

# Assembly of nanosize metallic particles and molecular wires on electrode surfaces

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This article highlights recent developments in the assembly of nanosize materials on electrode surfaces. A brief historical background of the field is given, followed by a selection of topics of particular current interest. We focus especially on the assembly of nanosize metallic particles and molecular wires on gold and silicon electrode surfaces. The fabrication, properties, and characteristics of functional nanostructured biointerfaces on electrode surfaces are also described.

## Introduction

Nanotechnology has attracted the attention of scientists from different fields in search of new functional materials.<sup>1</sup> Numerous nanometer-scale ( $10^{-9}$  m in length) materials have been shown to exhibit unusual and interesting physical properties different from those of the corresponding bulk materials. The attachment of nanosize structures to flat surfaces is an important prerequisite to exert their function on matrixes for application in the field of nanoscience. In particular, much effort has been devoted to the immobilization strategy of metallic nanoparticles or nanosize coordination polymers on electrode surfaces.

Transition-metal nanoparticles have attracted a great deal of attention in the last 10 years. Nanoparticles are generally

defined to be less than 100 nm in length, and their preparation, structure determination, and applications are topics of current interest.<sup>2</sup> General methods to prepare nanoparticles are the chemical reduction of metal salts in the presence of capping materials such as polymers or surfactants. The preparation of nanoparticles using alkanethiols as the capping material has been greatly facilitated by the methods of Brust *et al.*<sup>3</sup> The mild conditions used in this process are compatible with a wide range of ligand functionality (Fig. 1(a)). Nanoparticle size can be controlled through the stoichiometry of the metal salt to the capping ligand, provided that the size is in the range of 1.0 to 10 nm. Many approaches have been employed to prepare important classes of novel functionalized nanoparticles. Among them, the place-exchange reaction on the nanoparticle surface is a straightforward and widely exploited way to introduce novel functionalities on the nanoparticle without drastic experimental synthetic conditions.<sup>4</sup> It is noteworthy that protecting reagents not only stabilize the nanoparticle but also create further functionalization with various ligands based on the desired applications.

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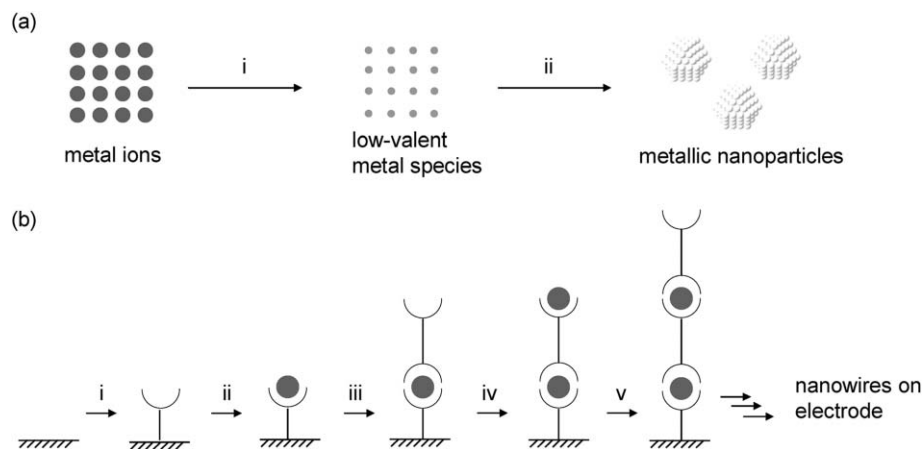
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**Fig. 1** (a) Preparation of metal nanoparticles. (i) reduction with reducing reagents or energy, (ii) protection with capping materials. (b) Layer-by-layer surface functionalization. (i) immobilization of surface-anchoring ligand, (ii) complexation with metal ion, (iii) complexation with linker ligand, (iv) complexation with metal ion, (v) complexation with linker ligand.

Controlling the structure and length of nanowires is also one of the challenging goals of contemporary material science. One prospective approach to this problem is the preparation of coordination polymers with ordered structure based on organometallic and coordination chemistry.<sup>5</sup> A layer-by-layer technique on electrodes has been demonstrated as a means to assemble multilayer inorganic (metal)–organic (ligand) structures (Fig. 1(b)). The main advantage of this technique is its simplicity and flexibility for preparing multiple complex layers without special instruments.

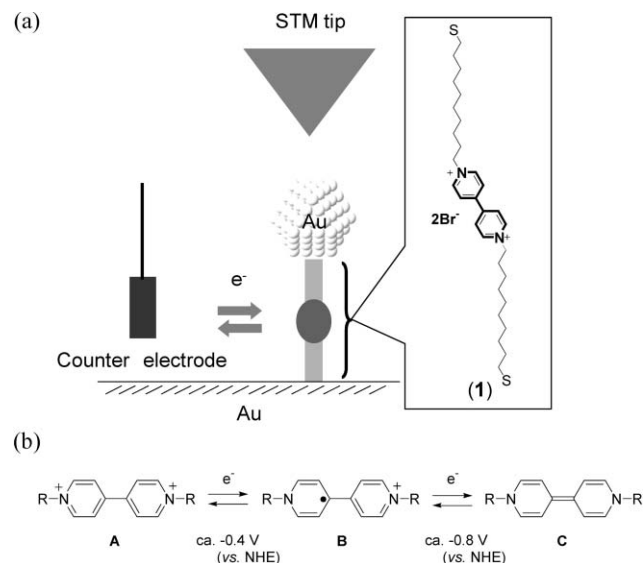
The nanostructures mentioned above can be easily synthesized, but assembling them on substrates for device applications in an ordered fashion remains a challenge. This article describes the recent representative advances in the simple and versatile immobilization processes of nanostructures, such as nanoparticles and nanowires, on electrode surfaces.

### Assembly on gold electrode surface

In recent years self-assembled monolayers (SAMs) on metal substrates have attracted the attention of many physicists and chemists for their ability to form ordered organic films with well-defined compositions and thicknesses.<sup>6</sup> They are potentially versatile building blocks for the development of advanced materials such as molecular electronic devices, and are prepared simply by immersing a substrate into a solution of the surface-active material. The driving force behind the spontaneous formation of the 2D assembly includes chemical bond formation of molecules with the surfaces and intermolecular interactions. In particular, the self-assembly of organosulfur compounds on a gold surface has been extensively studied, because thiol molecules are linked to a gold electrode surface by a strong S–Au bond ( $167 \text{ kJ mol}^{-1}$ ). Since self-assembled techniques have been widely studied and can help to construct a highly ordered nanoscale monolayer, it is beneficial to create a functional electrode surface.

Chen and Murray reported that gold nanoparticle (diameter *ca.* 2.0 nm) monolayers, fabricated by using ligand-exchange reactions with  $\alpha,\omega$ -dithiols as the chemical linkers, exhibited discrete charge-transfer features in differential pulse

voltammogram (DPV) measurements.<sup>7</sup> The single-electron transfer characteristics on the Au surface demonstrate the application potentialities of the use of these nanoscale entities as the building blocks for the fabrication of novel electronic devices. Schiffrin and Nichols reported a simple and unambiguous measurement of single-molecule resistance, achieved using a gold surface modified by gold nanoparticles (diameter: 6 nm) stabilized by redox switchable groups, 4,4'-bipyridinium dibromides (viologen molecules),<sup>8</sup> as chemical bridges (Fig. 2(a)). The layers were assembled by alternate dipping of an Au(111) film electrode in methanol solution of the viologen molecule and gold nanoparticle dispersion in toluene. The viologen group can be switched between its oxidized (A) and reduced (B and C) states by control of the potential (Fig. 2(b)). Using an external scanning tunneling microscope (STM) tip, they found that the viologen moieties were electrochemically addressable and exhibited electron-mediating properties on the modified surface.<sup>9</sup> The system is

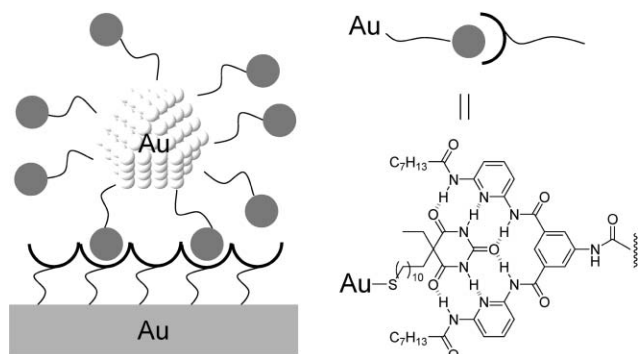


**Fig. 2** (a) Gold nanoparticle linked with a redox active molecule (1) on the gold surface. (b) Electrochemical properties of viologen molecule.

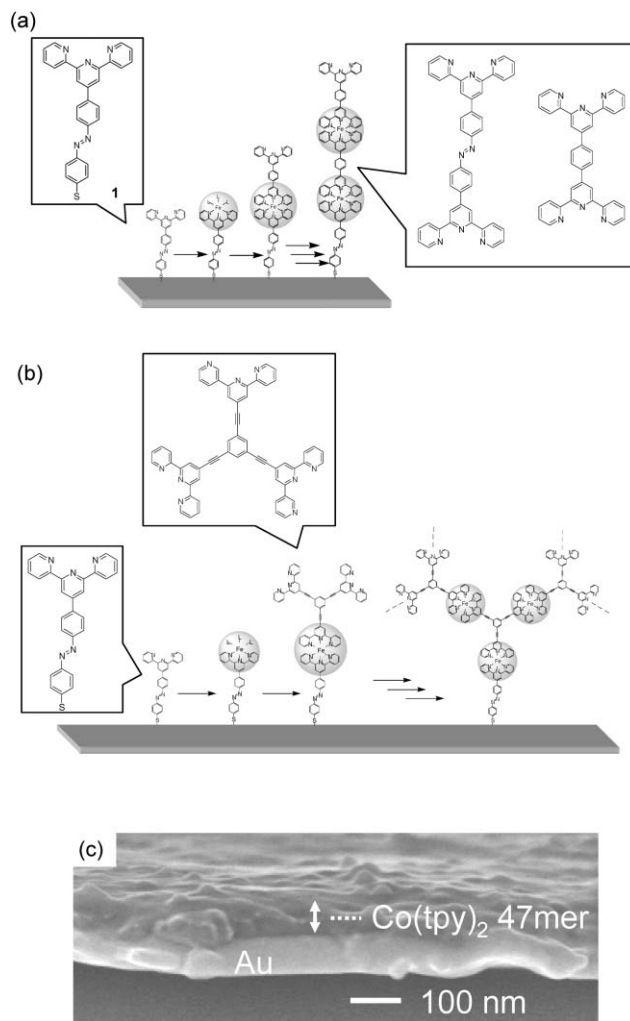
expected to serve as a nanosize electronic switch. Zirbs *et al.* reported the binding of gold nanoparticles to a surface *via* multiple hydrogen bonds (Fig. 3).<sup>10</sup> Moderate control of particle density was achieved by controlling the receptor density on the self-assembled monolayer surface. This method opens a general approach to nanoparticle and small object binding onto patterned surfaces.

Uosaki and co-workers reported that multilayers of gold nanoparticles covered by self-assembled monolayers containing a mixture of hexanethiol, ferrocenyl hexanethiol and mercaptoundecanoic acid were constructed on a Au(111) surface based on the electrostatic interaction between a carboxylate anion and metal cation.<sup>11</sup> Electrochemical measurements showed the electron is transferred between ferrocene and the Au(111) electrode through the gold nanoparticle cores and/or the ferrocene groups. Yamada and Nishihara reported that transition-metal nanoparticles (Au and Pd) protected by oligoferrocenethiol or anthraquinonethiol derivatives were electrochemically deposited onto a gold surface at a constant distance.<sup>12</sup> The prepared films exhibit specific spectroscopic characteristics derived from dipole-dipole interactions among adjacent particles densely fixed in the film. These characteristics cannot be explained by the behavior of single particles. This system can be utilized as a novel method for fabricating versatile metal nanoparticle films comprised of multiple layers by changing partners in the deposition processes.

Coordination chemistry provides a flexible method for creating organic-inorganic assemblies by incorporating metal ions with desired electrical, magnetic or optoelectric properties and organic ligands.<sup>13</sup> Monolayer films with a reactive terminal group have been extended into coordination polymers or supramolecular structures through covalent chemical reactions using layer-by-layer nanostructural growth.<sup>14</sup> If the building blocks were redox-active metal complexes, they would be of great interest in the investigation of fundamental aspects of charge transfer processes.<sup>15</sup> Recently, our group prepared  $\pi$ -conjugated bis(2,2':6',2''-terpyridine)metal polymer chains (Fig. 4(a)) and tris(2,2':6',2''-terpyridine)metal dendritic wedges (Fig. 4(b)) on gold surfaces using a sequential complexation process after the immobilization of surface-anchoring terpyridine ligand **1**.<sup>16</sup> In that study, we characterized the stepwise quantitative film formation by

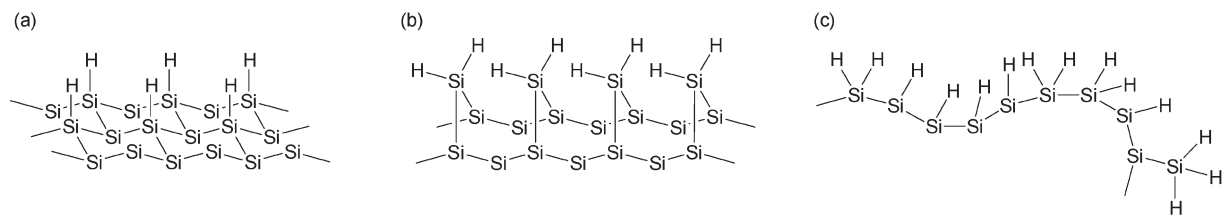


**Fig. 3** Concept of nanoparticle binding mediated by multiple hydrogen bonds.



**Fig. 4** Schematic representation of layer-by-layer growth with linear (a) and branched (b) terpyridine ligands with transition-metal ions on gold surface. (c) A side-view SEM image of a film composed of 47  $\text{Co}^{2+}$  complex units on a gold surface.

electrochemical techniques, water contact angle, UV-vis spectra and STM measurement at each step of monolayer formation. The SEM photograph of films with 47 layers of  $\text{Co}^{2+}$  and linear ligand indicates the growth of the film to a thickness of *ca.* 100 nm on Au in the side-view image (Fig. 4(c)). This thickness is in good agreement with the calculated result (2 nm (molecular unit length)  $\times$  47 layers). This method allows the formation of desired numbers of polymer units and desired sequences of hetero-metal structures in the polymer chain. In addition, the electron transport mechanism and kinetics of linear and branched oligomer wires were analyzed by potential-step chronoamperometry in detail owing to their highly organized structures. The observation suggested that the redox conduction in the oligomer films occurs not in a random-walk process (diffusion) but by successive electron hopping between neighboring redox sites through a molecular wire. Electrochemical studies of the redox-active monolayers on electrodes contributed to the understanding of long-range electron transfer<sup>17</sup> between metal electrodes and redox molecules, and these new types of



**Fig. 5** Schematic representations of hydrogen-terminated (a) Si(111), (b) Si(100) and (c) porous silicon surfaces.

redox-polymer films will be useful for the development of molecular electronics.

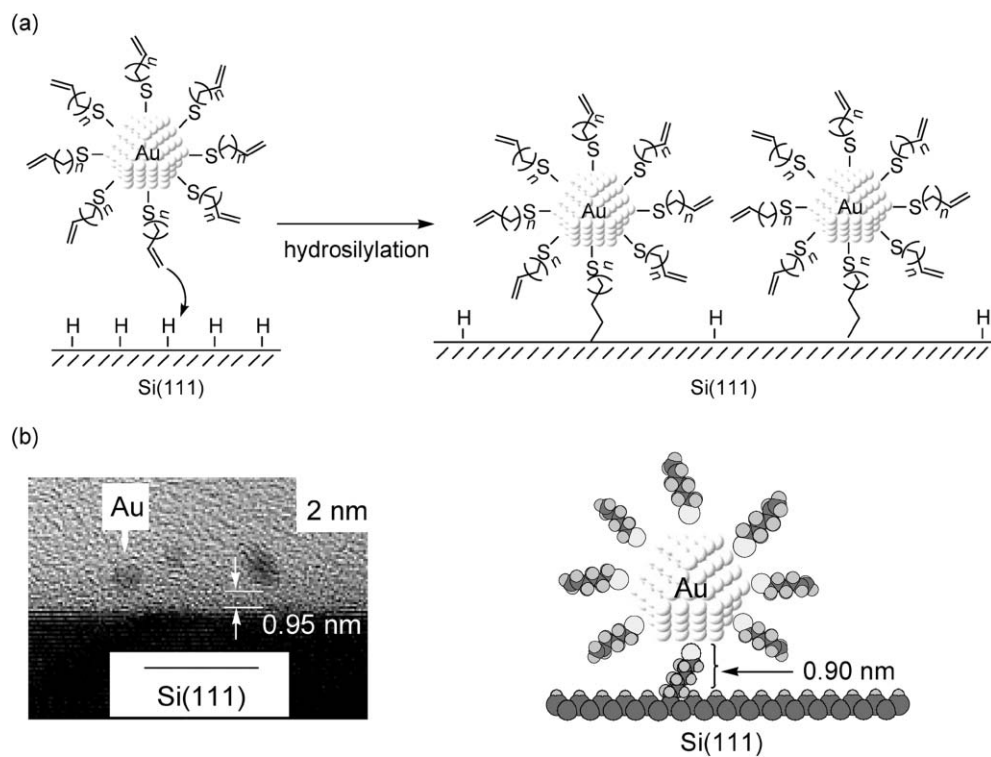
### Assembly on silicon electrode surface

Silicon is one of the most important materials in modern technology, and there has been strong interest in the chemical modification of silicon surfaces. Several techniques have been published on the self-assembly of ordered monolayer arrays on such surfaces. One approach to modifying silicon surfaces is to use silica-supported alkylsiloxane layers.<sup>18</sup> Although these layers are easily prepared by reacting alkyltrichlorosilane with an oxidized silicon surface, an insulating oxide layer is not desirable for many applications, such as electronic devices or sensor materials.

An alternative strategy is to prepare monolayers covalently bonded to a hydrogen-terminated silicon surface with 1-alkene molecules.<sup>19</sup> The reaction has been performed on both hydrogen-terminated crystalline Si(111) and Si(100) surfaces and on porous silicon (Fig. 5). Especially, hydrogen-terminated Si(111) is a kinetically stable silicon surface that

is an attractive starting point for the synthesis of novel modification surfaces. The monolayer is thermally highly stable, owing to the attachment of organic molecules to the surface *via* a stable covalent Si–C bond ( $340 \text{ kJ mol}^{-1}$ ). This hydrosilylation reaction is known to be promoted under thermal activation<sup>20</sup> or the irradiation of light<sup>21</sup> to form directly stable silicon–carbon covalent bonds on the silicon surface. A variety of organic monolayers have been demonstrated to attach covalently to silicon surfaces through silicon–carbon bonds. Such organic monolayers offer the potential for effective electron transfer at the silicon/organic layer interface, since there is no insulating layer (*i.e.*, no silicon oxide layer).

Considering the potential application of hydrogen-terminated silicon surfaces mentioned above, gold nanoparticles protected by functional surfactants such as  $\omega$ -alkene-1-thiols could be immobilized on a silicon surface through robust Si–C bonding (Fig. 6).<sup>22</sup> Moderate control of particle density on the silicon surface was achieved by controlling the reaction conditions. Gold nanoparticles immobilized on silicon surfaces were directly observed with cross-sectional TEM. Fig. 6(b) shows a cross-sectional TEM image of 5-hexene-1-thiolate



**Fig. 6** (a) Schematic representation of the immobilization of  $\omega$ -alkenene-1-thiol-functionalized gold nanoparticles on a hydrogen-terminated Si(111) surface. (b) Cross-sectional TEM image of 5-hexene-1-thiolate-protected gold nanoparticles on a hydrogen-terminated silicon surface (left) and calculated height in the formation of a silicon surface modified by 5-hexene-1-thiolate-protected gold nanoparticles (right).

immobilized on a silicon surface. The image clearly shows gold nanoparticles in the near surface layer surrounded by 5-hexene-1-thiol. Thus, the distance between the particle and the surface was estimated to be 0.95 nm, in fairly good agreement with the expected distance. This strategy can be applied to molecular architectures on semiconductor surfaces, leading to a promising technique for electronic applications such as single-electron transistors.

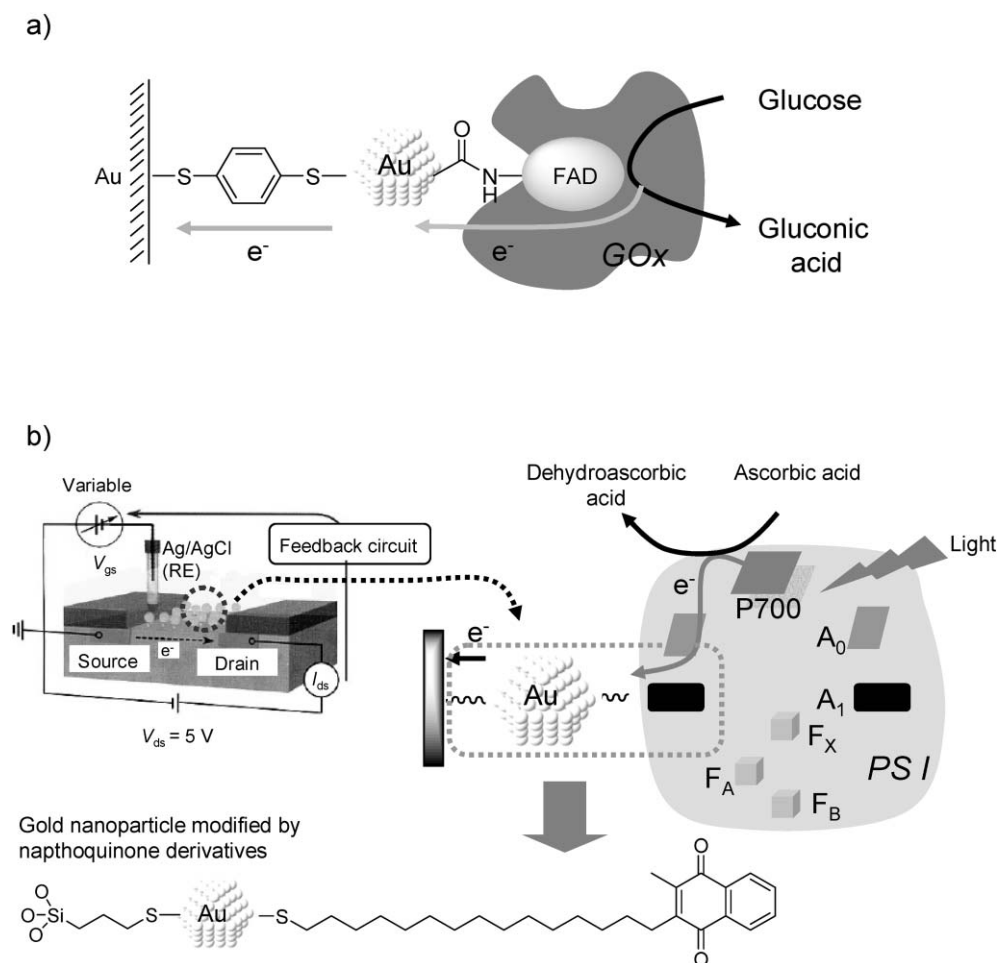
Quite recently, Altavilla *et al.* reported a similar method to prepare a film of magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ; 7 nm) covalently linked to a hydrogen-terminated silicon(111) surface.<sup>23</sup> They measured the field dependence of the magnetization of the immobilized particles at 2.5 K. At high fields, the magnetization saturates to a value that corresponds to  $3.8 \times 10^{-5} \text{ emu cm}^{-2}$  of the Si surface. This value is of the same order of magnitude as that expected for a regular, close-packed monolayer of an 8 nm coated  $\text{Fe}_3\text{O}_4$  nanoparticle (*ca.*  $8.5 \times 10^{-5} \text{ emu cm}^{-2}$ ). The modified silicon surface is a promising candidate for the fabrication of ultrahigh-density magnetic storage media or magneto-optical devices.

Although these reports presented here are still preliminary, they provide clear evidence that the synthetic procedure proposed can effectively provide a uniform extended layer of particles strongly bound to the substrate.

## Fabrication, properties, and application of bioconjugated nanostructures on electrode surfaces

Recently, opportunities for applying nanotechnology to biotechnology have increased, because many nanotechnological and biological systems operate on the same size scale.<sup>24</sup> Electronic communication of biomaterials with electronic transducers is a fundamental challenge in the rapidly developing field of bioelectronics.

Willner and co-workers reported that the electrical communication of glucose oxidase (GOx) was accomplished by the reconstitution of the apo-GOx on a flavin adenine dinucleotide (FAD) functionalized gold nanoparticle (diameter: 1.4 nm), which was linked to a gold electrode surface by a 1,4-benzenedithiol monolayer (Fig. 7(a)).<sup>25</sup> This study indicated that unprecedented effective electron transfer from the FAD moiety to the electrode occurred through the gold nanoparticle (electron transfer turnover rate  $4500 \text{ s}^{-1}$ ). In a control experiment, a gold electrode modified with an FAD monolayer on which apo-glucose oxidase was reconstituted lacked electrical communication with the electrode. This unprecedented efficient electron transfer communication between the redox protein and the electrode originated from the mediated electron transfer by a single gold nanoparticle that is



**Fig. 7** Electron transfer process of nanostructured biointerfaces on the electrode surface. (a) Enzyme-gold nanoparticle-gold electrode and (b) PSI-gold nanoparticle-FET gate.

conjugated to the protein assembly. This effective electron transfer communication between the nanoengineered redox enzyme and the electrode has important consequences for the sensitivity and selectivity of the enzyme electrode.

Photosynthesis has fascinated a large number of scientists who have expended much effort to imitate this process.<sup>26</sup> Photosystem I (PSI) in natural bio-components has already achieved extremely high and ultimate performance as the result of many cycles of natural selection and mutation, and it is well known that the quantum yield of charge separation at the reaction center is almost 100% in photosynthesis.<sup>27</sup> The high performance of PSI is the result of its well-designed spatial configuration (position, direction, etc.). Although a large number of trials on the application of PSI to electronic devices have been reported, successful artificial induction of PSI has been rare.<sup>28</sup> Hiraga (applied physics), Inoue (biology), Nishihara (synthetic chemistry), Minakata (electronics), Fujii (spectrochemistry), and their co-workers reported on the first successful output of electrons directly from PSI of thermophilic cyanobacteria to the gate of a field-effect transistor (FET) by bypassing electron flow *via* artificial vitamin K1 and gold nanoparticles (Fig. 7(b)).<sup>29</sup> Photo-electrons generated by the irradiation of the reconstituted PSI on the gate were found to control the FET. This biophotosensor system can be used to interpret gradation in images. Moreover, the biophotosensor is sufficiently stable for use for more than a year. The final goal of this system is to sense a small number of photons by utilizing the single transfer ability of a gold nanoparticle. Clearly, interdisciplinary research combining chemistry, physics, biology, microelectronics and material science will further develop the challenging topics of molecular electronics and machinery in functional science.

In the future, the molecular architecture of the bioconjugated nanostructure will play an important role in tailoring the requirements of a new generation of bio-nano hybrid devices. Although there remain a number of problems regarding the modification of nanostructured biointerface electrodes in a more controlled way, the ability to functionalize these nanostructures with biological molecules has opened new fields to utilize these nanostructure-bioconjugates for the fabrication of functional nanostructured biointerfaces in bioelectrochemical systems.

## Summary and outlook

The article has presented recent work on the assembly of nanosize materials, such as metallic nanoparticles and molecular nanosize wires, on gold and silicon electrode surfaces for biological application. These molecular assembly systems create a new class of materials at the molecular level. The advantage of the method is the possibility of introducing electro- and/or photo-functional chemical structure at desired positions in the wire or on the metallic nanoparticles. The application of such modified surfaces is proving invaluable for the interfacing and ordering of nanosize components. The assembly process described here is simply and broadly applicable, and can find applications in a variety of fields including the development of nanoelectronics and biosensors. For practical application it will be necessary to improve the

directional alignment and length disparity of nanosized materials on the surface. Further exciting developments in nanoscale science and technology are expected.

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