



## Regular article

## Tunable porosity in bimetallic core-shell structured palladium-platinum nanoparticles for electrocatalysts

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## ABSTRACT

A porous bimetallic palladium-platinum (Pd@Pt) nanoparticles (NPs) are prepared by using two different surfactants, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (Pluronic® F-127) and polyethylene glycol hexadecyl ether (Brij® 58). Using the Pluronic® F-127 results in a more porous structure and a larger electrochemically active surface area, even though the sizes of the Pd@Pt NPs prepared using the two different surfactants are similar, approximately 100 nm. It is revealed that the Pluronic® F-127 surfactant can introduce more electrochemically active sites into the Pd@Pt NPs nanoparticles, results in enhanced bisphenol A detection with better sensitivity.

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Noble metal nanoparticles (NPs) have attracted much attention in various fields, such as catalysts, sensors, biomedical applications, etc. [1–4]. In recent years, they have been reported many studies on bi- and tri-metallic nanoarchitectures [5–7]. In particular, palladium (Pd) based NPs are highly attractive as an alternative to platinum (Pt) NPs in terms of cost-effectiveness [8,9]. By combining them with carbons and other metals, the electrocatalytic properties of the Pd NPs can be further maximized [10,11].

Porous metals have been developed by various soft-template methods including lyotropic liquid crystals [12,13]. In general, structure-directing agents with low- and high-molecular-weight amphiphilic molecules can be used for preparing porous noble-metal-based NPs [14]. Amphiphilic surfactants and block copolymers (*i.e.*, Brij 58® (Brij 58), Pluronic® F-127 (F-127), and Pluronic® P-123 (P-123)) have been mostly utilized to prepare nanoporous metals. [14,15]. Brij 58 has hydrophobic alkyl chain and hydrophilic PEO block, while F-127 is composed of poly(ethylene oxide)-poly(propylene

oxide)-poly(ethylene oxide) (PEO-PPO-PEO), where the PEO is hydrophilic and the PPO consists of hydrophobic blocks. In the case of F-127, the hydrophilic units of the amphiphilic molecules accommodate the metal atoms during the formation of the porous structured NPs.

Porous noble metals have widely used as electrode for detecting glucose [16], phenolic compounds [17], and others biological important organics [18]. Recently, bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl) propane) is known to be produced by the polycarbonate plastics and epoxy resin, especially from various products (*i.e.* food containers and drink packaging) [8,17]. Unfortunately, the BPA can lead to some diseases including cancers and birth defects in our daily lives. Of the various methods for detecting BPA, electrochemical detection methods have been widely employed due to their advantages, such as; cost effective instruments, short analysis time, simplicity, and great sensitivity.

With research background, the main target of the present work is to discuss the effect of structure-directing agents on the resulting porous architectures. Here we prepared two types of porous Pd@Pt NPs with different surfactants (Brij 58 and F-127) using a sonochemical method under the same conditions except structure-directing agents. To confirm the electrochemically active surface area (ECSA), composition, and morphology, transmission electron microscopy (TEM), wide-angle powder X-ray diffraction (XRD), and cyclic voltammetry (CV) were

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carried out for the two different Pd@Pt NPs samples. Finally, the BPA sensor performances were compared and evaluated toward practical applications.

With regard to reagents and materials, potassium tetrachloroplatinate (II) ( $K_2PtCl_4$ ), sodium tetrachloropalladate(II) ( $Na_2PdCl_4$ ), chloroplatinic acid hexahydrate ( $H_2PtCl_6$ ), Pluronic® F-127, polyethylene glycol hexadecyl ether (Brij 58®,  $HO(CH_2CH_2O)_{20}C_{16}H_{33}$ ), hydrochloric acid (HCl), bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl) propane), and L-ascorbic acid (AA) were obtained from Sigma-Aldrich Co. USA. A 0.1 M phosphate buffer solution (PBS) was prepared using 0.1 M disodium hydrogen phosphate and 0.1 M sodium dihydrogen phosphate (Sigma-Aldrich Co. USA).

For synthesis of porous bimetallic Pd@Pt NPs, 0.6 ml of  $Na_2PdCl_4$  (20 mM), 1.2 ml of  $K_2PtCl_4$  (20 mM), 1.8 ml of  $H_2PtCl_6$  (20 mM), and 60  $\mu$ l of HCl (6 M) were thoroughly mixed in two vials. Brij 58® (60 mg) and Pluronic® F-127 (60 mg) was then added into the reaction vials, respectively. Each surfactant was completely dissolved, and 3.0 ml AA solution (0.1 M) was added. Then, the mixed vials were sonicated in a water bath for 4 h at 40 °C. The final products were collected by centrifugation at 12,000 rpm for 10 min and were washed with ethanol and water.

In order to prepare Pd@Pt NPs electrode for bisphenol A detection, two kinds of porous Pd@Pt NPs (4  $\mu$ g) with different Brij 58 and F-127 surfactants were dropped on screen-printed carbon electrodes, respectively [17]. As-prepared electrodes were activated by potential cycling from  $-0.6$  to  $+1.2$  V in 0.5 M sulfuric acid (scan rate:  $0.1$  V  $s^{-1}$ , cycles: 30). Cyclic voltammograms (CVs) were recorded using a potentiostat/galvanostat (Ivium, Netherlands). The morphology and structure of the Pd@Pt NPs (prepared with Brij 58 and F-127) were observed using transmission electron microscopy (TEM; H-7600, HITACHI, Japan). Wide-angle powder XRD patterns were obtained by on a GBC MMA XRD (scan rate of  $2^\circ \cdot min^{-1}$ ).

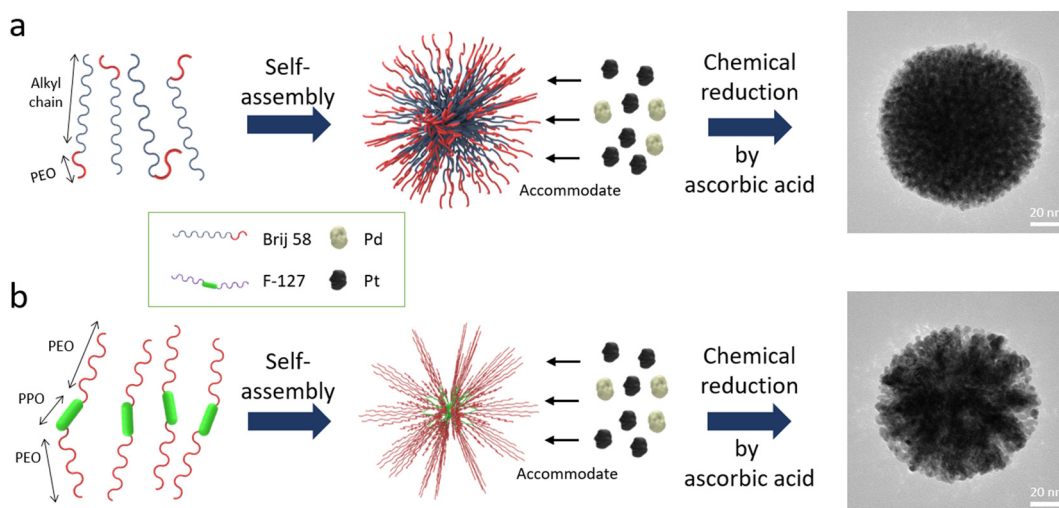
To synthesise the two different kinds of porous Pd@Pt NPs,  $Na_2PdCl_4$ ,  $H_2PtCl_6$ , and  $K_2PtCl_4$ , with either Brij 58 or F-127, were reacted using the sonochemical method in aqueous solution (Fig. 1). The chemical formulae of the used surfactants are shown in Fig. S1. The Pd (20 mM) and Pt (20 mM) precursors and the HCl (6 M) solution were thoroughly mixed, and then Brij 58 or F-127 was added into each reaction solution. In this step, the surfactants formed self-assembled micelles, where the hydrophilic heads were exposed to the aqueous face and the hydrophobic tails faced the micelle centre. Ascorbic acid (AA) was added as a reducing agent to each prepared solution under ultrasonication [19]. The final products were collected, followed by washing with deionized (DI) water and ethanol to thoroughly remove the remaining reactants and

surfactant. Before synthesising the final products, we initially examined the effect of the ratio of two different Pt precursors ( $K_2PtCl_4$  and  $H_2PtCl_6$ ), to which the final particle size can be attributed.

More interestingly, the standard reduction potential of Pd ( $PdCl_4 \rightarrow Pd$ :  $E^0 = +0.59$  V) is lower than for Pt ( $[PtCl_6]^{2-} \rightarrow [PtCl_4]^{2-}$ :  $E^0 = +0.68$  V and  $[PtCl_4]^{2-} \rightarrow Pt$ :  $E^0 = +0.76$  V). In the general process, it is thus expected that the reduction of Pt species is easier than for Pd species, resulting in the Pt@Pd structure. Our bimetallic NPs did not follow the general process, however. This is probably because our reduction kinetics related to the nuclei and the coordination effects are strongly governed by the specific experimental condition [20,21]. As results, we obtained the core-shell Pd@Pt structure in this study.

The shape and size of Pd@Pt NPs were characterized by SEM and TEM, as can be seen in Fig. 2. The average diameter of two different Pd@Pt NPs was estimated to be around 100 nm (Fig. 2a, b and d, e). It is to be noted that Pd@Pt NPs prepared with F-127 have a relatively narrow size distribution. As can be seen in Fig. S2, the morphology of Pd@Pt NPs prepared with Brij 58 is denser than for the Pd@Pt NPs prepared using F-127. The selected area diffraction (SAED) patterns of both Pd@Pt NPs samples indicate a face-centred cubic (fcc) crystal structure with concentric rings from the (111), (200), (220), and (222) planes, respectively (Fig. S2c and f). Fig. S3 shows the XRD patterns of the Pd@Pt NPs prepared using Brij 58 and F-127, where the patterns also indicate the fcc structure. To further confirm the structures of the Pd@Pt NPs samples, element mappings were performed on the two kinds of Pd@Pt NPs that were synthesised using the different surfactants, Brij 58 (Fig. 3a) and F-127 (Fig. 3b). As can be seen in Fig. 3, the Pd (red) mainly exists in the core of the NPs, while the Pt (green) is located on the outer shell. This can be supported by the line scan element mapping (Fig. 3). As a result, the Pd@Pt NPs prepared using Brij 58 are much denser than Pd@Pt NPs prepared using F-127. We thus expected that the Pd@Pt NPs prepared with F-127 would have a relatively large ECSA compared to Pd@Pt NPs prepared using Brij 58. Hence, we evaluated the ECSA values of the Pd@Pt NPs prepared with the two different surfactants, respectively.

For this purpose, CVs were recorded for Pd@Pt NPs prepared using the different surfactants, Brij 58 (red dotted line) and F-127 (blue solid line), in 0.5 M sulfuric acid ( $H_2SO_4$ ) solution from  $-0.6$  V to  $+1.2$  V (scan rate:  $0.05$  V  $s^{-1}$ ) (Fig. 4a). The ECSAs from the H atom adsorption region are 11.26 and 16.37  $m^2 g_{Pt}^{-1}$  for the NPs prepared using Brij 58 and F-127, respectively (Fig. S4). The ECSA for the F-127 Pd@Pt NPs is larger than for those prepared using Brij 58. This indicates that electrochemically active sites could be tuned by surfactants having different chain lengths and structures.



**Fig. 1.** Illustrations of the synthesis of porous bimetallic Pd@Pt nanoparticles using two different surfactants: (a) Brij 58 (polyethylene glycol hexadecyl ether) and (b) F-127 (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)).

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