Azide-Modified Graphitic Surfaces for Covalent Attachment of Molecular Species by ‘Click’ Chemistry

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Molecular Species-Attached Graphitic Surfaces

Motivation
- Graphite as electrode material: inexpensive, stable to oxidation and hydrolysis, and electrically conductive
- Attaching molecular species (e.g., electrocatalysts) to graphite electrodes can find applications in:
  - fuel cells
  - electrochemical synthesis
  - sensors

Challenges
- The catalyst should be coupled to the substrate by a robust linker, that is oxidatively and hydrolytically stable
- The linker should provide adequate electrical coupling between the substrate surface and the molecular catalyst

Our Approach using ‘Click’ Chemistry
- Use azide-modified graphite surfaces as a platform to covalently couple ethynyl-terminated molecular catalysts by a 1,2,3-triazole linker formed via the Cu(I)-catalyzed 1,3-Huisgen cycloaddition, popularly known as a ‘click’ reaction

Advantages of using the Click Reaction
- High yield (almost 100% yield)
- Low quantity of reagents required (μM concentration sufficient)
- Fast reaction time (in minutes)
- Inertness to a range of reaction conditions (aqueous, non-aqueous, acidic, basic etc.) and allows a broader range of molecular catalysts be coupled to the surface
- The triazole is a robust aromatic linker, stable to hydrolysis and air oxidation

Preparation of Azide-Modified Graphitic Surfaces and Attaching Ethynylericocene to the Surfaces

A method to prepare azide-terminated graphite surfaces that can be used to couple ethynyl-terminated species to graphite surfaces has been developed by the Chidsey Group, Stanford University

IN$_3$ Reaction is Selective to Edge-Plane Graphite

Figure 2: Schematic diagram showing the preparation of azide-modified graphitic surface using iodine azide as the reagent and subsequent coupling of ethynylericocene via the ‘click’ reaction

Figure 3: XPS data showing the presence of azide on the graphite surface and formation of the triazole after the click reaction

IN$_3$ Reaction is Selective to Edge-Plane Graphite

Figure 4: XPS data showing the presence of Fe 2p peaks due to the ethynylericocene coupled to the surface

Figure 5: Voltammetric data showing the presence of redox peaks due to the ethynylericocene coupled to the surface

surface coverage of ethynylericocene obtained in pyrolyzed photoresists (graphitic substrate): 2.5 x 10$^{-11}$ molecules cm$^{-2}$

IN$_3$ Reaction is Selective to Edge-Plane Graphite

Figure 6: Cyclic voltammograms obtained at A) edge-plane graphite and B) basal-plane graphite surfaces after treating the surfaces with iodine azide and subsequently attaching ethynylericocene.

Hydrolytic Stability of the Triazole Linker

1-ethyl-4-(trifluoromethyl)benzene was attached to the azide-modified graphite surface by click chemistry. The surface was immersed in 1M HCl for 1 h at 55°C. The stability of the triazole linker was monitored following the F 1s spectra.

Figure 7: XPS data showing the stability of the triazole linker towards hydrolysis treatment. Top row: before hydrolysis treatment, bottom row: after hydrolysis treatment.

Cu(phen)/3-ethylphen-coupled Graphite Surfaces

Figure 8: Cyclic voltammograms obtained at a 3-ethylphen-coupled surface and a Cu(phen)(3-ethylphen)-coupled surface.

Future directions:
- Coupling coordination complexes with Pt, Ru, and Pd and exploring their electrocatalytic properties
- Extending the ‘click’ chemistry method to other substrates relevant to energy applications