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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 graphitic 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

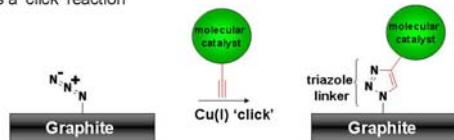


Figure 1: Schematic diagram showing the covalent coupling of ethynyl-terminated molecular catalyst to azide-modified graphitic surface by the 'click' reaction

Advantages of using the Click Reaction

- high yield** (almost 100% yield)
- low quantity of reagents** required (μM concentration sufficient)
- fast reaction time** (in minutes)
- insensitive 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

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Reference

- Devadoss, A.; Devaraj, N. K.; Chidsey, C. E. D. U.S. Patent Provisional Application no. 60/880,249
- Devadoss, A.; Chidsey, C. E. D., J. Am. Chem. Soc. 2007, 129, 5370-5371.

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

A method to prepare azide-terminated graphitic surfaces^{1,2} that can be used to couple ethynyl-terminated species to graphitic surfaces has been developed by the Chidsey Group, Stanford University

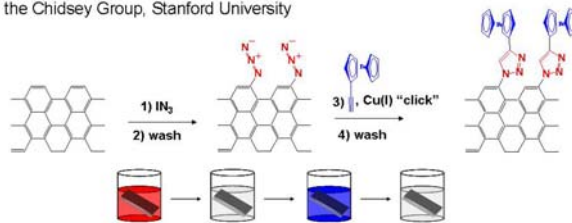


Figure 2: Schematic diagram showing the preparation of azide-modified graphitic surface using iodine azide as the reagent and subsequent coupling of ethynylferrocene via the 'click' reaction.

Monitoring Click Chemistry at Azide-Modified Graphitic Surfaces by X-ray Photoelectron Spectroscopy (XPS)

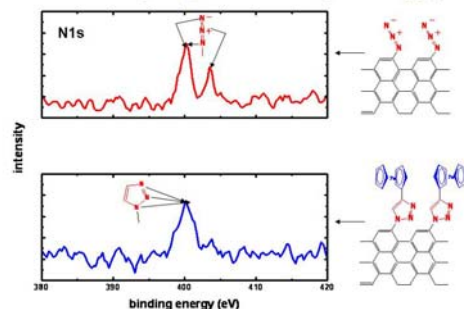


Figure 3: XPS data showing the presence of azide on the graphite surface and formation of the triazole after the click reaction

XPS and Electrochemical Characterization of Ferrocene-Attached Graphitic Surfaces

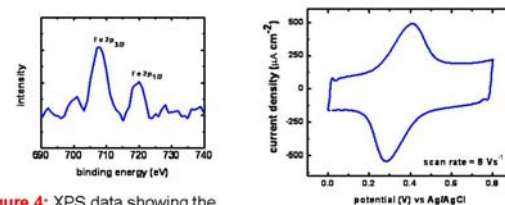


Figure 4: XPS data showing the presence of Fe 2p peaks due to the ethynylferrocene coupled to the surface

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

surface coverage of ethynylferrocene obtained in pyrolyzed photoresists (graphitic substrate)= 2.5×10^{13} molecules cm^{-2}

IN_3 Reaction is Selective to Edge-Plane Graphite

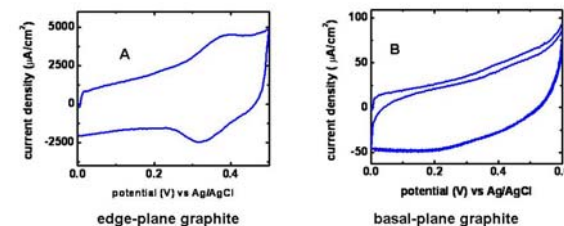
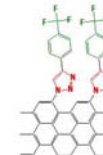


Figure 6: cyclic voltammograms obtained at A) edge-plane graphite and B) basal-plane graphite surfaces after treating the surfaces with iodine azide and subsequently attaching ethynylferrocene.

Hydrolytic Stability of the Triazole Linker



1-ethynyl-4-(trifluoromethyl)benzene was attached to the azide-modified graphitic 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 by following the F 1s spectra.

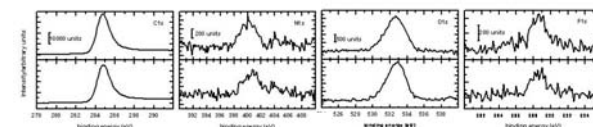


Figure 7: XPS data showing the stability of the triazole linker towards hydrolysis treatment **top row**: before hydrolysis treatment, **bottom row**: after hydrolysis treatment

Cu-1,10-Phenanthroline (phen)-coupled Graphite Surfaces

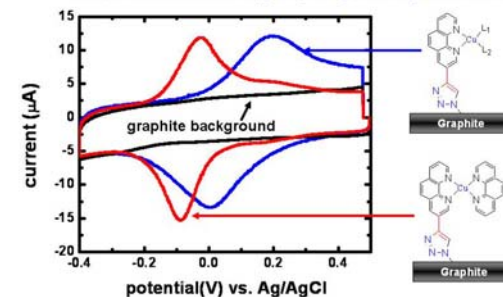


Figure 8: cyclic voltammograms obtained at a 3-ethynyl-phen-coupled surface and a Cu(phen)(3-ethynyl-phen)-coupled surface.

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