



Platinum nanoparticles functionalized with acetylene derivatives and the influence of ligand length on their electrocatalytic activity



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ABSTRACT

Platinum nanoparticles were prepared by sodium borohydride reduction of Pt(II) precursors and stabilized by the self-assembly of acetylene derivatives of different lengths (phenylacetylene, 4-ethylphenylacetylene, and 4-butylphenylacetylene). Transmission electron microscopic measurement showed that these nanoparticles exhibited similar average core sizes of 2.22 ± 0.83 nm, 2.09 ± 0.91 nm, and 2.18 ± 0.77 nm, respectively. FTIR study confirmed that the Pt cores were capped by these acetylene ligands with the breaking of the terminal $\equiv\text{C}-\text{H}$ vibrational stretch and a substantial red-shift of the $\text{C}\equiv\text{C}$ vibration. X-ray photoelectron measurements showed that platinum is in the metallic form. Pt nanoparticles all exhibited typical exponential decay profiles with some difference in small absorption peaks before 360 nm in UV–vis measurements. In $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot, band gap decrease is related with the increase of ligand chain length. The Pt nanoparticles all showed apparent photoluminescence with a clear red-shift of the excitation and emission peak positions as compared to those of the free monomers, due to intraparticle charge delocalization between the particle-bound acetylene moieties. Electrochemical measurements showed that the nanoparticles exhibited electrocatalytic activity towards the oxidation of methanol and hydroquinone oxidation, and the activity was found to increase with increasing ligand chain length.

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1. Introduction

Noble metal nanoparticles have been gaining extensive attention primarily because of their unique optical, electronic, and magnetic properties [1–4] and hence potential applications in diverse fields, such as catalysis [5–8], sensing [9–11], photonics [12,13], and biolabeling [14, 15]. In these studies, organic molecules (e.g., mercapto derivatives) are generally employed for the stabilization and functionalization of the nanoparticles [7,16–22], such that the nanoparticle materials properties may be readily manipulated by the chemical nature of the metal cores and the organic capping ligands [23,24]. More recent studies have shown that the nanoparticle chemical and physical properties can also be tuned by metal–ligand interfacial bonding interactions, in particular in the regulation of the dynamics of interparticle and intraparticle charge transfer [17,25–27], which may be exploited for a wide range of applications.

Of these, Pt nanoparticles represent a kind of important nanoparticles because of their high and effective catalytic performance in a number of chemical reactions. For instance, platinum nanoparticles have

been used extensively as the effective catalysts for the anodic oxidation of methanol, a critical process in direct methanol fuel cells (DMFC) [28–30], as well as for the hydroquinone/benzoquinone (HQ/BQ) redox reaction that plays an important role in the oxidative phosphorylation or photosynthesis [31,32] and electrochemical degradation of quinine-based environmental pollutants [33–35]. However, because of the high costs and scarce reserves in nature, it is imperative to minimize the amount of platinum used in these reactions [36] and meanwhile to enhance the catalytic activity beyond the state of the art. Within this context, Pt is generally dispersed as nanosized particles on a substrate support of a large surface area, where the catalytic performance may be readily manipulated by the particle size, shape, and metal–substrate interfacial interactions. More recently, metal–ligand interfacial bonds have emerged as a new variable that may tune the electronic properties of the metal cores and hence the electronic interactions with reaction intermediates [37–40].

Herein, Pt nanoparticles were synthesized by sodium borohydride reduction of Pt(II) precursors and functionalized with various acetylene derivatives. The structures of the Pt nanoparticles were characterized by a wide range of microscopic and spectroscopic measurements. The electrocatalytic activity of the nanoparticles in methanol oxidation and HQ/BQ redox reactions were studied and compared, and the results showed improved performance with increasing ligand chain length.

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2. Experimental

2.1. Chemicals

Potassium tetrachloroplatinate(II) (K_2PtCl_4 , Mascot, Tianjin, China), phenylacetylene (PA, 99%, Aladdin), 4-ethylphenylacetylene (EPA, 98%, J&K Scientific LTD.), 4-butylphenylacetylene (BPA, 98%, Energy chemicals), sodium borohydride ($NaBH_4$, 98%, Sinopharm Chemical Reagents Co., Ltd), hydrochloric acid (HCl, 36.0%–38.0%, Shanghai Lingfeng Chemical Reagents Co. Ltd.), tetra-*n*-octylammonium bromide (TOABr, 98%, Sinopharm Chemical Reagents Co., Ltd), sulfuric acid (H_2SO_4 , 98 wt.%, Shanghai Lingfeng Chemical Reagents Co. Ltd.), methanol (99.5%, Sinopharm Chemical Reagents Co., Ltd), hydroquinone (HQ, Sinopharm Chemical Reagents Co., Ltd), conductive carbon black (Ketjenblack, EC-600JD, Akzo Nobel), Nafion 520 (5 wt.%, Dupont), and a commercial Pt/C catalyst (20 wt.%, E-TEK) were used as received. All other organic solvents were purchased from commercial sources and used without further treatment. Water was supplied by a Milli-Q system (>18.0 M Ω cm, Millipore).

2.2. Synthesis of alkyne-capped Pt nanoparticles

The Pt nanoparticles were prepared by $NaBH_4$ reduction method, a procedure that has been used in previous work [17,38]. In a typical reaction, for example, approximately 41.5 mg of K_2PtCl_4 (0.1 mmol) was dissolved in 1 mL of HCl under heating. After cooling to room temperature, the red Pt(II) ions was transferred to 10 mL toluene with 0.3 mmol TOABr. The toluene phase was collected and immersed in an ice bath for at least 30 min, into which was then added 22 μ L of PA (28 μ L of EPA, or 35 μ L of BPA). The solution was under magnetic stirring for 30 min before 40 mg of $NaBH_4$ (10 fold excess equivalents) in 20 mL of water was added dropwise with a pipet. The color of the solution changed rapidly to dark brown, signifying the formation of platinum nanoparticles. The organic phase was collected and toluene was removed by rotary evaporation. The resulting sample was then washed several times with acetonitrile and ethanol to remove TOABr and excess ligands, affording purified nanoparticles that were denoted as PtPA, PtEPA, and PtBPA, respectively. Finally, the purified Pt nanoparticles were dissolved in dichloromethane (DCM), and the solution presents pale yellow color.

2.3. Sample characterization

The morphology and sizes of the nanoparticles were examined by transmission electron microscopic measurements (TEM, JEOL, JEM-200CX) at an acceleration voltage of 200 kV. The samples were prepared by placing a drop of the particle solution (~1 mg/mL in DCM) onto a standard carbon-coated copper grid (200 mesh). FTIR measurements were performed with an FTIR spectrometer (Nicolet iS5, spectral resolution 0.8 cm^{-1}) within the wave number range of 500 to 4000 cm^{-1} , where the samples were prepared by dropcasting the nanoparticle DCM solutions onto a ZnSe disk. UV–vis spectra were collected on a Shimadzu UV3600 spectrometer with a resolution of 1 nm, using a 1 cm quartz cuvette. Fluorescence characteristics were examined with an Agilent Cary Eclipse fluorescence spectrophotometer. X-ray photoelectron (XPS) spectra were obtained with a ULVAC-PHI 5000 Versaprobe using a monochromated Al K_{α} X-ray operated at 350 W and 5×10^{-7} Pa. Silicon wafers were washed and ultrasonicated with ethanol and then used as substrates.

Electrochemical measurements were carried out in a conventional three-electrode cell with a CHI 660D electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China), with a Pt wire as the counter electrode (CHI 150) and a saturated calomel electrode (SCE, CHI 115) as the reference electrode at room temperature. The working electrode was a glassy carbon disk electrode (GCD, diameter 3.00 mm, CHI 104) for methanol and hydroquinone oxidation. The

GCD electrodes were polished with 1.0, 0.3 and 0.05 μ m Al_2O_3 slurries and rinsed thoroughly with ethanol and water. A calculated amount of the Pt nanoparticles prepared above was mixed with conductive carbon black and Nafion (Pt:C = 1:4 w/w, Nafion 0.05%), to form a well dispersed suspension. A calculated volume of the mixed suspension was loaded onto the surface of the freshly polished glassy carbon electrode. Once the suspension was dried, a dilute ethanol solution of Nafion (0.1 wt.%, 2 μ L) was dropcast onto it. Finally, the electrode was washed with pure water and ethanol, and then dried in N_2 . A commercial Pt/C catalyst was also deposited onto the GCD electrode in the similar manner, and used as a benchmark to assess the electrocatalytic activity of these acetylene-capped Pt nanoparticles. The mass loading of Pt was 10 μ g in all cases. The current densities were calculated on the basis of the electrochemical surface area (ECSA) of the Pt electrode.

3. Results and discussion

The mean diameter and size distribution of the synthesized Pt nanoparticles structures were characterized by TEM measurements. Fig. 1 depicted the representative TEM micrographs of PtPA (a), PtEPA (c) and PtBPA (d) nanoparticles. It can be seen that these nanoparticles were well dispersed and roughly in spherical shape, indicating the effective protection of the nanoparticles by these acetylene ligands. Furthermore, the nanoparticles exhibited well-defined crystalline lattice fringes with a spacing of 0.229 nm (Fig. 1d), which was consistent with the *d*-spacing of the (111) planes of *fcc* Pt [6,7]. Fig. 1b showed the core size histogram, where most of the PtPA nanoparticles fell within the range of 1.5 to 3.5 nm, and statistical analysis based on >400 nanoparticles showed that the nanoparticle average core diameter was very close, 2.22 ± 0.83 nm for PtPA, 2.09 ± 0.91 nm for PtEPA, and 2.18 ± 0.77 nm for PtBPA.

The structures of the capping ligands on these nanoparticles were then characterized by FTIR measurements. Fig. 2 showed the FTIR spectra of PtPA (red curve), PtEPA (blue curve) and PtBPA (magenta curve) nanoparticles, along with those of PA (black curve), EPA (green curve) and BPA (cyan curve) monomers. One can see that the PA, EPA and BPA monomers all exhibited a strong and well-defined vibrational band at about 3300 cm^{-1} due to the $\equiv C-H$ stretch; yet this band disappeared in the nanoparticle samples, indicating the effective breakage of the $\equiv C-H$ bond when the ligands self-assembled onto the nanoparticle surface. Concurrently, a broad and weak band appeared at about 2066 cm^{-1} for the three Pt nanoparticles, in contrast to the sharp peak at 2110 cm^{-1} observed for the ligand monomers due to the $C\equiv C$ stretch. Such a red-shift has been observed previously and ascribed to effective charge delocalization due to the conjugated bonding interactions between the acetylene moieties and the Pt metal cores [38, 41].

In addition, the PA monomers exhibited multiple vibrational bands within the range of 3019 to 3086 cm^{-1} due to the aromatic $C-H$ stretches; in comparison, these $C-H$ vibrational stretches red-shifted markedly with the PtPA nanoparticles to the region between 2967 and 2840 cm^{-1} , again, indicating the strong electronic interactions between aromatic π electrons and Pt cores [27]. Similar red shifts can also be observed with PtEPA and PtBPA nanoparticles, as compared to EPA and BPA monomers. Furthermore, one may see a slight red-shift in these Pt nanoparticles (<10 cm^{-1}) of the aromatic ring skeleton $C=C$ vibrations, also because of intraparticle charge delocalization among the particle-bound acetylene groups, whereas the overtone and/or combination [7] of aromatic ring skeleton deformations at about 1600, 1500, and 1450 cm^{-1} [42,43] can be identified for both the monomeric ligands and the Pt nanoparticles.

The structures of the Pt nanoparticles were further analyzed by XPS measurement. Fig. 3 depicted the representative XPS spectra of Pt 4f electrons of (a) PtPA, (b) PtEPA, and (c) PtBPA nanoparticles. The spectra of all Pt 4f were composed of two well-defined peaks, ones were at the binding energies of about 71 eV (71.1 eV for PtPA, 71.2 eV for

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