

Electrostatic Catalysis using Functionalized Silicon Electrodes

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Abstract

External electric fields that are oriented are increasingly emerging as "smart effectors" of chemical processes. The main difficulties in researching electrostatic catalysis experimentally are I regulating the direction of fields along the reaction axis and carefully modifying the magnitudes of electrostatic stimuli. Surface models offer a flexible framework for addressing the direction of electric fields with regard to reactants and managing the trade-off between charged species solubility and electric field intensity. In this mini-review, we discuss recent breakthroughs in the study of the electrostatic influence on chemical reactions on monolayer-functionalized silicon surfaces. We are primarily interested in determining the mediator/catalysis role of static electric fields induced by either solid/liquid electric double layers at electrode/electrolyte interfaces or space charges in semiconductors, indicating that electrostatic aspects are important in semiconductor electrochemistry, redox electroactivity and chemical bonding. The functionalization of silicon surfaces allows scientists to investigate electrostatic catalysis from the nanoscale to the mesoscale; more importantly, it provides glimpses of the broad potentials of oriented electric fields for turning on/off macroscale synthetic organic electrochemistry and living radical polymerization.

Keywords: Polymerization; Electroactivity

Introduction

At the moment, there is a lot of interest in using directed electric fields as "smart reagents" to catalyse non-electrochemical processes, namely electrostatic catalysis. A controllable electric field allows chemists to control catalysis/inhibition of chemical/biological reactions at will, establishing a new approach to future chemistry and biology, from adjusting enzyme activity in biological processes to manipulating barrier heights of chemical reactions or functions of molecular devices. However, electrostatic catalysis is still in its infancy in experimental studies, but it is widely used in theoretical predictions. This is due to the inherent constraint of an electric field as a vector in altering its orientation against the reaction axis and assessing the precise intensity of the electric field supplied to the reactions. Furthermore, electrostatic effects are strong in the gas phase and gradually diminish with increasing polarity of media, whereas charged residue solubility is poor in non- or less-polar solvents. To expand electrostatic catalysis to practical processes, two issues must be addressed: I directing the direction and strength of an external electric field at will, and balancing the trade-off between the solubility of charged species and the size of electric field provided proof of concept that an electric field could accelerate a carbon-carbon bond-forming reaction through Scanning Tunnelling Microscope-Break Junction (STM-BJ) experiments in 2016, and this nanoscale technique was later chosen as a versatile platform to trigger some chemical changes by deliberately controlling the orientation and intensity of electric fields. Although this provided the opportunity to use easily accessible model systems to investigate electrostatic catalysis phenomena experimentally, the proposed STM-BJ surface system is not on a practical scale, and only a limited number of molecules/specific reactions are used to match this experimental setup; for example, some single-molecule junctions are built using gold-carbon bond formation. To extend electrostatic catalysis beyond individual molecules, it is necessary to be able to design monolayer surface systems by linking

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interested molecules to the strength of a solid device. The semiconductor silicon electrode, the most significant electrode material of our day, is still accelerating the development of electrochemistry, molecular electronics, quantum computing, and spintronics. The following are the primary reasons for using a silicon electrode in the electrostatic catalysis study: It exhibits outstanding photoelectrochemical characteristics at the electrode–electrolyte interface, and it is conveniently accessible for surface-sensitive X-ray spectroscopic characterizations using the Si/C contrast. Because of these benefits, the silicon electrode has become a suitable platform for studying electrostatic catalysis in mesoscale processes. The functionalization of silicon substrates and semiconductor electrochemistry will be explained briefly below so that readers may understand how the electrostatic effect works on monolayer films. We present a detailed overview of the advances in electrostatic catalysis of redox and non-redox reactions on functionalized silicon electrodes, implying that electric fields can be used as "smart reagents" for regulating organic surface synthesis and switching ON/OFF nitroxide-mediated polymerization.

Organic monolayer assembly on silicon surfaces

Silicon surface models provide an efficient technique for addressing the direction of external electric fields with regard to reactants and balancing the mismatch between the solubility of charged species and the amplitude of external electric fields. Our first focus is on the fabrication of stable silicon monolayer films, minimizing/avoiding the development of silicon oxides during measurements, and guaranteeing that electric fields have catalytic effects. There are various procedures available for generating chemically well-defined organic monolayers on silicon electrodes, including Si-C, Si-O, and Si-N bonded layers. One of the most popular covalent attachments on a silicon electrode is Si-C bound surface modifications. To obtain the robust Si-C linked monolayers and thus precise electron-transport studies, the insulating silicon oxide layers on silicon substrates are typically passivated by chemical etching in either fluoride-containing solution or alkaline aqueous, resulting in hydrogen-terminated (Si-H) silicon surfaces. The resultant Si-H surfaces are unmistakably favourable for molecular monolayer adhesion through wet chemical processes. This is due to the Si-H functionality's fascinating features, such as its ease of preparation, short-term endurance to atmospheric and aqueous media, and inert reactivity toward typical organic media. This review introduced two widely used methods for preventing silicon oxide formation: (1) insertion of an unsaturated molecule (i.e., alkenes and alkynes) into Si-H bonds, known as hydrosilylation, and (2) formation of a Si-C linkage on non-oxidized Si-H surfaces, which can be accomplished by thermal-triggered hydrosilylation under appropriate conditions. Photochemical irradiation, on the other hand, can enhance hydrosilylation of unsaturated molecules at normal temperature by homolytic breaking of Si-H bonds. The necessary processes will be described in full in the sections that follow.

Voltammograms with suboptimal resolution in semiconductor electrochemistry

When working with redox reactions in semiconductor electrodes, scientists occasionally encountered non-ideal voltammograms [anti-thermodynamic inverted redox peaks and 90.6 mV Full Width at Half Maximum (FWHM) value]. Because the current signal obtained from an electrified contact was always viewed as an indication of an overall rate, these non-idealities were quickly dismissed as electrochemical faults or artefacts. We just discovered that these non-ideal electrochemical events may be recreated and are not erroneous data; they are the result of an electrostatic interaction between surface charged species and space charges in semiconductors. According to investigation the electrochemical behaviour of nitroxide in liquids with varying dielectric constants by anchoring 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) monolayers to a poorly doped Si(100) electrode. Under illumination, cyclic voltammograms (CVs) with only sweeps toward the anodic direction were recorded, and the light source was promptly turned off at the anodic vertex. Following that, we discovered that the FWHM is significantly reliant on the surface coverage of electroactive units, with values dropping from 142 mV to 55 mV to 75 mV for ferrocene-modified weakly doped Si (111) electrodes when ferrocene concentrations shift from 2.9×10^{10} to 1.7×10^{10} mol cm², respectively. It was, investigated the electrochemical behaviour of nitroxide in liquids with varying dielectric constants by anchoring 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) monolayers to a poorly doped Si (100) electrode. Under illumination, Cyclic Voltammograms (CVs) with only sweeps toward the anodic direction were recorded, and the light source was promptly turned off at the anodic vertex. These effects are due to the conversion of the dominant electrostatic forces from repulsive interactions between ferrocenes (142 mV FWHM) to attractive interactions between ferrocenium and space charges (55 mV to 75 mV FWHM). The degree of band-bending in the depleted semiconductor space charge is heavily dependent on external stimuli; for example, the band would bend more as the external illumination intensity increased or the surface-confined redox probe decreased, indicating that the electrostatic interaction on the surface-tethered species is favoured by attractive forces, with the G value increasing above zero. Furthermore, when the dielectric constant of the solvent decreases, the influence of space charge on the electrostatic interaction becomes more apparent. These findings have obvious implications for a thorough grasp of kinetic and thermodynamic studies of charge transport at the

electrified semiconductor/liquid interface, as well as for gaining a better understanding of electrostatic impacts on chemical reactivity.

Alkoxyamine cleavage catalyzed by electrostatics

Beyond using electric fields to catalyse redox or single-molecule reactions on silicon substrates, chemists are working hard to use an external electric field to catalyse non-redox processes. Alkoxyamines are undoubtedly the most important precursors in the fields of nitroxide-mediated polymerization, smart material design, and theranostics. However, they require either rather high temperatures or high-energy irradiation to initiate their homolytic activity, which might result in either undesired side effects or cancer of live cells. Recently, electrochemically controllable C-ON cleavage was reported using electricity as an alternative stimulus of alkoxyamine decomposition at room temperature, indicating that alkoxyamine electrochemical cleavage is sensitive to electrostatic environments such as molecular structure and supporting electrolytes and solvents. The creation of an alkoxyamine molecular junction in the STM-BJ setup quantifies the amount of the electrostatic influence on the homolytic cleavage of alkoxyamines. It, on the other hand, can undergo a one-electron electrochemical oxidation to generate an unstable cation radical intermediate that rapidly breaks into a nitroxide and a carbocation, signalling a sequential Electrochemical–Chemical–Electrochemical (ECE) process. A series of voltammetric tests using digital simulations and quantum calculations show that electrostatic surroundings (i.e., solvents, ion-pairing, and electrolytic concentration) in the electrolytes have a major impact on the collapse of the alkoxyamine cation radicals. Importantly, when alkoxyamines are grafted on the silicon surface, the amount of fragments may be controlled by varying the anodization period of applied positive biases, implying a flexible technique for creating in situ active nitroxides and carbocations utilised to govern chemical synthesis. We covalently bonded an alkoxyamine derivative to a Si (100) surface and used an anodic bias to cause its breakdown into a diffusive nitroxide radical and a surface-tethered carbocation, for example. By varying the anodization period applied to alkoxyamine monolayers, the density of active carbocations and hence the coverage of a generated redox probe tagged monolayer can be controlled. The electrostatic effect is extended to the control of organic electrosynthesis in this proof-of-concept experiment.

Conclusions and future prospects

Since the first experimental evidence of electrostatic catalysis of C–C bond formation at individual-molecule interfaces, scientists have had a novel idea to revolutionise conventional reactions catalysed by specific catalysts: using oriented electric fields as smart catalysts to catalyse chemical synthesis. Although electrostatic catalysis has received much attention, research into electrostatics as a chemical change effector is still in its infancy. Because of the orientation and strength issues, most work on electrostatic effects has been limited to theoretical investigations and individual-molecule studies; thus, the development of versatile platforms to control the orientation and intensity of an external electric field at will is an extremely appealing approach toward electrostatic catalysis experiments. The functionalization of the semiconductor silicon surface follows the evolution of the electrostatic effect from directing chemical bonding research at the nanoscale to manipulating chemical processes at the mesoscale. We summarised the progress of electrostatic catalysis based on a monolayer-functionalized silicon surface in this review, and the contents include: 1) developing wet chemistry methods for preparing stable monolayers on silicon electrodes; 2) revealing the effect induced by space charge on non-ideal voltammetric behaviours in semiconductor electrochemistry; and 3) investigating the effect of electrostatic interactions on the electrochemical reactivity of a redox nitride. These investigations, however, are unlikely to be useful for chemical processes at the preparative scale. The prospects of electrostatic catalysis are to establish the static electric field as a "smart reagent" a catalyst or inhibitor in a wide range of chemical reactions; this will bring electrostatic catalysis into the realm of chemical methods that are both clean and green, as well as capable of processing workable quantities of materials. The discovery that the electroactivity of nitroxide radicals may be controlled by electrostatic forces should assist in the creation of electrocatalytic heterogeneous systems related to the homogeneous reactions of surface-confined monolayers. In comparison to grafting TEMPO molecules on highly doped silicon surfaces, the heterogeneous oxidation potential of bromide to bromine is driven contrathermodynamically by up to 500 mV under light when attaching the redox mediator of TEMPO monolayers to weakly doped silicon electrodes. Polymerization strategy development is also of tremendous present importance in both basic investigations and practical applications of surface polymers. Electrostatically controllable C-ON homolysis of alkoxyamine molecules opens up a new avenue for future surface grafting methodologies controlled by electric fields in the absence of initiators, stabilisers, and dispersants, which is far less dangerous than traditional thermal and irradiation-triggered polymerizations.