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Research Paper

Self-assembled monolayers of N-heterocyclic carbene on gold: Stability under ultrasonic circumstance and computational study

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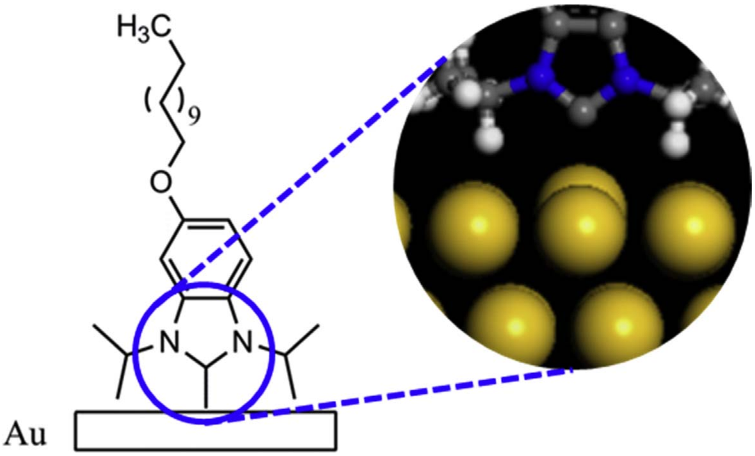
GRAPHICAL ABSTRACT



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ABSTRACT

Self-assembled monolayers (SAMs) of N-heterocyclic carbene (NHC) are built up on gold substrate. Electrochemical impedance spectroscopy (EIS) tests show that the NHC-based SAMs exhibit high stability under ultrasonic circumstance, over 90% of NHC molecules being retained at gold surfaces after ultrasonic treatment of 10 min in water. Computations of density functional theory (DFT) demonstrate the preferential adsorption of NHC molecules at atop sites of Au (1 1 1) plane, and the strong interaction between NHC molecules and Au surfaces is attributed to the bonding between 2-position C atoms and Au atoms by the hybridization of the C 2*p* orbitals with the Au 5*d* and 6*s* orbitals.

1. Introduction

Due to their wide applications in construction of functional surfaces, self-assembled monolayers (SAMs) on flat gold surfaces have attracted more and more attention since the landmark report on thiol-based SAMs on gold by Nuzzo and Allara in 1983 [1,2]. The poor stability of thiol-based SAMs on gold, however, seriously impedes their applications in ambient and aqueous environments [3,4], even though much effort has been made for the improvement in stability.

Recently, it was demonstrated in several reports that N-heterocyclic carbenes (NHCs) as an alternative to thiol compounds can strongly bind to gold surfaces to form stable SAMs [5–8]. It is reported that NHC-

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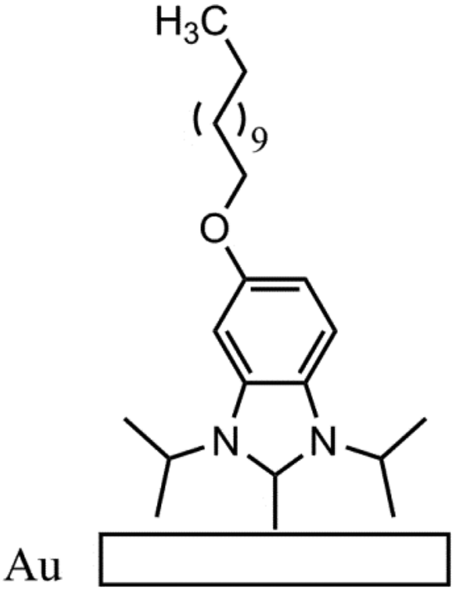

Fig. 1. NHC-based SAM on gold.

based SAMs exhibit better chemical stability than thiol-based SAMs in both organic and aqueous solutions [7]. In contrast, physical stability of SAMs was paid little attention. In surface modification area, for instance, ultrasound is a common technique wildly used to remove fouling on substrates or inclusion in functionalized layers of surfaces. Therefore, it is necessary to investigate the stability of NHC-based SAMs in ultrasonic circumstance.

In comparison to imidazole-based carbene analogues, furthermore, benzimidazole-based carbenes can form more stable SAMs on gold because of an extended π-system [7]. Moreover, the synthetic flexibility of benzimidazole-based carbenes with various substituents on the benzenoid segments could facilitate their potential applications in surface functionality. Herein we pay much attention to a long-chain benzimidazole-based carbene (Fig. 1) because of its potential applications in the fabrications of modified electrodes and superhydrophobic surfaces.

Although NHCs has been used to functionalize the surfaces of both gold nanoparticle and planar gold, the adsorption mechanism of NHCs on gold remains unclear [6–12]. In previous reports, density functional theory (DFT) calculations shows NHCs bind at ‘atop’ sites via a single Au-C bond and the bond strength is approximately 25 kJ/mol stronger than Au-S bond on Au (1 1 1) [7,12]. However, the details of the interaction between NHCs and gold surfaces are still deficient. In this work, we perform DFT calculations to achieve the optimized adsorption configuration, and then analyze the state densities of bonding atoms to explore both hybridization of orbitals during formation of Au-C bond and roles of Au atoms and C atoms in electron transfer.

2. Experimental and methods

2.1. Materials

NHC (Fig. 1) was synthesized through a modified procedure according to reference [7] (see Supplementary material). Gold-coated silicon wafers (50 nm gold deposited on a 10 nm chromium adhesion layer) were cut into 1.0 cm × 1.0 cm pieces, and then were mounted to a glass-made cell by a PTFE holder with an exposed area of 0.28 cm^2 as working face. Prior to use, the wafer pieces were ultrasonically cleaned in ultrapure water for 5 min, followed by rinsing with ethanol and dried with N_2 stream.

2.2. Fabrication of SAMs on gold

Before fabricating SAMs, 10 cycles of cyclic voltammetry were carried out for Au surfaces in 0.1 M H_2SO_4 at a scanning rate of 100 mV/s with the potential range from −0.1 V to 1.5 V (vs. SCE). After dried with N_2 stream, the wafer pieces were immediately immersed in an anhydrous toluene solution of NHC with a concentration of 1.0 mM for 24 h at 25 °C under nitrogen atmosphere in a glove box, followed by rinsing with anhydrous THF and dried with N_2 stream. X-ray photoelectron spectroscopy (XPS) analysis confirms the formation of NHC-SAMs on gold (see Supplementary material).

2.3. Tests for stability of SAMs

The NHC-functionalized surfaces were immersed in pure water. After 24 h the wafer pieces were withdrawn out of the solutions and dried with N_2 stream, and then electrochemical impedance spectroscopy (EIS) measurements for those surfaces were performed in 5 mM/5 mM $K_4Fe(CN)_6/K_3Fe(CN)_6$ aqueous solutions with 0.1 M $NaClO_4$ as the supporting electrolyte with a counter electrode of Pt sheet. A saturated calomel electrode (SCE) was employed as reference for all potential measurements. EIS were recorded at open-circuit potential over the frequency range of 100 kHz–0.01 Hz with a perturbation of 5 mV amplitude (peak to peak) at 25 ± 1 °C. Additionally, stability of NHC-based SAMs was also tested at room temperature (25 °C) in an sonicator (Durasonic PS-30, China) with an ultrasonic frequency of 40 kHz and an ultrasonic power of 180 W. EIS of NHC-functionalized surfaces were recorded in $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ aqueous solution at open-circuit potential (ca. 188 mV vs. SCE) after being successively sonicated in pure water. All electrochemical measurements were carried out on an IVIUM Vertax electrochemical workstation controlled by IVIUM software.

2.4. Computational details

Periodic DFT calculations were performed without any symmetry constraint using $Dmol^3$ module in Materials Studio software 6.0. A fcc unit cell of gold was first optimized prior to further operation. Then *p* (3 × 2) supercells of Au (1 1 1) containing four atomic layers were created on the basis of the optimized unit cell. The slabs were separated from their periodic images in the *z*-direction by a vacuum space of 35 Å. NHC molecules were then added near to the upper surfaces of the slabs at positions corresponding to atop, bridge, hcp hollow and fcc hollow sites, respectively (Fig. 2). The initial distances between gold atoms and 2-position carbon atoms of NHCs were set at 4.0 Å. In all calculations, the bottom two layers of Au atoms were fixed at the bulk positions, whereas the atoms in the two topmost layers as well as the adsorbed molecule were allowed to fully relax.

All electron calculations with the relativistic core treatment were made with double-numeric basis set (DNP 4.4) with both *d* and *p* orbital polarization functions in all DFT calculations [13]. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE)

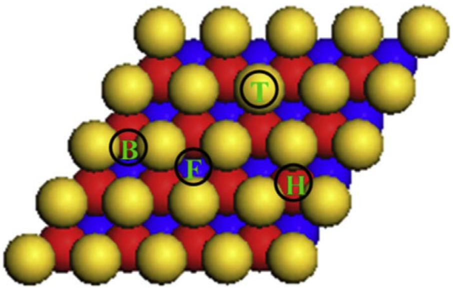

Fig. 2. Adsorption sites for NHC on Au (1 1 1). T: atop; B: bridge; H: hcp hollow; F: fcc hollow. Yellow: first layer Au atoms; red: second layer; blue: third layer.