Electronic Supplementary Information

Direct synthesis of H_2O_2 catalyzed by Pd nanoparticles encapsulated in multi-layered polyelectrolyte nanoreactors on a charged sphere

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Experimental Section

Materials

Poly(allylamine hydrochloride) (PAH, Mw 56,000), poly(diallyldimethylammonium chloride) (PDDA, Mw <100,000, 35wt% in H_2O), poly(ethyleneimine) (PEI, Mw 25,000), poly (4-styrenesulfonate, sodium salt) (PSS, Mw 70,000), poly(acrylic acid) (PAA, Mw 100,000, 35wt% in H_2O), potassium tetrachloropalladate (K_2PdCl_4), palladium nitrate ($Pd(NO_3)_2$), cesium nitrate ($CsNO_3$), and heteropolyacid ($H_3PW_{12}O_{40}$) were purchased from Aldrich and used without further purification. Four types of resins such as K2621 (SO_3^-), MP500 (NR_3Cl^-), VPOC1065 (NH_2), K2635 (Pd^{2+}/K2621) were kindly provided by Lanxess. Detailed physical properties of resins are summarized in Table S1.

Preparation of polyelectrolytes, metal precursor, and reducing agent solutions

All the polyelectrolytes were prepared as 10 mM solutions (based on the repeat-unit molecular weight) in deionized water. The polyelectrolytes solutions were adjusted to pH 9 with 0.1 M HCl or 0.1 M NaOH except for PEI (pH 5). 1 mM of aqueous palladium precursor solution (K_2PdCl_4) was adjusted to pH 3 and stored away from light.

Preparation of catalysts

Representative construction of polyelectrolyte multilayers (PEMs) on anionic macro resin (K2621, Lanxess) was carried out by alternative adsorption of PAH and PSS. Before use, 100g of resin was washed three times with water. The rein was immersed in 1500 ml of PAH solution (10 mM, pH 9) and stirred for 20 min (**G1**). The decanting the residual solution, **G1** was thoroughly washed three times with 1500 ml of water to remove excess PAH. After then,

deposition of PSS (10 mM, pH 9) on **G1** was carried out with a similar manner (**G2**). This procedure was repeated until 7 multilayers were formed on resin (**G7**). For metal complexation with PEMs, the resulting **G7** was added in 1500 ml of 1 mM K_2PdCl_4 solution (pH 3) and stirred for 30 min. After thorough washing, subsequent reduction of Pd metal ions was performed by H_2 (200ml/min) for 2 h under vigorous stirring. The resulting catalyst was washed three times with water. During whole catalyst preparation process, pH variation was monitored using pH meter (S40 Sevenmulti pH meter, Mettler Toledo).

Stacking of PEMs on cationic macro resin (MP500 or VPOC1065) was performed simply by changing the order of polyelectrolyte depositions. For example, PSS and PAH were alternatively adsorbed on MP500 until 6 multilayers were formed (**G6**). After then, sequential metal complexation and reduction yields **PEM(Pd^0)/MP500** or **PEM(Pd^0)/VPOC1065**.

Palladium-exchanged insoluble heteropolyacid ($Pd_{0.15}Cs_{2.5}H_{0.2}PW_{12}O_{40}$) catalyst was prepared by an ion-exchange method [S. Park, S. H. Lee, S. H. Song, D. R. Park, S.-H. Baeck, T. J. Kim, Y.-M. Chung, S.-H. Oh and I. K. Song, *Catal. Commun.,* 2009, **10,** 391.].

Characterization

High-resolution transmission electron microscopy (HRTEM) was carried out using a JEOL JEM-3000F transmission electron microscope equipped with an EDS (energy dispersive spectroscopy) detector (Oxford Co.). The specimens were prepared by cryogenic microtoming of the catalyst imbedded in epoxy resin. Binding energies of Pd ions in the catalyst were measured with XPS (Thermo VG Scientific ESCA 2000 spectrometer). Data were acquired employing a pass energy of 40 eV, a step increment of 0.1 eV, and an Al anode. XPS peak positions were referenced to the carbon (1 s) peak at 284.6 eV.

Activity test

Catalytic activity test was carried out in an upflow fixed bed reactor (10 mm ID x 300 mm L) equipped with cooling jacket. In a typical run, 20 cc of catalyst loaded in a reactor was rinsed with pure methanol for 3 hr at 30^{o}C. After the pressure was raised to 50 Bar with nitrogen, methanol feed-in was stopped and a liquid feed consisting of methanol admixed with 1.47 x 10^{-4} M HBr was fed to the reactor at total rate of 15 ml/hr. Reaction was started with changing nitrogen to gas mixture feed containing 3% hydrogen, 47% oxygen, 50% nitrogen. The gas hourly space velocity (GHSV) of a reaction was 2400 h^{-1} and gas to liquid ratio is 3200. During a reaction, liquid product and off-gas were periodically withdrawn from the reactor for analysis. H_2O_2 content was measured by titration with Cerium(IV) sulfate standard solution (0.25 N in 2~3 N sulfuric acid) and Ferroin indicator (0.1wt% solution in water). The off-gas was analyzed by gas chromatography for hydrogen concentration.

Table S1 Physical properties of various resins

Resin	K2621	MP500	VPOC1065
Functional group	SO_3^-	NR_3Cl^-	NH_2
Total capacity (min. eq/l)	1.4-1.5	1.1	2.2
Bead size (mm)	0.4-1.3	0.62 (+/- 0.05)	0.315-1.25

Fig. S1 pH variation during polyelectrolyte multilayer stacking, meal complexation and subsequent reduction.

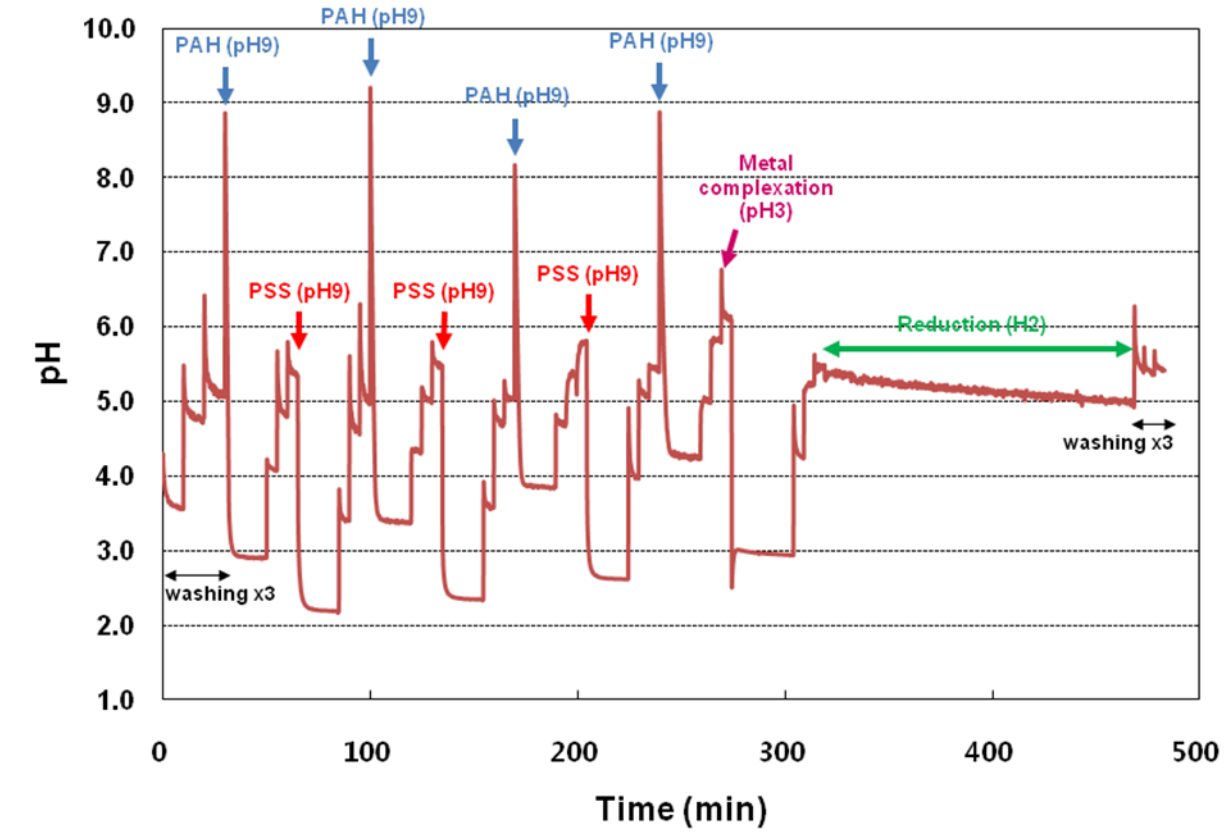

Fig. S2 XPS spectra of PEM-encapsulated Pd^0 on sulfonated resin (a) and Pd^{2+} ion doped sulfonated resin (b).