

Electronic Supporting Information

Tuning azolate ionic liquids to promote surface interactions with titanium nanoparticles leading to increased suspension stability and passivation

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I. Materials and Methods

Chemicals. 1-Methylimidazole, 1-chlorobutane, 5-amino-tetrazole, 4,5-dicyano-imidazole, 4-NO₂-imidazole, 2-Me-4-NO₂-imidazole, potassium carbonate, and anhydrous acetone were purchased from Sigma-Aldrich (St. Louis, MO). 1-Methylimidazole was redistilled and kept under Argon prior to use while all other chemicals were used without any further purification. Titanium(0) nanoparticles (< 100 nm in diameter) were purchased from Sigma-Aldrich as a dispersion in mineral oil. The dispersion was washed with freshly distilled n-hexane while under inert atmosphere in a VAC-Omni drybox (Hawthorne, CA) to remove mineral oil. Titanium(IV) dioxide rutile nanopowder (< 100 nm) was purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Ultra-pure Argon (> 99.999%) was purchased from Airgas (Radnor Township, PA) and used as received.

Thermogravimetric Analysis (TGA). All experiments were conducted with a TA Instruments (New Castle, DE) model 2950 thermogravimetric analyzer. The instrument's internal temperature was calibrated by observing the Curie point of Nickel (358.15 °C). In order to investigate the decomposition profile of the titanium loaded ILs, samples of 5-25 mg were analyzed on a platinum pan under a purge of argon and under a stream of compressed air and measured *via* dynamic heating. Samples were heated from room temperature to 75 °C at 5 °C/min and with a 30 min isotherm at 75 °C in order to ensure excess volatiles or residual solvents were removed. Following the isotherm, samples were heated to 800 °C at 5 °C/min. Decompositions temperatures are recorded as the onset to 5% weight mass loss (T_{5%dec}).

X-Ray Photoelectron Spectroscopy (XPS). All XPS analyses were run on a Kratos Axis 165 XPS/Auger (Manchester, UK) containing an Al X-ray source. Samples were prepared neat by applying droplets of either neat IL or dispersions of Ti in an IL to a copper stub with a depression to allow the liquid to reside. Samples were brought under high vacuum (~1 X 10⁻⁸ torr) in the antechamber before allowed to enter the sampling chamber (~1 X 10⁻⁹ torr).

Spectroscopy. All Nuclear Magnetic Resonance (NMR) spectra were recording utilizing a Bruker Avance Spectrometer Bruker/Magnex UltraShield 500 MHz magnet (Madison, WI) or a Bruker Spectrospin DRX 400 MHz UltrashieldTM spectrometer (Madison, WI). ¹H (500 MHz) and ¹³C (125 MHz) were collected using DMSO-*d*₆ as the solvent with TMS as the internal standard and shifts reported in δ (ppm). Infrared (IR) spectra were collected using a Bruker ALPHA-FTIR by direct measurement *via* attenuated total reflectance of the neat samples (or loaded with titanium nanoparticles) on a diamond crystal.

Viscosity. Viscosity measurements were taken at 40 °C with a Cambridge Viscosity (Medford, MA) Viscometer, VISCOLab 3000. Approximately 1 mL of each IL was placed in the sample chamber. The correct sized piston corresponding to the expected viscosity range was added and the measurement was taken.

Density. Density measurements were taken at 40 °C with an Anton Paar USA (Ashland, VA) density meter, DMA 500. Samples of IL (~1 mL) were inserted *via* a syringe directly into

the instrument. The value for density was recorded and the sample was washed out with methanol and water.

Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-Ray Analysis (EDX). Measurements for STEM were carried out on a FEI (Hillsboro, OR) Tecnai F-20 TEM under high vacuum conditions ($\sim 1 \times 10^{-9}$ torr) at 200 kV. EDX measurements were taken at an accelerating voltage of 200 kv with an α tilt of 15.38 degrees at an input full width at half maximum of 150 eV @ 5.9 keV. Samples were prepared on a copper disc and blotted to remove excess ionic liquid.

II. Synthesis

Synthesis of [BMIM][Cl]¹

1-Methylimidazole (150.00 g, 1.83 mol) was distilled directly into the reaction flask and a 1.1 molar excess of 1-chlorobutane (204.64 g, 2.00 mol) was added and the reaction was refluxed under a constant stream of Argon utilizing Schlenk-line techniques. The reaction was monitored by NMR until all peaks of 1-methylimidazole were no longer visible, approximately 96 h. The remaining excess of 1-chlorobutane was removed under reduced pressure and the product was slowly cooled to a white crystalline solid, collected into small vials, and immediately capped. ¹H NMR (360 MHz, *DMSO-d*₆) δ ppm: 9.124 (1H, s), 7.929 (1H, s), 7.847 (1H, s), 4.223 (2H, t, *J* = 7.132 Hz), 3.898 (3H, s), 1.773 (2H, quintet, *J* = 7.427 Hz), 1.250 (2H, sextet, *J* = 7.538 Hz), 0.890 (3H, t, *J* = 7.310 Hz).

Metathesis Reactions using a Modified Literature Synthesis²

[BMIM][5-NH₂-Tetra]

5-NH₂-Tetrazole (6.447 g, 50 mmol) was combined with K₂CO₃ (13.8205 g, 100 mmol) in 250 mL of anhydrous acetone and stirred for 2 h to deprotonate the azole. [BMIM][Cl] (8.734 g, 50 mmol) was added piecewise maintaining anhydrous conditions and stirred for 72 h. The mixture was filtered and the acetone was removed under reduce pressure. The resulting oil was dissolved in anhydrous acetone and filtered again and the acetone was removed under reduced pressure and high vacuum techniques. The resulting liquid was freeze thawed with liquid N₂ under high vacuum to remove excess dissolved gas. The resulting red viscous liquid was stored under argon. ¹H NMR (360 MHz, *DMSO-d*₆) δ ppm: 9.580 (1H, s), 7.892 (1H, s), 7.814 (1H, s), 4.212 (2H, t), 3.891 (3H, s), 1.771 (2H, quintet), 1.254 (2H, sextet), 0.883 (3H, s); ¹³C NMR (125 MHz, *DMSO-d*₆) δ ppm: 164.681 (s), 137.366 (s), 124.099 (s), 122.828 (s), 48.917 (s), 36.175 (s), 31.873 (s), 19.233 (s), 13.711 (s). *T*_g: -67 °C³

[BMIM][4,5-DiCN-Imid]

4,5-Dicyano-imidazole (5.96 g, 50 mmol) was combined with K₂CO₃ (13.8205 g, 100 mmol) in 250 mL of anhydrous acetone and stirred for 2 h. [BMIM][Cl] (8.734 g, 50 mmol) was added

piecewise maintaining anhydrous conditions and stirred for 72 h. The mixture was filtered and the acetone was removed under reduce pressure. The resulting oil was dissolved in anhydrous acetone and filtered again and the acetone was removed under reduced pressure and high vacuum techniques. The resulting liquid was freeze thawed with liquid N₂ under high vacuum to remove excess dissolved gas. The resulting yellowing non-viscous liquid was stored under argon. ¹H NMR (360 MHz, *DMSO-d*₆) δ ppm: 9.618 (1H, s), 7.735 (1H, s), 7.675 (1H, s), 7.312 (1H, s), 4.165 (2H, t), 3.876 (3H, s), 1.780 (2H, quintet), 1.280 (2H, sextet), 0.889 (3H, t); ¹³C NMR (125 MHz, *DMSO-d*₆) δ ppm: 149.226 (s), 136.985 (s), 124.127 (s), 122.788 (s), 117.986 (s), 117.352 (s), 49.130 (s), 36.230 (s), 31.786 (s), 31.786 (s), 19.529 (s), 13.602 (s). *T*_g: -74 °C²

[BMIM][4-NO₂-Imid]

4-NO₂-imidazole (5.829 g, 50 mmol) was combined with K₂CO₃ (13.8205 g, 100 mmol) in 250 mL of anhydrous acetone and stirred for 2 h. [BMIM][Cl] (8.734 g, 50 mmol) was added piecewise maintaining anhydrous conditions and stirred for 72 h. The mixture was filtered and the acetone was removed under reduce pressure. The resulting oil was dissolved in anhydrous acetone and filtered again and the acetone was removed under reduced pressure and high vacuum techniques. The resulting liquid was freeze thawed with liquid N₂ under high vacuum to remove excess dissolved gas. The resulting yellow-orange non-viscous liquid was stored under argon. ¹H NMR (360 MHz, *DMSO-d*₆) δ ppm: 9.381 (1H, s), 7.835 (1H, s), 7.773 (1H, s), 7.758 (1H, s), 7.171 (1H, s), 4.177 (2H, s), 3.891 (3H, s), 1.757 (2H, quintet), 1.242 (2H, sextet), 0.873 (3H, t); ¹³C NMR (125 MHz, *DMSO-d*₆) δ ppm: 146.512 (s), 137.152 (s), 132.058 (s), 131.951 (s), 124.112 (s), 122.773 (s), 49.060 (s), 36.088 (s), 31.862 (s), 19.219 (s), 13.459 (s). *T*_g: -72 °C³

[BMIM][2-Me-4-NO₂-Imid]

2-Me-4-NO₂-imidazole (9.349 g, 72.8 mmol) was combined with K₂CO₃ (20.1277 g, 145.6 mmol) in 250 mL of anhydrous acetone and stirred for 2 h. [BMIM][Cl] (12.719 g, 72.8 mmol) was added piecewise maintaining anhydrous conditions and stirred for 72 h. The mixture was filtered and the acetone was removed under reduce pressure. The resulting oil was dissolved in anhydrous acetone and filtered again and the acetone was removed under reduced pressure and high vacuum techniques. The resulting liquid was freeze thawed with liquid N₂ under high vacuum to remove excess dissolved gas. The resulting dark orange non-viscous liquid was stored under argon. ¹H NMR (360 MHz, *DMSO-d*₆) δ ppm: 9.308 (1H, s), 7.827 (1H, s), 7.748 (1H, s), 7.660 (1H, s), 4.165 (2H, t), 3.869 (3H, s), 2.138 (3H, s), 1.752 (2H, quintet), 1.243 (2H, sextet), 0.876 (3H, t). ¹³C NMR (125 MHz, *DMSO-d*₆) δ ppm: 154.895 (s), 147.984 (s), 137.175 (s), 133.801 (s), 124.084 (s), 122.751 (s), 48.997 (s), 36.145 (s), 31.852 (s), 19.264 (s), 18.022 (s), 13.666 (s).

III. Nanofluid Characterization

Details of Purification of the ILs. The isolated and purified EILs (as determined by NMR), were dried under high vacuum at 60 °C while being stirred for 48 h. The ILs were dried through freeze-thawing the IL with N_{2(l)} while under high vacuum to remove excess gas trapped in the IL. The ILs were stored and sealed after being back filled with Ar.

Viscosity.

Compound	Viscosity (cP)	% Error
[BMIM][4,5-DiCN-Imid]	32.56	1.9
[BMIM][5-NH ₂ -Tetra]	245.3	1.7
[BMIM][4-NO ₂ -Imid]	42.52	2.0
[BMIM][2-Me-4-NO ₂ -Imid]	150.2	2.0

Infrared Spectroscopy.

[BMIM][4,5-DiCN-Imid]

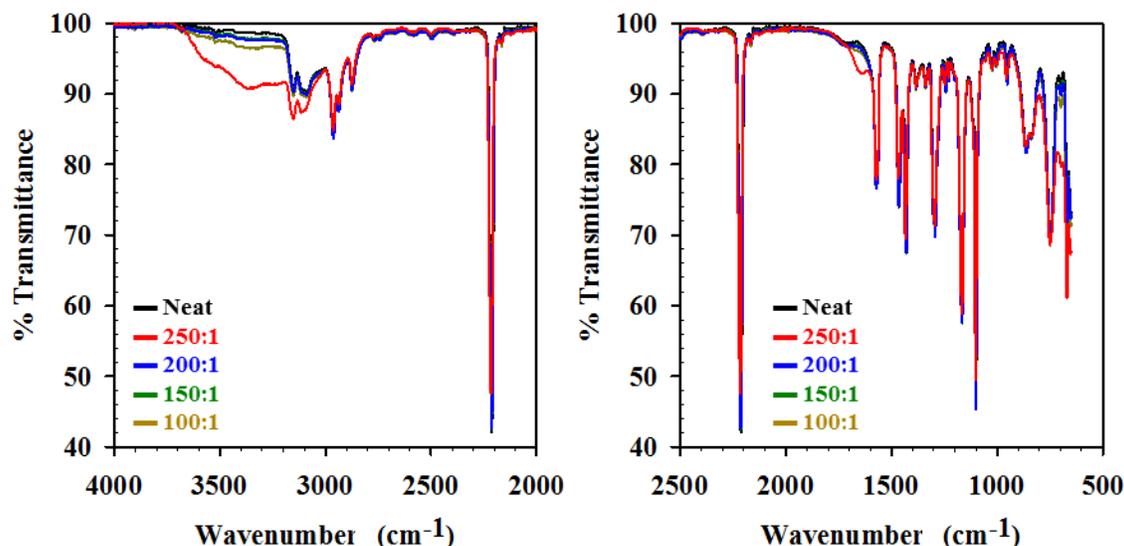


Figure S1. Infrared Spectra of [BMIM][4,5-DiCN-Imid] loaded with various concentrations of Ti nanoparticles

The Ti loaded sample at 250:1 for [BMIM][4,5-DiCN-Imid] was contaminated with water. The top was inadvertently unscrewed while it was in the sonication bath.

[BMIM][2-Me-4-NO₂-Imid]

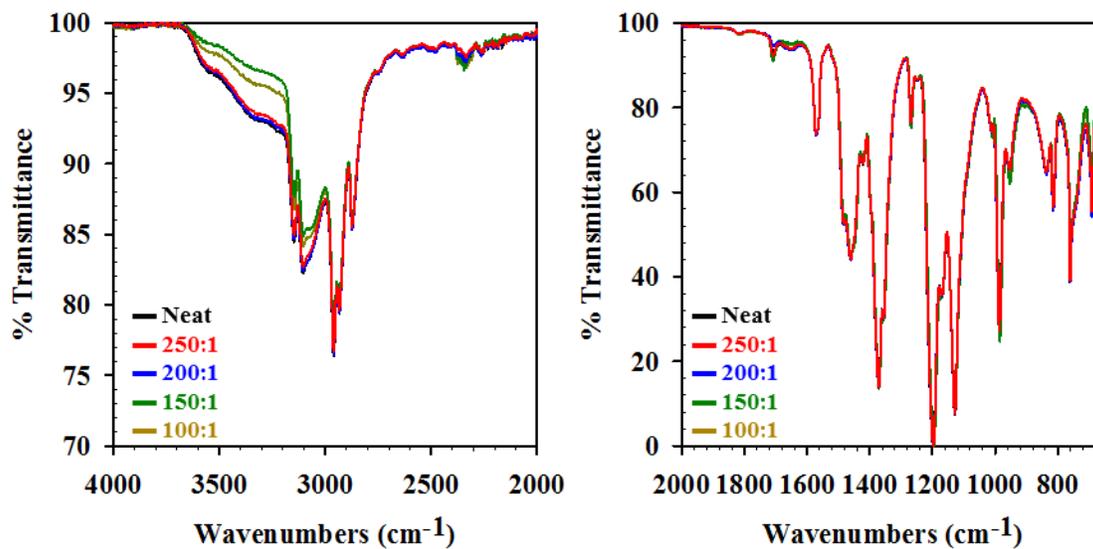


Figure S2. Infrared Spectra of [BMIM][2-Me-4-NO₂-Imid] loaded with various concentrations of Ti nanoparticles

X-Ray Photoelectron Spectroscopy.

[BMIM][4,5-DiCN-Imid]

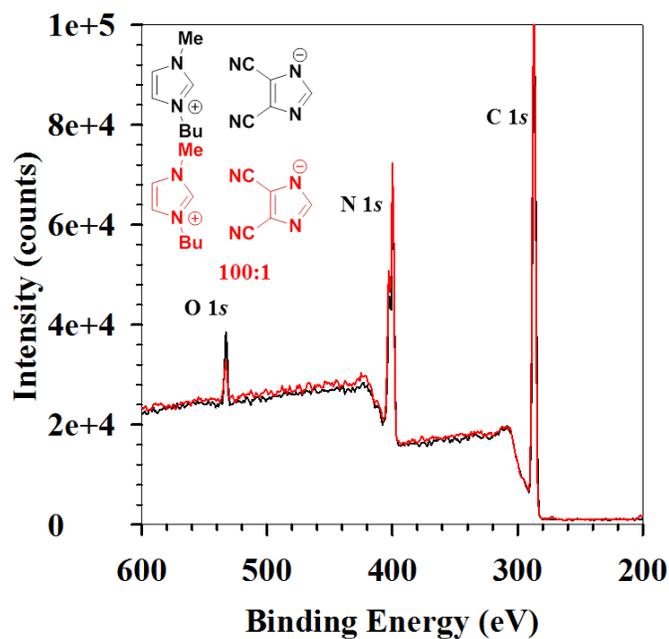


Figure S3. XPS Spectra of [BMIM][4,5-DiCN-Imid] neat (black) and with Ti(0) (red)

[BMIM][4-NO₂-Imid]

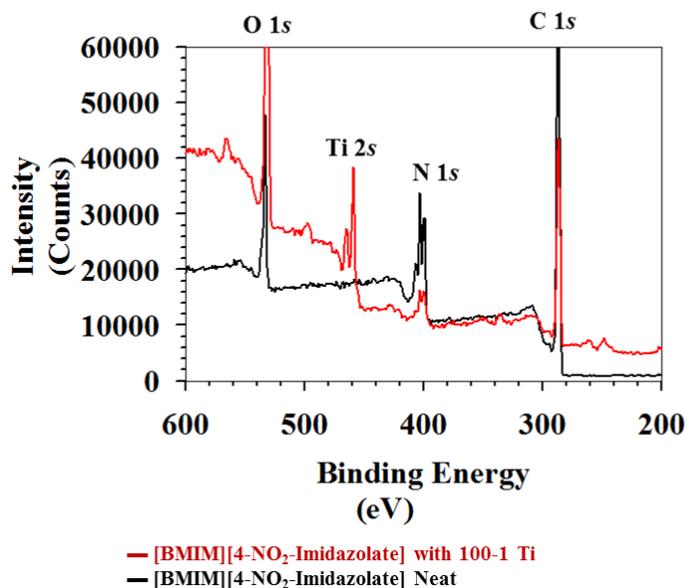


Figure S4. XPS Spectra of [BMIM][4-NO₂-Imid] neat (black) and with Ti(0) (red)

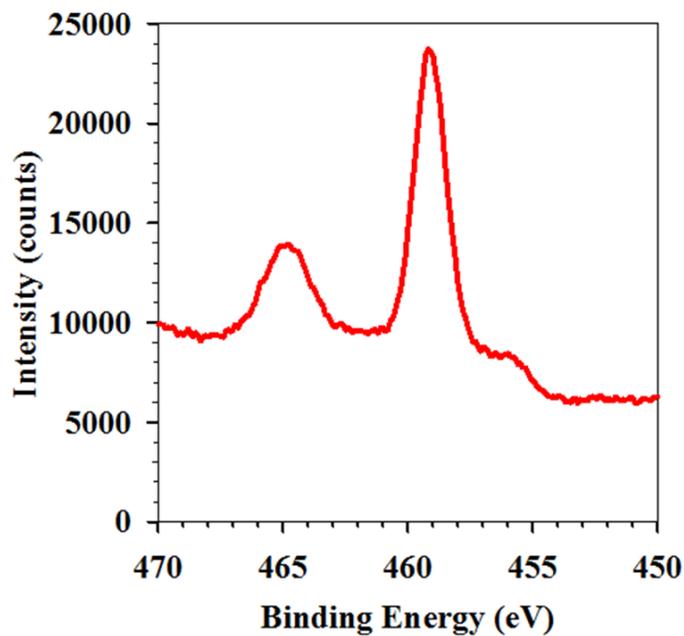


Figure S5. High resolution XPS spectra focusing on Ti 2p_{3/2} orbital for [BMIM][4-NO₂-Imid], which correctly corresponds to a Titanium oxide surface

Thermogravimetric Analysis.

[BMIM][4,5-DiCN-Imid]

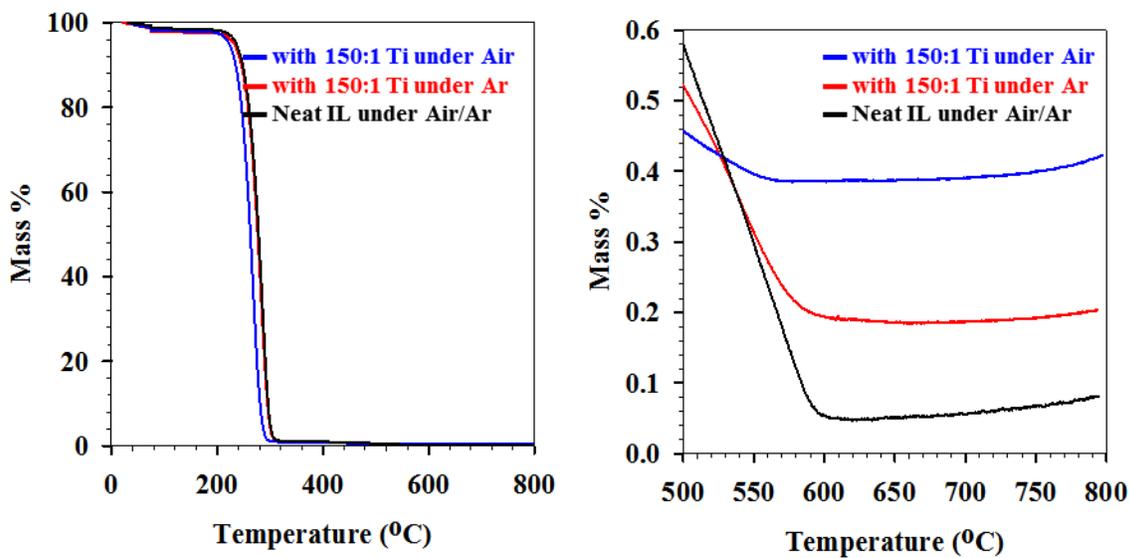


Figure S6. Thermogravimetric analysis of [BMIM][4,5-DiCN-Imid] with Ti in Air or Argon

[BMIM][2-Me-4-NO₂-Imid]

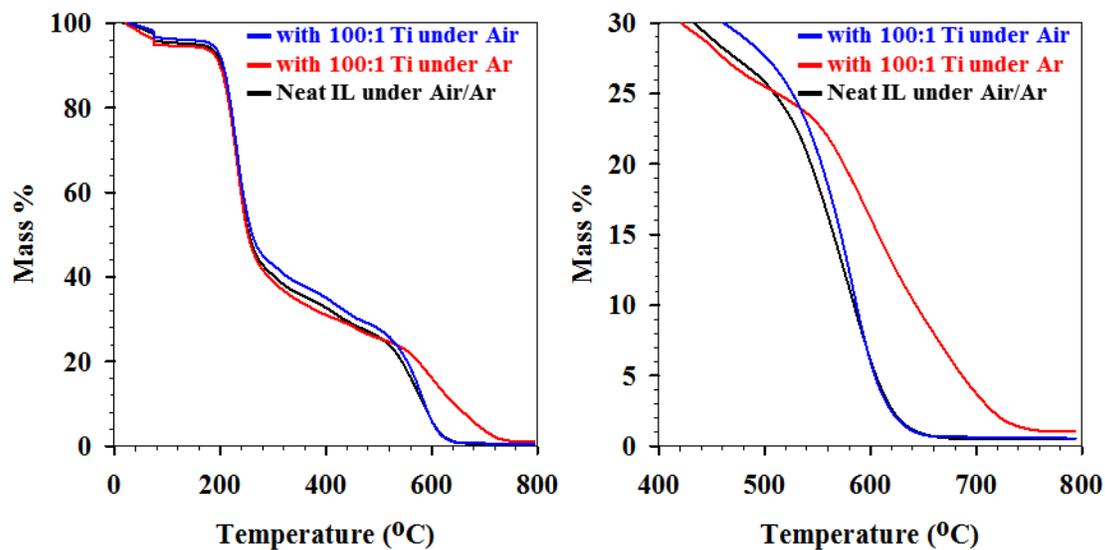


Figure S7. Thermogravimetric analysis of [BMIM][2-Me-4-NO₂-Imid] with Ti in Air or Argon

STEM and EDX Spectroscopy.

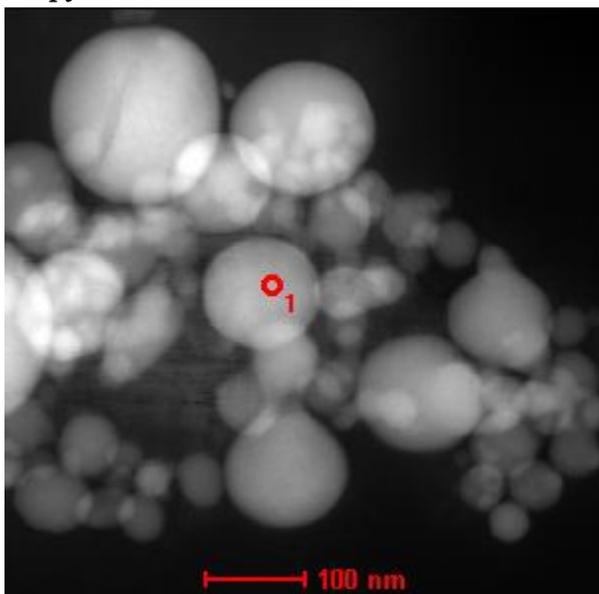


Figure S8. TEM Micrograph of Ti nanoparticles loaded into [BMIM][4-NO₂-Imid] at 100-1 ratio, which demonstrates size and morphology of added Ti nanoparticles.

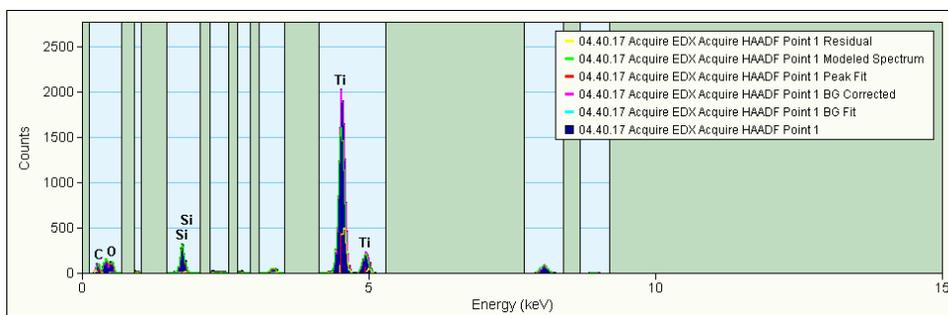


Figure S9. EDX spectra for location shown in Figure S8 demonstrating the presence of Ti with no metallic impurities.

- 1 P. D. McCrary, P. A. Beasley, O. A. Cojocaru, S. Schneider, T. W. Hawkins, J. P. L. Perez, B. W. McMahon, M. Pfeil, J. A. Boatz, S. L. Anderson, S. F. Son and R. D. Rogers, *Chem. Commun.*, 2012, **48**, 4311.
- 2 M. Smiglak, C. C. Hines, T. B. Wilson, S. Singh, A. S. Vincek, K. Kirichenko, A. R. Katritzky and R. D. Rogers, *Chem. Eur. J.*, 2010, **16**, 1572.
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