Computational Chemistry and Electrochemical Studies of Adsorption Behavior of Organic Additives during Gold Deposition in Cyanide-free Electrolytes

Xuefeng Ren[a], Ying Song[a], Anmin Liu[a], Jie Zhang[a], Guohui Yuan[a], Peixia Yang[a], Jinqiu Zhang[a], Maozhong An[a,*], Daniel Matera[b], Gang Wu[b,**]

[a] State Key Laboratory of Urban Water Resource and Environment, School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China
[b] Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States

ARTICLE INFO

ABSTRACT

In this work, a combined approach using density functional theory (DFT), molecular dynamic simulations, and electrochemical experiments was developed to study organic additives used for a cyanide-free gold electrodeposition process. When 5,5-dimethylhydantoin (DMH) is used as the complexing agent, organic additives with either imino groups or nitrogenous heterocyclic rings including polyethyleneimine (PEI), 2,2′-bipyridine, and nicotinic acid (NA) were systematically investigated. Electronic properties and orbital information of these studied additives were determined by quantum chemical calculations based on DFT. Compared to the other additives, PEI was predicted as the most promising one for the introduced DMH based gold electrodeposition. The theoretical prediction was further verified by using experimental results. In particular, the cathodic polarization of the gold electrodeposition was significantly improved in the presence of PEI. Also, the resulting gold electrodeposit shows obviously finer crystalline particles largely. In addition, molecular dynamic simulations determined that PEI molecules possess optimized adsorption behavior on the gold surface, suggesting its effectiveness to be additive in the studied cyanide-free Au-electrodeposition electrolytes.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Due to their excellent physical, chemical, and electrochemical properties, electrodeposited gold films are widely used for numerous decorative and functional applications [1–3]. Nowadays, the majority of operational gold electroplating electrolytes are still cyanide-based, capable of providing dense and uniform gold films at low cost. The cyanide-based gold electroplating electrolytes also have high current efficiency and good stability, regardless of alkaline, neutral or acidic conditions. Unfortunately, cyanide is an extremely toxic chemical, yielding high risks to human health and the environment, especially when operated at a relatively high temperature [4]. To solve this problem, a number of attempts have been made in the past few decades to develop cyanide-free gold electroplating electrolytes [5–10].

Due to its ability to coordinate with many metal ions, including Au³⁺ [11–13], 5,5-dimethylhydantoin (DMH), a derivative of hydantoin, was selected herein for use as a complexing agent to replace the toxic cyanide, The solubility of DMH in alkaline solutions is better than that in neutral or acid solutions due to the ionization reaction provided in equation (1):

$$DMH \rightleftarrows DMH^- + H^+. \tag{1}$$

Thus, a stable cyanide-free gold electroplating electrolyte can be utilized with DMH as the complexing agent. However, standalone DMH still cannot provide a gold electrodeposit of sufficient quality, and proper additives are needed to improve the electrodeposited Au films [11,14]. Unfortunately, investigating potential additives through experimental approach is both expensive and time-consuming. Therefore, it is highly desirable to create a more effective approach when designing and optimizing additive structures for utilization in cyanide-free gold electroplating.

* Corresponding author. Tel/fax: +86 451 86418616.
** Corresponding author.
E-mail addresses: mzan@hit.edu.cn (M. An), gangwu@buffalo.edu (G. Wu).

In the past decades, quantum chemical calculations and molecular dynamic (MD) simulations have emerged as an effective technique for the calculation [15–19] and simulation [20–23] of small chemical systems to understand and predict their properties at the molecular level. Especially, both theoretical methods have been widely used to investigate the molecular configurations, electronic structures, reactivity of additives [24–26] and inhibitors [27–29] as well as the adsorption property of various organic molecules on metal surfaces [30–34]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) eigenvalues and the HOMO-LUMO gap (ΔE) are the most commonly used parameters to interpret the interaction mechanisms occurring between organic additives and metal surfaces at the molecular level [35–37]. MD simulations are also widely employed to study the adsorption interactions between organics and metal surfaces [18,38–40], and can provide insight into the understanding of additives with superior properties and interaction energies to explain the influence of additives during the process of metal electrodeposition [41]. Particularly, high binding energy values mean that organic additive molecules will give high inhibition on the metal electrodeposition. Therefore, combining quantum chemical calculations and MD simulations with experimental investigation and experimental validation have emerged as a highly efficient methodology to study additives during the electrodeposition process [42–46].

Regarding the gold electrodeposition, several polyamines or nitrogenous heterocyclic compounds have been demonstrated as good additives [47–49]. However, their performance are still not sufficient to deposit high-quality Au films. Also, these explorations to identify effective additives are only relied on time-consuming and high-cost electroplating experiments. In this work, we developed a new approach to theoretically predicting additive performance, which was further verified by experimental studies. In particular, polyethyleneimine (PEI), 2,2′-bipyridine, and nicotinic acid (NA) containing either imino groups or nitrogenous heterocyclic rings were selected to be the potential additives for the DMH-based gold electroplating electrolytes. At first, quantum chemical calculations were employed to investigate the electronic

properties and orbital information of these studied additives. Molecular dynamic simulations were employed to study the adsorption behavior of PEI, 2,2′-bipyridine, NA, and DMH on a gold surface. Then, the adsorption of studied additives on cathodic metal surfaces was predicted. Experimentally, cathodic polarization curves, macroscopic images of gold deposits, and scanning electron microscope (SEM) images were analyzed for further selection of additives. As a result, PEI, one polymer with many imino groups, was demonstrated to be an excellent additive for the gold electroplating electrolyte using DMH as the complexing agent.

2. Theoretical methods and experimental details

2.1. Quantum chemical calculations and MD simulations

All quantum chemical calculations were carried out by density functional theory (DFT) using the B3LYP functional method. In the geometry optimization and molecular orbital characteristic analysis, a 6-311G basis set was used for all atoms of the studied systems. All calculations on these systems under investigation were performed using the Gaussian 09 program package at 318 K with water as solvent in the IEFPCM theoretical model.

MD simulations of the adsorption interactions between PEI, 2,2′-bipyridine, NA, or DMH molecules and Au (111) surface were carried out in simulation boxes with periodic boundary conditions using Materials Studio (from Accelrus Inc). The MD simulation boxes consisted of a gold surface (cleaved along the (111) crystal face), a liquid phase and a vacuum layer of 1 nm height. The liquid phase was composed of water molecules with a density of 1 g/cm³ and two PEI molecules, four 2,2′-bipyridine, NA, or DMH molecules, respectively. NVT ensemble and COMPASS force field were employed, with a time step of 1 fs and simulation time of 500 ps at 318 K. The interaction energy $E_{\text{organic-surface}}$ between the organic and metal surface is calculated as according to equation (2).

$$E_{\text{organic-surface}} = E_{\text{total}} - E_{\text{organic}} - E_{\text{surface}} \tag{2}$$

Where E_{total} is the total energy of the organic together with the metal surface, E_{organic} and E_{surface} are the total energy of the organic
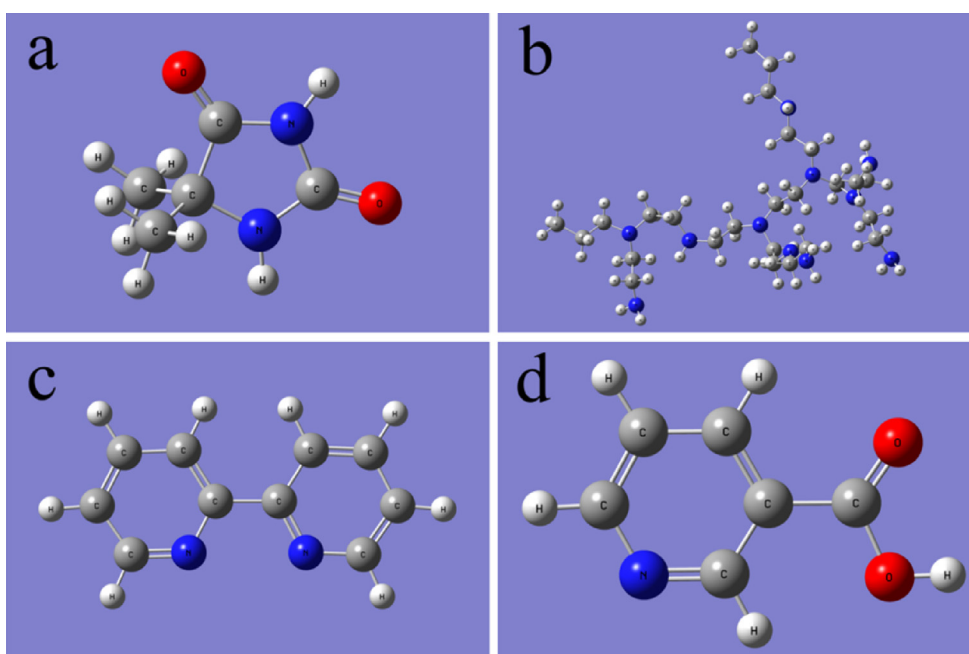

Fig. 1. Molecular structures of (a) DMH, (b) PEI, (c) 2,2′-bipyridine, and (d) NA.