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Feature article

Metal complex oligomer and polymer wires on electrodes: Tactical constructions and versatile functionalities

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ABSTRACT

This review covers recent progress in the construction of metal complex wires on various substrates via the stepwise coordination method, their functions, and the electrochemical evaluation of bis(terpyridine) metal complex oligomer wires on electrodes. In the layer-by-layer process of metal complex wire construction, various combinations of anchor ligands, metal sources, and bridging ligands have been used. The prepared structures show multiple functions, including photocurrent generation, catalytic activity, insulation properties, and long-range electron transport abilities. The electron transport behavior, and the long-range electron transport abilities from the terminal redox site to the electrode via bis(terpyridine)metal complex wires, were evaluated using potential step chronoamperometry. The remarkable long-range electron transport abilities were evidenced in the small values for the attenuation factor, β. The influence of the building blocks in the metal complex wires on the β value and the electron transfer rate constant was demonstrated.

1. General introduction

In recent decades, the size of semiconductor-based electric devices has shrunk from a few hundred micrometers to a few nanometers, and their performance has improved drastically. These electric devices are manufactured using the top-down method, which is the technique that is most commonly used to construct nano-size structures (an example of a technique that can be used in this process is photolithography). However, there is a belief that the top-down method will reach a limit in the near future, because of the restriction on the patterning resolution that is imposed by the wavelength of light used in the photolithography process, the leak current from the nanometer-scale electric circuits, and the enormous manufacturing costs. In order to resolve these problems, another approach to the fabrication of nano-size structures (i.e., the bottom-up approach) has become attractive. In this method, structures are constructed by assembling nano- or angstrom-size elements; for example, molecules, atoms, ions, and nanoparticles. These elements will automatically assemble to form the desired structures via electric, hydrophilic/hydrophobic, and various intermolecular interactions among them. This phenomenon is called self-assembly. The self-assembly bottom-up technique allows fabricating a large number of nanometer systems easily and inexpensively. Therefore, many researchers have studied the bottom-up method to create new materials or systems, and to establish techniques to control the self-assembly process. In this review, we will present recent researches related to the structures created on substrates via molecular self-assembly using the stepwise coordination process, and we evaluate their electrochemical properties.

2. Modification of substrate surfaces by self-assembled monolayers

2.1. Introduction

The fabrication of electric devices composed of molecules is one of the ultimate goals of nanotechnology. It is expected that molecular-based electronic devices would have magnetic, photophysical, and chemical properties derived from the compositional molecules; this is different from known silicon-based electric devices. Many research groups have fabricated and reported the basic components of molecular devices such as switches [1] and diodes [2]. In the construction of molecular electric systems, the signal detection from molecules is important to input or output information. In addition, high stability is required in the long-term performance and the responsivity to signals. The immobilization of molecules on electrodes is one of the methods that can be used to fulfill these requirements. Molecules immobilized on electrode surfaces should show more rapid responses and higher durability

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than molecules in solution. Thus, surface modification with molecules is an important process for the achievement of molecular-based devices.

Langmuir–Blodgett (LB) films [3–5], electropolymerization [6,7], chemical vapor deposition (CVD) [8–10], and self-assembled monolayers (SAMs) are the most commonly used surface modification techniques; the preparation of SAMs on various substrates (such as metal, semiconductor, or metal oxide material surfaces) can be achieved easily via immersion in a solution.

2.2. Fabrication of self-assembled monolayers on substrates

Typical combinations of substrates and molecules are listed in Table 1. The SAM fabrication has been performed on various substrates. Among these, gold, indium tin oxide (ITO), and silicon are most usually used as the platforms for SAMs. Gold is the metal that is most commonly applied as electrodes. Gold has excellent thermal and electric conductivity, and a surface that is inert against heat, humidity, oxidation, and a number of chemical reactions. Gold-coated electrodes are typically prepared using vapor deposition on a silicon or mica substrate, followed by annealing with a hydrogen flame to form an Au(111) surface before use. The treated Au electrode is then immersed in a solution of compounds containing thiol, disulfide, SCN, or SAc moieties to fabricate an SAM [11–25]. The formation process, arrangement, electrochemical properties and conductivity of SAMs on Au electrodes have been investigated previously.

The ITO is a transparent electrode material, and is attractive for electrodes in dye-sensitized solar cells and organic electric luminescence devices. For the modification of ITO surfaces, usually phosphoric acid, trialkoxysilane, and carboxylic acid [28–34] are used. Many studies have reported the photochemical properties of SAMs on ITO surfaces, because the transparency of ITO is suitable for photo-irradiation experiments. Matsuo et al. modified ITO with a mixed SAM containing a C_{60} fullerene and an iron atom-doped C_{70} fullerene, and demonstrated that this modified electrode generated a bidirectional photocurrent under irradiation with 340 nm and 490 nm light [31]. Nesterov and coworkers prepared thiophene SAMs on ITO, and performed additional modifications using electrochemical polymerization [32]. The photocurrent generation in ITO modified with SAMs and poly(3,4-ethylenedioxythiophene) was evaluated in the presence of methyl viologen as an electron carrier, and its photovoltaic performance was superior to that of a control device prepared using the spin-coating method. Our laboratory has also reported photochemically functional SAMs on ITO (Fig. 1) [33]. We modified ITO with 3-ferrocenyl-4′-carboxylazobenzene, and succeeded in the *cis*- and *trans*- isomerization of the azobenzene unit with a single wavelength (546 nm), and in the control of the ferrocene valence state. In another study, we sequentially prepared porphyrin-terminated $M(tpy)_2$ (tpy = 2,2′:6′,2″-terpyridine, M = Fe^{2+}, Co^{2+}, Zn^{2+}) wires on an ITO surface modified with 4-[(2,2′:6′,2″-terpyridin)-4″-yl]benzoic acid [34]. The photo-electron conversion abilities of these wires were evaluated in an Na_2SO_4 aqueous solution containing triethanolamine, and the $Co(tpy)_2$-bridged system showed the highest quantum efficiency.

Silicon is the most widely used semiconductor and core material in the electronics field. The SAMs on SiO_2 and hydrogen-terminated Si have been reported. Trialkoxysilane or trichlorosilane moieties are used for the modification of SiO_2 surfaces, and SAMs are prepared using the thermal method or the vapor phase method [35–39]. The thermal stability of an organic silane SAM has been investigated, and the SAM was not destroyed at 300 °C under vacuum conditions [39]. Hydrogen-terminated silicon is an attractive substrate, due in part to the fact that Si–C bonds can be formed between the substrate and the immobilized molecules without any SiO_2 insulating layer [40–43,45–50]. The connection of SAMs to a silicon surface via covalent bonds allows making a direct evaluation of the electric properties, and this process also results in high thermal and chemical durability. The hydrosilylation reaction between Si–H bonds and alkyne or alkene molecules is one of the most popular methods for the modification of hydrogen-terminated silicon surfaces. This reaction is typically performed under heated conditions or UV light irradiation, but reactions under mild conditions [48] and under visible light irradiation [49] have also been reported. Recently, Huck and Buriak reported that aromatic electron acceptors (e.g., chlorobenzene) accelerated the UV-

Table 1
Combinations of molecules and substrates for the formation of SAMs.

Substrate	Molecule	Ref.	Substrate	Molecule	Ref.
Au	R–SH	[11–25]	X–Si (X = Cl, Br, I)	R–OH	[51–55]
	R–S–S–R			R–MgBr	
	R–SCN			R–Na	
	R–SAc				
Pt	R–SH	[26,27]	GeO_2	$R–SiX_3$ (X = Cl, OMe, OEt)	[61]
	R–NC		X–Ge (X = Cl, Br)	R–MgBr	[62–66]
				R–SH	
ITO	$R–SiX_3$ (X = Cl, OMe, OEt)	[28–34]	H–Ge	Alkenes	[67–69]
	$R–PO(OH)_2$			R–SH	
	R–COOH		H–C	Alkenes	[70–74]
				R–I	
				R–N=N–R	
SiO_2, glass	$R–SiX_3$ (X = Cl, OMe, OEt)	[35–39]	X–C (X = Cl, Br)	R–MgBr	[75–77]
				R–SH	
				R–SNa	
				Alkenes	
			Glassy Carbon	R–I	[78,79]
H–Si	Alkynes	[40–50]	GaAs	R–SH	[80–83]
	Alkenes		InP	R–SH	[84–86]
	R–OH		TiO_2	Alkenes	[87–89]
	R–CHO			$R–CO_2H$	
	R–SH			$R–PO(OH)_2$	
	R–MgBr		Aluminum Oxide	$R–PO(OH)_2$	[90–92,123]
	R–Li			$R–Si(OEt)_3$	
			SiC	Alkenes	[93–96]
				$R–Si(OMe)_3$	