Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2016

Supporting Information

Controllable Fabrication of N and B Co-Doped Carbon Shell on the Surface of TiO_2 as a Support for Boosting the Electrochemical Performances

Ying Chang, Conghui Yuan, Yuntong Li, Cheng Liu, Tong Wu, Birong Zeng, Yiting Xu, and Lizong Dai *

Fujian Provincial Key Laboratory of Fire Retardant Materials, College of Materials, Xiamen University, Xiamen, 361005, China.
E-mail：*lzdai@xmu.edu.cn

Synthesis of TAC and TAB

***Synthesis of TAC*:** Tris(4-aminophenyl)amine (1.0 mmol, 0.29 g) and a catalytic amount of concentrated HCl solution were dissolved in a solution containing 16.0 mL of anhydrous ethanol and 8.0 mL of dichloromethane. To this solution, 3,4-dihydroxybenzaldehyde (3.1 mmol, 0.428 g) in 6.0 mL of anhydrous ethanol solution was added. The reaction mixture was stirred at room temperature for 12 h under an Ar atmosphere and protected from light. Then, the reaction mixture was concentrated into ~10.0 mL. The resultant orange precipitate was collected by filtration, washed with cold ethanol and dried in vacuum. Yield: 83 %. ^{1}H NMR (400 MHz, DMSO-D_6) δ (ppm): 9.70 (s, 3H), 9.55 (s, 3H), 8.61 (s, 3H), 7.39 (d, 3H), 7.21 (d, 6H), 7.16 (d, 3H), 7.05 (d, 6h), 6.83 (d, 3H). ^{13}C NMR (400 MHz, DMSO-D_6): 159.23, 149.51, 147.11, 146.09, 145.34, 124.67, 122.80, 122.67, 122.36, 115.93, 114.54. ESI/MS m/z 649.78 $[M-H]^-$ (expected m/z= 649.69).

Synthesis of TAB: To a solution containing 16.0 mL of anhydrous ethanol, 8.0 mL of dichloromethane, Tris(4-aminophenyl)amine (1.0 mmol, 0.29 g) and a catalytic amount of concentrated HCl solution, was added 6.0 mL anhydrous ethanol solution of 4-formylphenylboronic acid (3.1 mmol, 0.464 g). After stirring at room temperature for 12 h, the reaction mixture was concentrated into ~5.0 mL. Then dichloromethane (25.0 mL) was added into the solution slowly at 0 ^{o}C. The resultant

yellow precipitate was collected by filtration, washed with a cold solvent containing both dichloromethane and ethanol (volume ratio: 5:1) and dried in vacuum. Yield: 81 %. ^{1}H NMR (400 MHz, DMSO-D_6) δ (ppm): 8.68 (s, 3H), 8.19 (s, 6H), 7.95-7.87 (d, 6H; d, 6H), 7.33 (d, 6H), 7.11 (d, 6H). ^{13}C NMR (400 MHz, DMSO-D_6): 159.71, 146.64, 145.88, 138.01, 134.87, 134.69, 127.89, 124.79, 123.03. ESI/MS m/z 745.32 $[M+59]^-$ (expected m/z= 745.15).

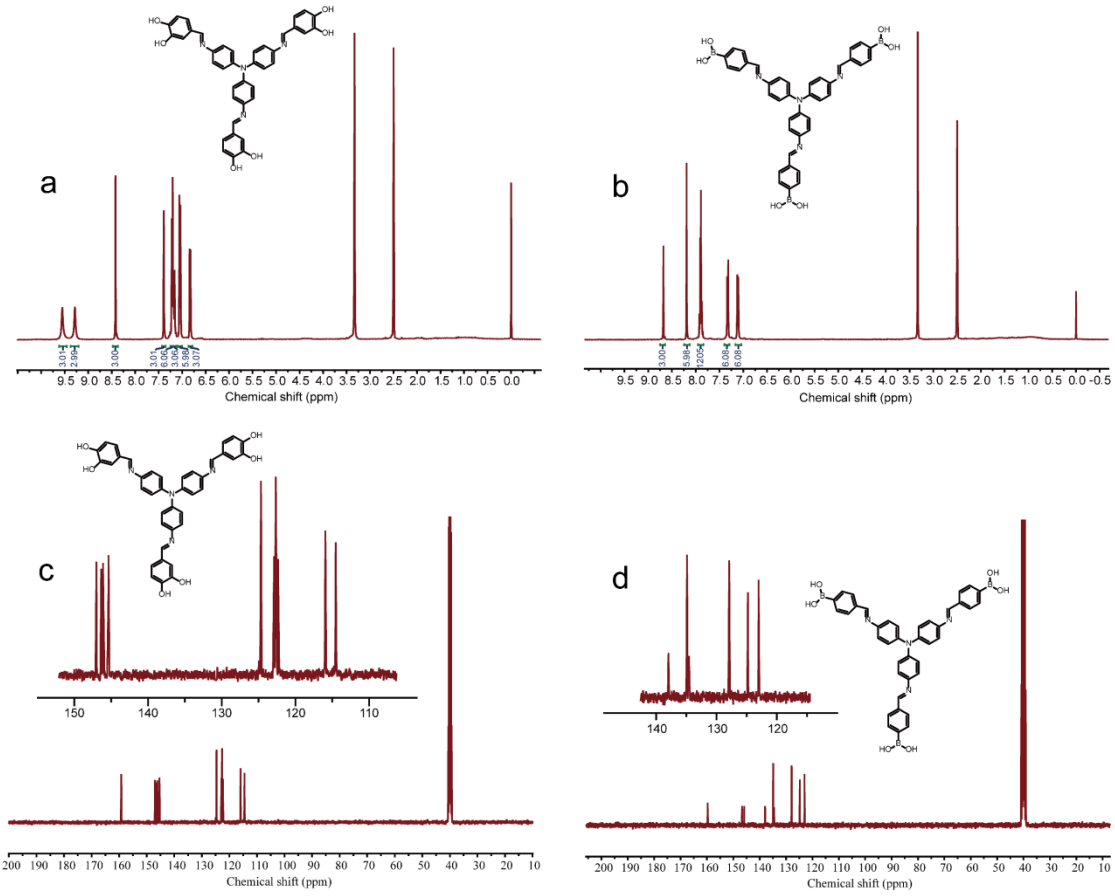

Fig. S1 ^{1}H NMR spectra of (a) TAC and (b) TAB, ^{13}C NMR spectra of (c) TAC and (d) TAB, solvent: DMSO-D_6.

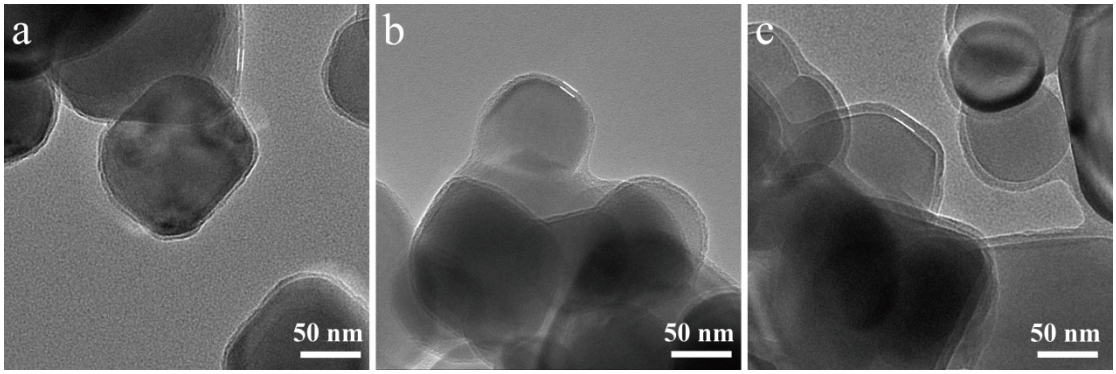

Fig. S2 TEM images of (a) TiO_2@polymer-1, (b) TiO_2@polymer-2 and (c) TiO_2@polymer-3 nanoparticles.

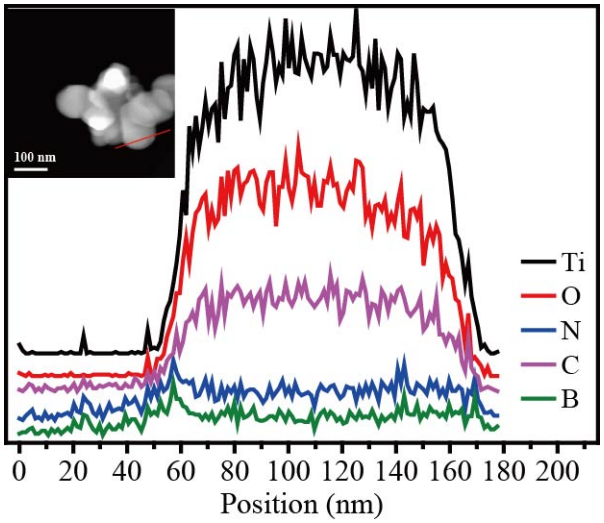

Fig. S3 The line scanning analyses of C, B, N, Ti and O elements on TiO_2@CNB-2 support. The inset is a HADDF-STEM image of TiO_2@CNB-2 support.

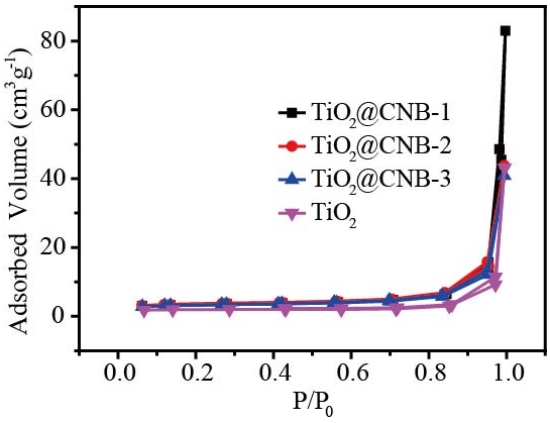

Fig. S4 N_2 adsorption and desorption isotherms of TiO_2@CNB-1, TiO_2@CNB-2, TiO_2@CNB-3 and TiO_2.

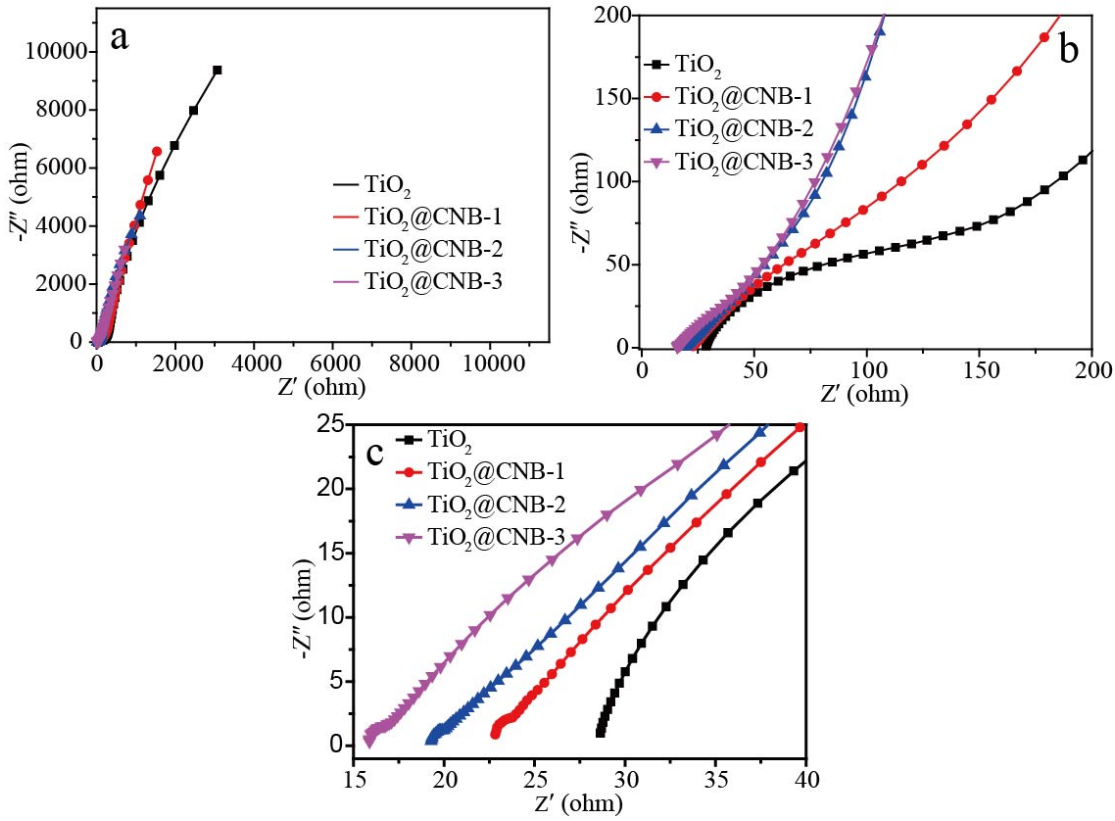

Fig. S5 Overview Nyquist plots of TiO_2, TiO_2@CNB-1, TiO_2@CNB-2 and TiO_2@CNB-3 using an amplitude of 5 mV at a frequency range from 100 KHz to 0.1 Hz (a); (b) and (c) are the magnified version of (a).

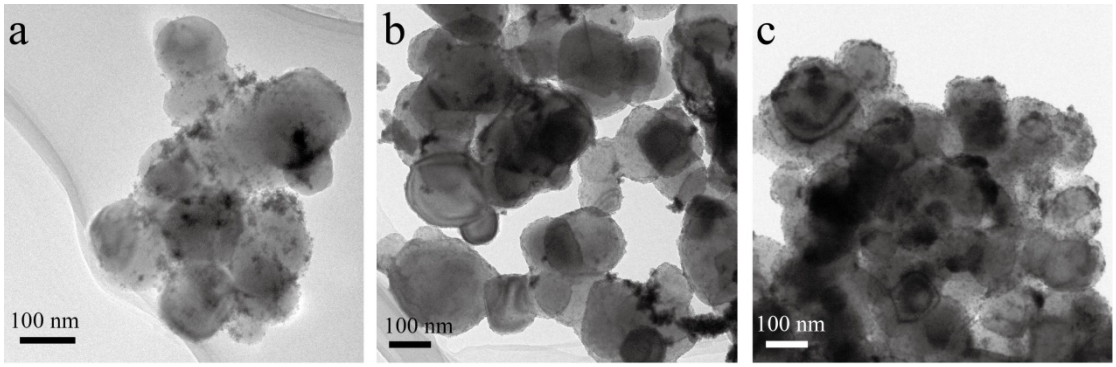

Fig. S6 TEM images of Pt supported TiO_2@CNB catalysts with various shell thickness: (a) Pt/TiO_2@CNB-1, (b) Pt/TiO_2@CNB-2 and (c) Pt/TiO_2@CNB-3 catalysts.

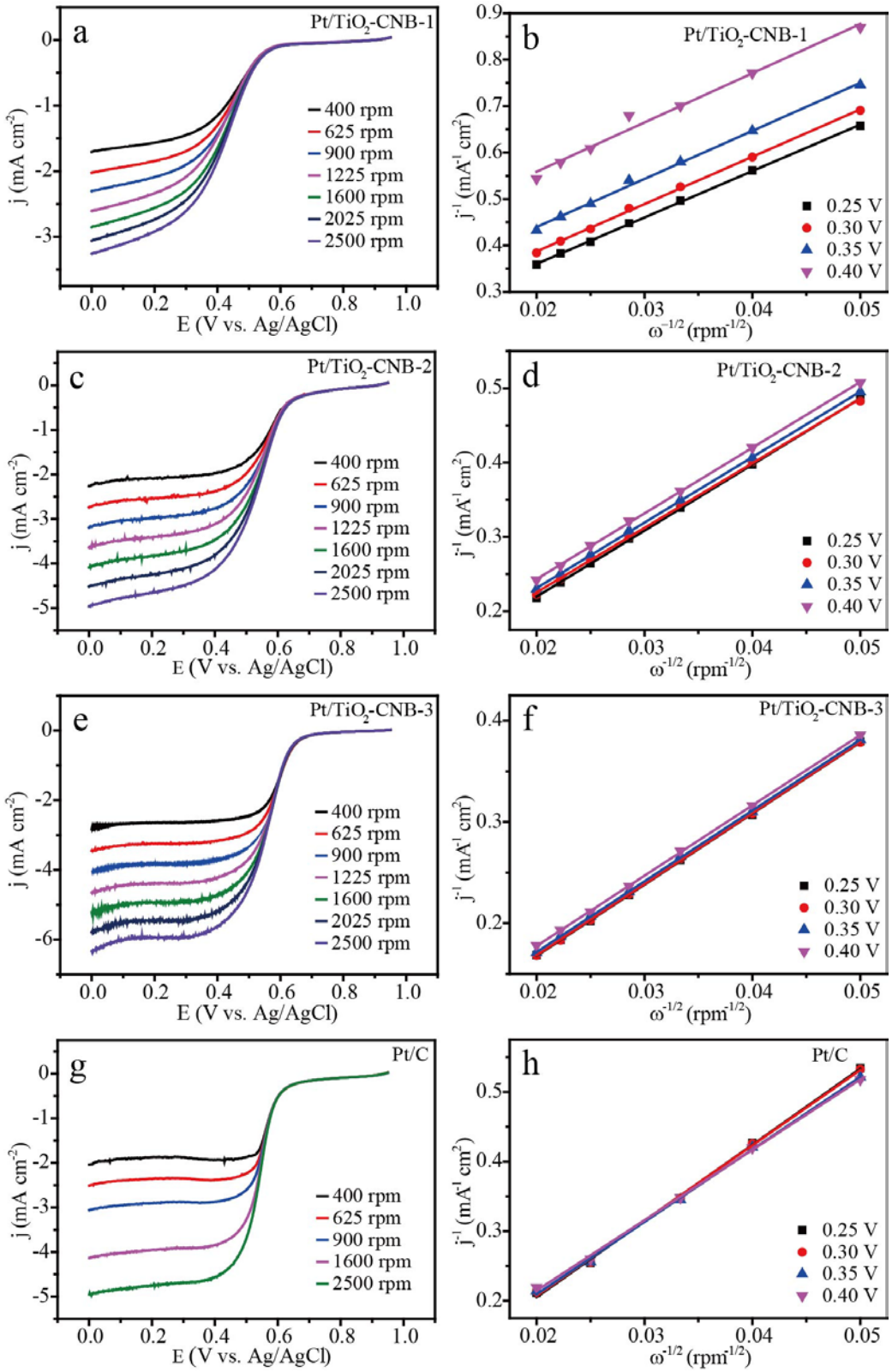

Fig. S7 LSV curves of (a) Pt/TiO_2@CNB-1, (c) Pt/TiO_2@CNB-2, (e) Pt/TiO_2@CNB-3 and (g) Pt/C at various rotation speeds. (b, d, f and h) the corresponding K-L plots at different potentials.

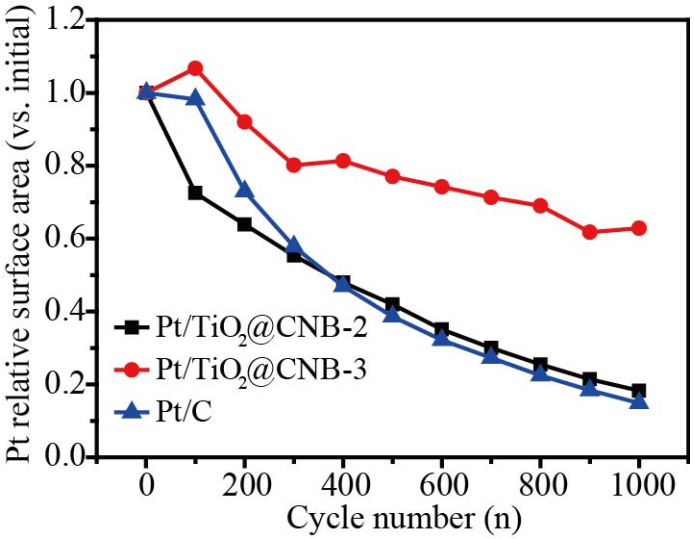

Fig. S8 Changes of ESA for Pt/TiO_2@CNB-2, Pt/TiO_2@CNB-3 and Pt/C catalysts with the increase of cycle number.

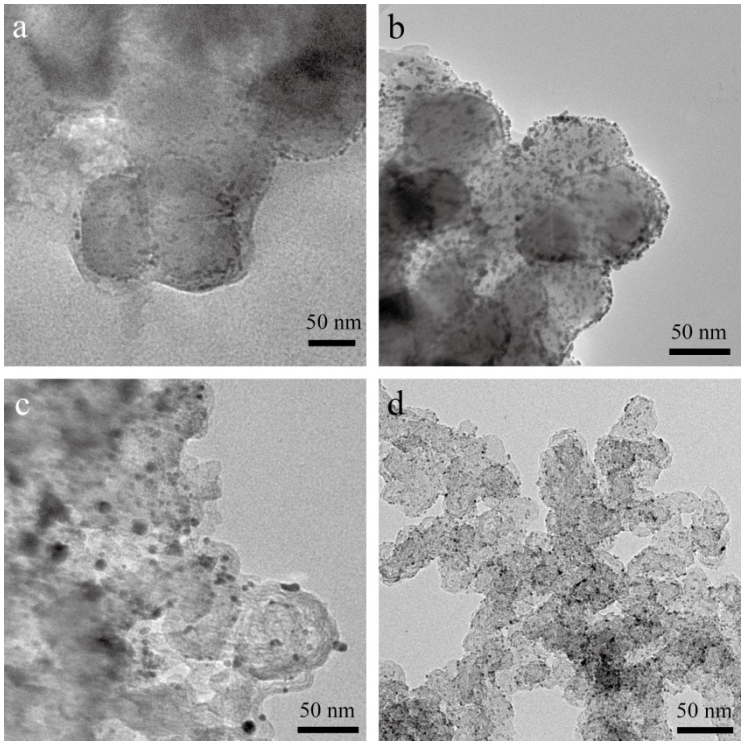

Fig. S9 TEM images of (a) Pt/TiO_2@CNB-2, (b) Pt/TiO_2@CNB-3 and (c) Pt/C catalysts obtained after the CV cycles. (d) showed the TEM image of Pt/C catalyst before the CV cycles.

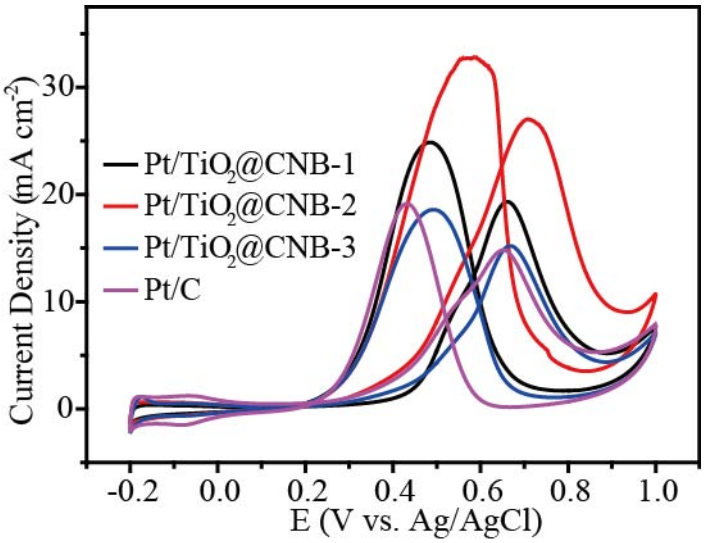

Fig. S10 CV curves of Pt/C and Pt supported TiO_2@CNB catalysts with various shell thickness in Ar-saturated 0.5 mol L^{-1} CH_3OH + 0.5 mol L^{-1} H_2SO_4 solution with a scan rate of 50 mV s^{-1}: area activity.

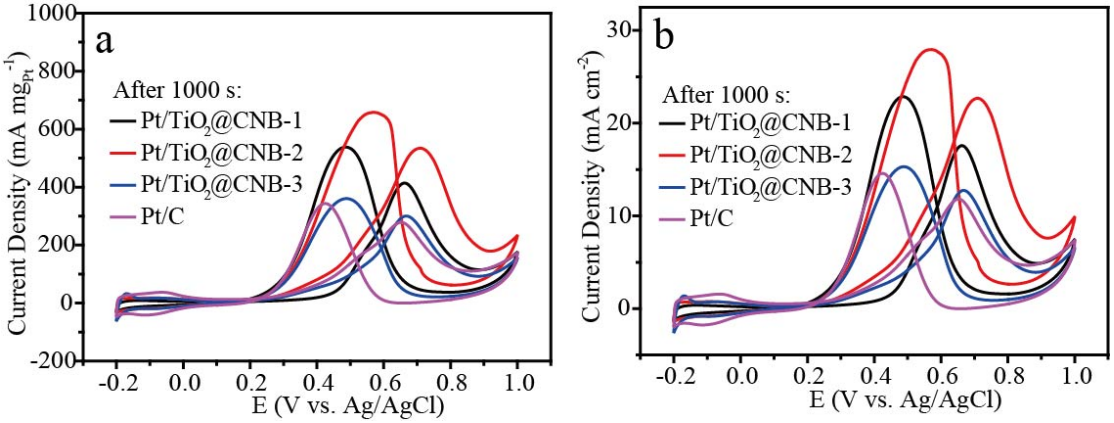

Fig. S11 CV curves of Pt/C and Pt supported TiO_2@CNB catalysts with various shell thickness after 1000 s in Ar-saturated 0.5 mol L^{-1} CH_3OH + 0.5 mol L^{-1} H_2SO_4 solution with a scan rate of 50 mV s^{-1}: (a) mass activity, (b) area activity.