

Supporting Information

Direct Surface Functionalization of Indium Tin Oxide Via Electrochemically-induced Assembly

Mun-Sik Kang, Hong Ma, Hin-Lap Yip, Alex K.-Y. Jen*

Department of Materials Science and Engineering, University of Washington

Box 352120, Seattle, WA 98185-2120

Contents

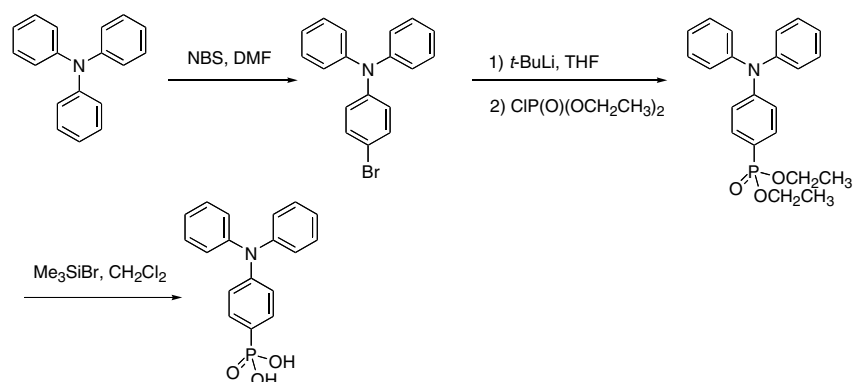
1. Characterization of electrochemically-induced assembly
2. Synthesis of TPAPA
3. Molecular structures of different organophosphonic acids
4. Cyclic voltammograms

1. Characterization of electrochemically-induced assembly

The efficiency of the electrochemical reaction was tested using 2.0 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ as an electroactive probe. All the electrochemical experiments were performed using a one compartment cell equipped with three electrodes, Pt mesh as the counter electrode, Ag/AgCl as the reference electrode and ITO modified with TPAPA as the working electrode. A set of experiments was performed to find the optimal electrochemical conditions by altering either the bias potential or the reaction time. The electrochemically-assembled monolayer on ITO was characterized with cyclic voltammetry (CV) and X-ray photoelectron spectroscopy.

2. Synthesis of TPAPA

All chemicals were purchased from Aldrich and used as received unless otherwise specified. Tetrahydrofuran (THF) was distilled under nitrogen from sodium with benzophenone as the indicator. Methylene chloride was distilled over P₂O₅. ¹H NMR spectra (200 MHz) were taken on a Bruker-200 FT NMR spectrometer. ESI-MS spectra were obtained on a Bruker Daltonics Esquire Ion Trap Mass Spectrometer. Elemental analysis was determined at QTI (Whitehouse, NJ).



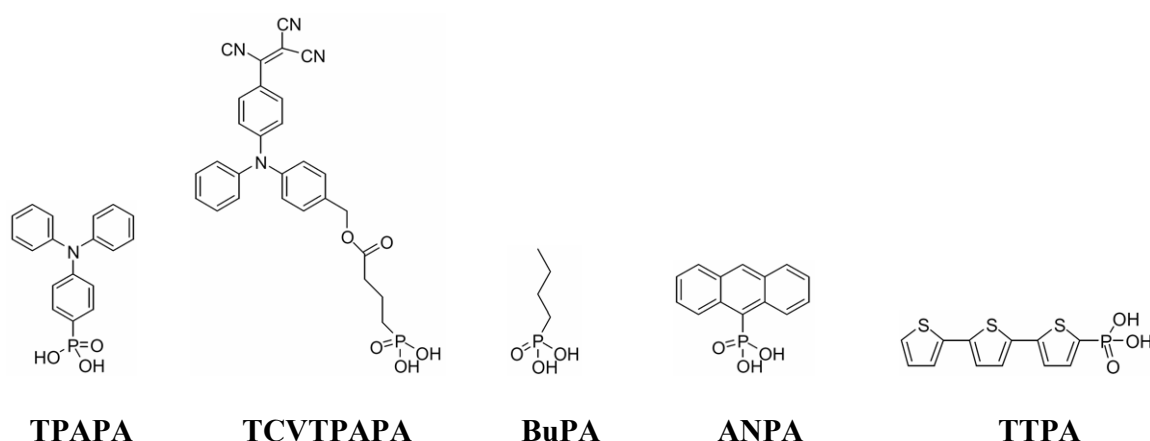
4-Bromotriphenylamine. To a solution of triphenylamine (9.81 g, 40.0 mmol) in *N,N*-dimethylformamide (DMF, 30 mL) was added dropwise the solution of *N*-bromosuccinimide (NBS, 7.12 g, 40.0 mmol) in DMF (20 mL) at room temperature under a nitrogen atmosphere. The solution was stirred overnight at room temperature. The reaction mixture was poured into water, and extracted with methylene chloride. The combined methylene chloride layers were washed with water, dried with Na₂SO₄, and concentrated. The crude product was purified over silica gel column chromatography with hexane to hexane/methylene chloride (5:1) as the eluents to afford a white solid (9.10 g, 70%). ¹H NMR (200 MHz, CDCl₃): δ 6.94-7.12 (8H, m), 7.25-7.40 (6H, m). C₁₈H₁₄BrN: Calcd C 66.68, H 4.35, Br 24.65; found C 66.79, H 4.27, Br 24.60. ESI-MS (*m/z*): Calcd. 323.0; Found 323.1.

Diethyl (4-diphenylamino)phenylphosphonate. To a solution of 4-bromotriphenylamine (2.59 g, 8.0 mmol) in dry THF (30 mL) was added dropwise *tert*-butyllithium (9.4 mL, 1.7 M in pentane) at -78 °C under a nitrogen atmosphere. The solution was stirred at -78 °C for 2 h followed by the dropwise addition of diethyl chlorophosphate (1.38 mL, 9.6 mmol). The reaction mixture was slowly warmed up to room temperature and stirred overnight. The reaction was then quenched with water and the THF

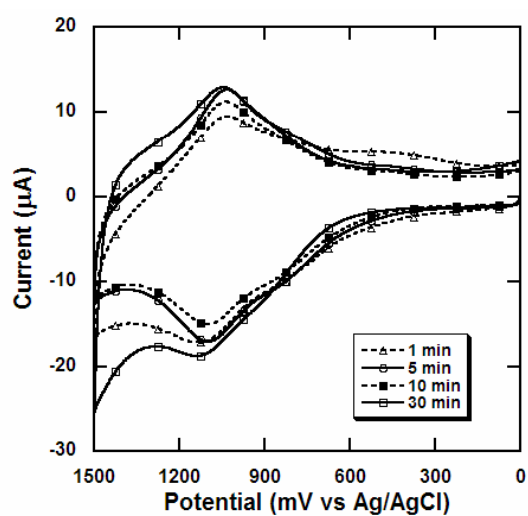
solvent was evaporated. The residue was extracted with methylene chloride. The combined methylene chloride layers were washed with water, dried with Na_2SO_4 , and concentrated. The crude product was purified over silica gel column chromatography with methylene chloride to ethyl acetate as the eluents to afford a slightly yellow solid (1.97 g, 65%). ^1H NMR (200 MHz, CDCl_3): δ 1.33 (6H, t, $J = 6.80$ Hz), 4.11 (4H, q, $J = 6.80$ Hz), 6.98-7.40 (12H, m), 7.50-7.70 (2H, m). $\text{C}_{22}\text{H}_{24}\text{NO}_3\text{P}$: Calcd C 69.28, H 6.34, N 3.67, P 8.12; found C 69.16, H 6.39, N 3.72, P 8.06. ESI-MS (m/z): Calcd. 381.2; Found 381.1.

4-Triphenylaminephosphonic acid. To a solution of diethyl (4-diphenylamino)-phenylphosphonate (0.76 g, 2.0 mmol) in dry methylene chloride (10 mL) was added dropwise bromotrimethylsilane (0.98 mL, 7.6 mmol) at room temperature under a nitrogen atmosphere. The solution was stirred overnight at room temperature. The reaction mixture was poured into water, extracted with methylene chloride. The combined methylene chloride layers were washed with water, dried with Na_2SO_4 , and concentrated to afford a white solid (0.51 g, 79%). ^1H NMR (200 MHz, CDCl_3): δ 6.98-7.35 (12H, m), 7.50-7.70 (2H, m), 8.55 (2H, br). $\text{C}_{18}\text{H}_{16}\text{NO}_3\text{P}$: Calcd C 66.46, H 4.96, N 4.31, P 9.52; found C 66.35, H 4.87, N 4.42, P 9.60. ESI-MS (m/z): Calcd. 325.1; Found 325.0.

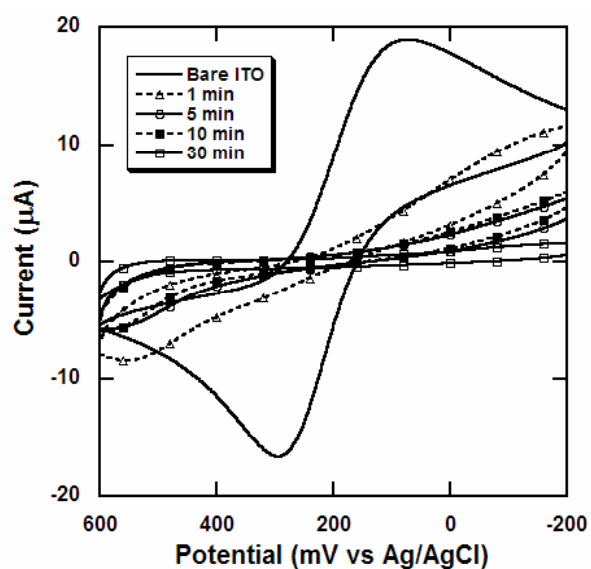
3. Supplement Figure S1. Molecular structures of different organophosphonic acids



4. Cyclic voltammograms

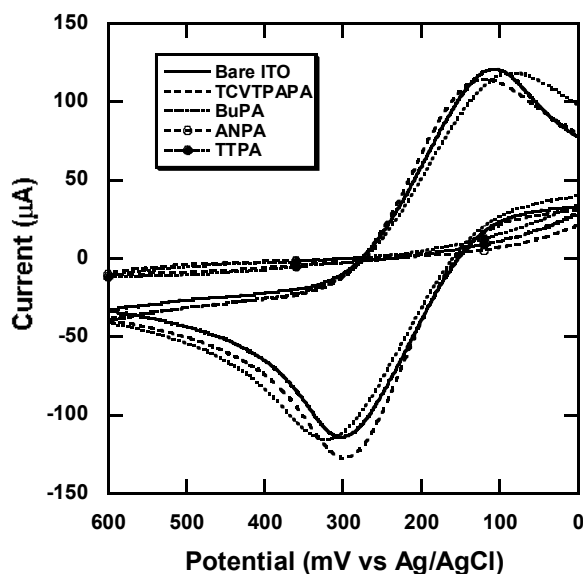


Supplement Figure S2. Cyclic voltammograms of TPAPA/ITO samples prepared under a bias potential of 1500 mV with different deposition times. Acetonitrile solution containing 0.1 M TBAHFP was used as electrolyte. The scan rate was 0.5 V/s and each CV curve was recorded after 6 repeated



cycles.

Supplement Figure S3. Cyclic voltammograms of a 2.0 mM ferricyanide solution in 0.1 M KCl aqueous electrolyte at the bare ITO surface and the TPAPA/ITO surfaces prepared under 1500 mV bias potential with different deposition times. The scan rate was 0.1 V/s.



Supplement Figure S4. Cyclic voltammograms of a 2.0 mM ferricyanide solution in 0.1 M KCl aqueous electrolyte at the bare ITO surface and a series of organophosphonic acid on ITO prepared by the electrochemically-induced assembly method. The scan rate was 0.1 V/s.