO₂-HS and the reported Pt-mesoporous hollow carbon sphere, the mass current density is noted to be less (270 vs 561 mA mg⁻¹) in the case of Pt-SiO₂-HS. This is plausibly due to the more conducting nature of the carbon spheres to that of silica spheres.

The third important parameter is the ratio of the currents in the forward scan to the reverse one (I_f/I_r). In the case of Pt-SiO₂-HS, an average value was noted to be 0.9 ± 0.1 . This value is rather small compared to the one recorded for the Pt-ETEK catalyst and reported for other similar systems (refer to Figure 4) which hinted at the plausible accumulation of intermediates including CO over the surface of the catalyst.

In spite of a moderate value for the (I_f/I_r) ratio, the peak current was found to be stable and in fact showed the tendency to increase with time. This is evidenced from repeated cycle voltammograms shown in Figure 5 and shows a significant increase in the current and a tendency to saturate after ca. 16

cycles, and a steady-state value was maintained even after 200 cycles.

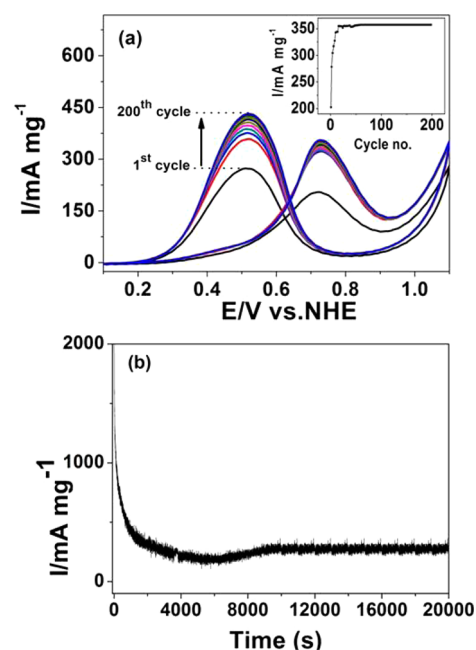


Figure 5. (a) Repeated cycle CVs on Pt-SiO₂-HS in 1 M methanol and 0.5 M H₂SO₄. The scan rate is 100 mV/s. Inset shows a plot for mass current density (forward oxidation) vs number of cycles (inset). (b) Chrono-amperometry curve recorded in 1 M methanol and 0.5 M H₂SO₄ on Pt-SiO₂-HS. The step potential was 0.80 V vs NHE.

In order to further test the stability of the catalyst, the current at the first oxidation peak was recorded vs time for the constant polarization at 0.80 V vs NHE, as shown in Figure 5(b). A more positive bias than the peak potential (0.72 V) was employed in this measurement to create enough oxidative situation to have a crash test. In spite of this, it gave a stable current density of ca. 329 mA mg⁻¹ which in fact showed increasing trend up to 9000 s and stable current response even after 20 000 s. This set of experiments further underlines the stability of the catalyst during the methanol oxidation.

On the contrary, in the case of Pt-mesoporous carbon spheres, the peak current during repeated cycles has been reported to decrease.²¹ The difference between this system and Pt-SiO₂-HS is associated with the presence of abundant -OH groups with silica, even in acidic pH. The adsorbed carbon monoxide CO_{ad} and the intermediates react with these -OH_{ad} via the Langmuir-Hinshelwood mechanism^{3,4} and cleared up the catalytic sites for the next cycle of reaction. Because of this, Pt-SiO₂-HS could maintain its activity even with repeated use. Thus, the moderate response in (I_f/I_r) ratio is compensated by the outstanding stability test displayed by Pt-SiO₂-HS. Figure 6 depicts the effect of mass loading of Pt-SiO₂-HS on the current response. The current density for both the peaks increases in a sigmoidal fashion and shows the tendency to saturation after ca. 0.39 μg of loading. This is attributed to the formation of an insulating layer of SiO₂ on the electrode after the optimum loading which perhaps impedes further electron transfer process.

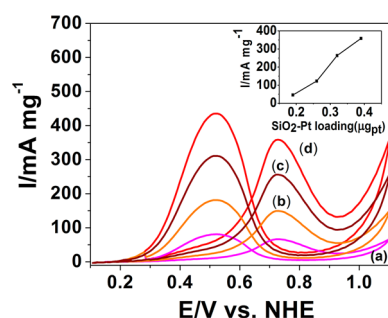


Figure 6. Cyclic voltammograms recorded at various Pt-SiO₂-HS loadings on a Au electrode: (a) 0.19 μg , (b) 0.26 μg , (c) 0.32 μg , and (d) 0.39 μg . The scan rate was 100 mV s^{-1} . The inset shows a plot for mass current density vs amount of Pt-SiO₂-HS loading.

CONCLUSION

This study is devoted toward an investigation of a novel Pt nanoparticle decorated SiO₂ hollow sphere composite as an electrocatalyst for the methanol oxidation reaction. The novelty of this work is use of SiO₂ hollow spheres which are decorated with Pt NPs by the γ -radiolysis method. Our results demonstrated that the Pt-SiO₂-HS shows no resistive current drop and in fact displayed superior performance to the reported champion systems. The presence of reactive hydroxyl groups on SiO₂ even in acidic pH and “clean” catalyst surface delivered by γ -radiolysis is responsible for the facile oxidation of CO to CO₂ which is manifested as less overpotential, higher current activity per Pt loading, and excellent stability over repeated use. So, we propose Pt-SiO₂-HS as a more promising electrocatalyst material for the DMFC applications.

ASSOCIATED CONTENT

Supporting Information

EDAX spectrum recorded on Pt-SiO₂-HS, cyclic voltammogram on Pt-SiO₂-HS in H₂SO₄, and method for the determination of electrochemical surface area. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Pt-SiO₂-HS, silica hollow spheres, loaded with platinum nanoparticles; EDAX, energy-dispersive X-ray analysis; XPS, X-ray photoelectron spectroscopy; HRTEM, high-resolution transmission electron microscopy; SEM, scanning electron microscopy; NHE, normal hydrogen electrode; CV, cyclic voltammetry; DMFC, direct methanol fuel cell; CO_{ad}, adsorbed carbon monoxide; OH_{ad}, surface hydroxyl groups; TEOS, tetraethylorthosilicate; APTES, aminopropyltriethoxysilane; LET, lauryl ester of L-tyrosine; ESA, electrochemical surface area; BET, Brunauer–Emmett–Teller; Pt-MWCNTs, platinum multiwalled carbon nanotubes

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