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SUPPORTING INFORMATION

Hydrolysis-induced immobilization of Pt(acac)₂ on polyimide-based carbon nanofiber mat and formation of Pt nanoparticles

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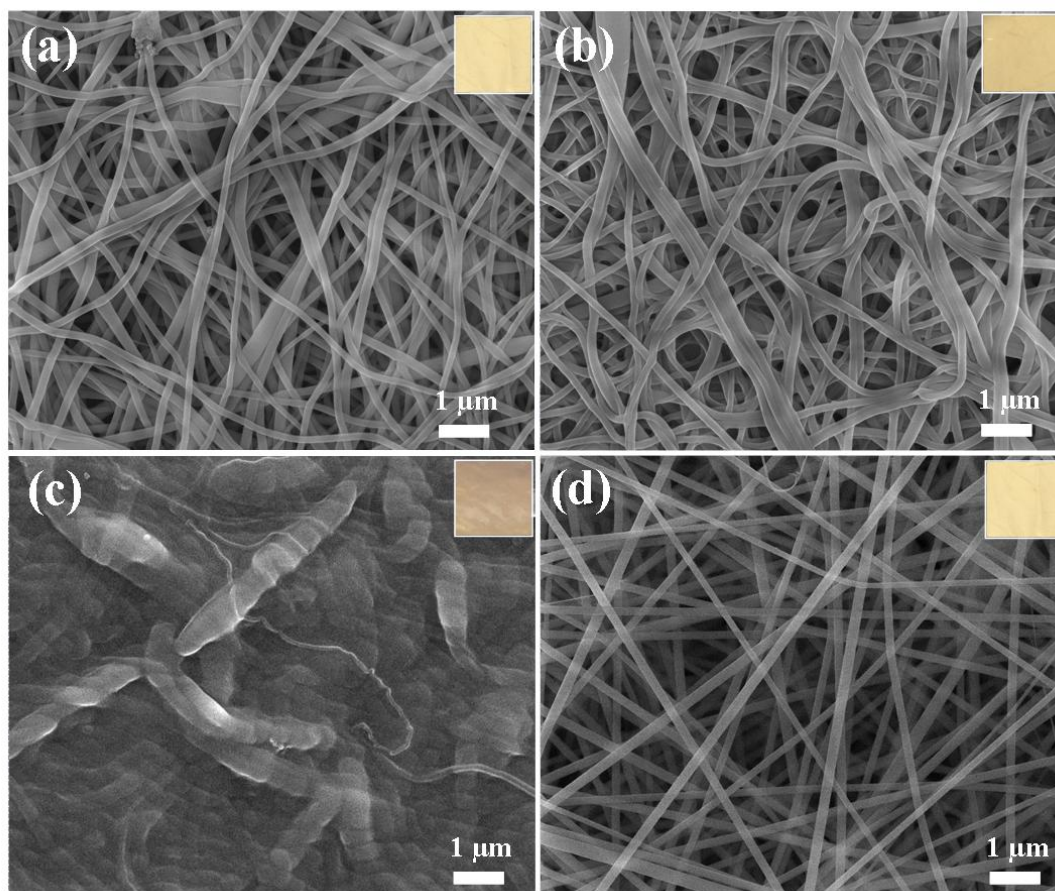


Fig. S1 SEM of the PI nanofibers hydrolyzed at different KOH concentrations for 30 minutes at 50 °C. KOH activity to PI nanofibers at 50 °C was much stronger than that at room temperature. (a) With 0.05 M of KOH solution, the PI nanofiber was partially melted but the fiber form was still retained. (b) With 0.1 M of KOH solution, the PI nanofibers were flattened and the porosity of the mat was diminished due to the sticking of nanofibers to each other. (c) With 0.2 M of KOH solution, the PI nanofibers were deformed severely and melted. (d) With 0.1M of KOH solution for 2 minutes at RT, the PI nanofibers were intact.

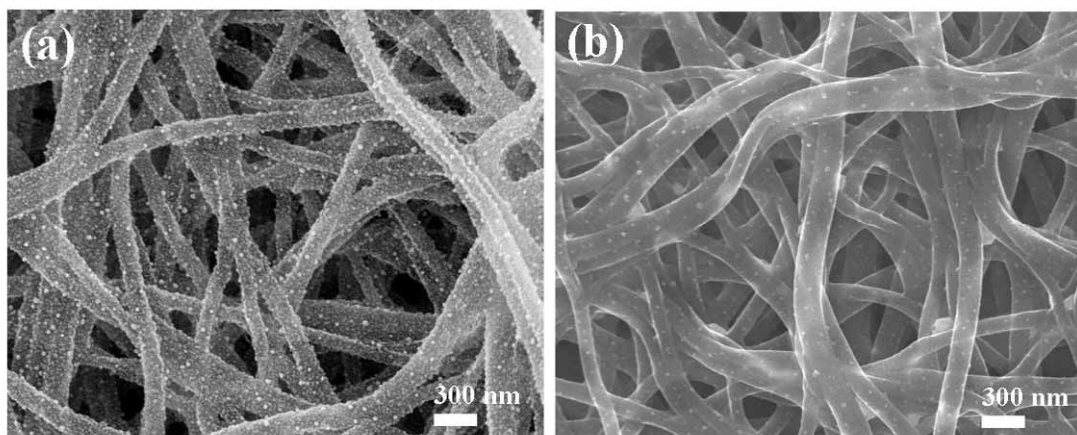


Fig. S2 After hydrolysis with KOH concentration of 0.2 M at room temperature for 30 minutes, the sample was left in air for several days. Pt solution was dropped onto the sample. Large sizes of Pt particles were formed with large separation distance between particles as shown in SEM image (a) high Pt concentration, and (b) low Pt concentration.

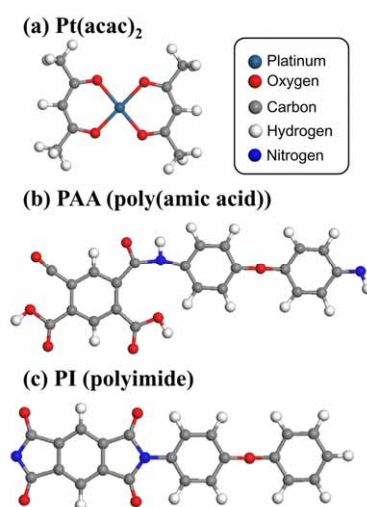


Fig. S3 Molecule structure of (a) $\text{Pt}(\text{acac})_2$, (b) PAA and (c) PI. Top views are shown here to make clear distinction in the geometry.

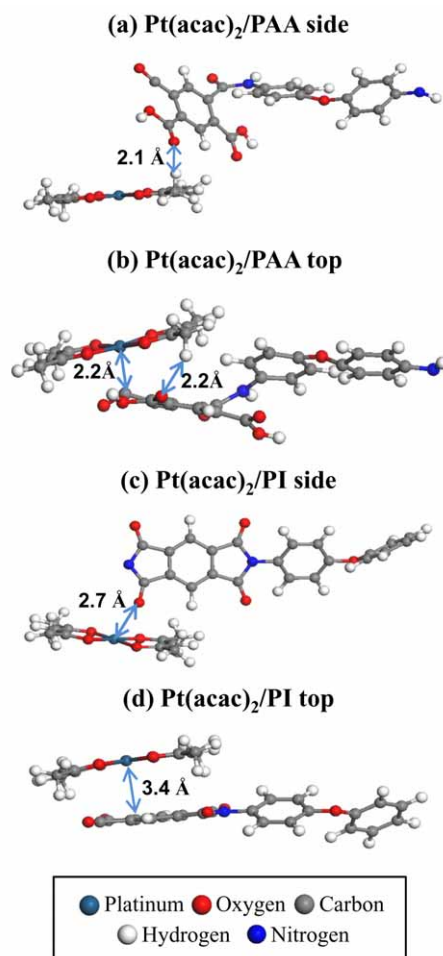


Fig. S4 The model of the absorption (a) Pt(acac)₂ molecule on PAA side, (b) Pt(acac)₂ molecule on PAA top, and (c) Pt(acac)₂ molecule on PI side, and (d) Pt(acac)₂ molecule on PI top.

Table S1. Adsorption energy and the closest separation distance between Pt(acac)₂ and PAA/PI, and the amount of charge transfer from Pt(acac)₂ to PAA or PI.

Model	Pt(acac) ₂ /PAA-side	Pt(acac) ₂ /PAA-top	Pt(acac) ₂ /PI-side	Pt(acac) ₂ /PI-top
Interaction site	acac ↔ O	Pt ↔ O/pentagon	Pt ↔ O	Pt ↔ pentagon top
Adsorption energy (eV)	-3.58	-4.35	-2.48	-3.19
Closest separation distance (Å)	2.1	2.2	2.7	3.4
Charge transfer (e)	0.05	0.04	0.38	0.39

Pt-O bonds were formed when Pt(acac)₂ was adsorbed on the side of PI (Fig. S4c), and Pt-pentagon interaction was involved in adsorption on top of PI (Fig. 4d), which was opposite the PAA adsorption. In spite of significant charge transfer of ~0.4 e from Pt(acac)₂ to PI for both cases, the adsorption was still dominated by the π-stacking interaction. Regardless of the type of adsorptions, the adsorption of Pt(acac)₂ is stronger on PAA than on PI. This is attributed to electric dipole moments originating from the carboxyl (-COOH) groups and the shorter distances between the interaction sites in PAA than those in PI. For the case of PI, the transferred electrons become delocalized at the PI nanofiber and do not contribute to the electrostatic interaction significantly. On the other

hand, relatively small amount of PtO bonds are formed in the case of PI adsorption. The adsorption energy of -3.19 eV is not strong enough to survive in the carbonization process. This explains why the loading of Pt particles by impregnating Pt(acac)₂ on PI surface was very difficult to achieve except under extreme supercritical conditions (15).