From Two- To Three-Dimensional Molecular Assemblies for Photoelectric Conversion

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Molecular assembling is one of the current interests in the field of bottom-up nanotechnology. Self-assembled monolayers of sulfur-containing molecules or supramolecular assemblies via surface sol-gel processes formed on conductive supports are chemically robust and can be easily fabricated without sophisticated instruments. We have fabricated various types of molecular assemblies consisting of donor-acceptor pairs on the surfaces of gold and indium-tin-oxide electrodes. Build-up of three-dimensional multistructures consisting of thiol dyes and gold nanoparticles also has been successful. These assemblies showed clear photocurrent responses in photoelectro-chemical cells. In this article, we will describe recent progress on photoelectric conversion using molecular assemblies especially focused on our research results.

key words: Photoinduced electron-transfer, Self-assembled monolayers, Photoelectric conversion, gold nanoparticles, surface sol-gel process

INTRODUCTION

Photoenergy conversion is primarily important for the development of clean energy generation systems such as solar cells, photoelectronic devices, and artificial photobiological systems. Organic compounds have promising advantages over inorganic compounds in terms of light absorptivity and easiness in thin film preparation. In addition, abilities of self-assembling or self-organization can be easily implanted in organic molecules. These characteristics have opened-up new approaches (that is, bottom-up approaches) in fabricating high-performance photoelectric conversion devices. Particularly, a dye-sensitized solar cell, in which an organic dye with functional groups was self-assembled (chemically bound) on the surfaces of a semiconductor thin film, was developed by several research groups.[1-3]

Photoinduced electron-transfer (ET) or charge-separation (CS) between an electron donor (D) and an electron acceptor (A) molecule is one of the most important photoreactions for photoenergy conversion, as has been verified in the reaction center of photosynthesis. Thus, build-up of those organic photoinduced ET systems on conductive supports make it possible to perform photoelectric conversion in monolayer or nanometer levels. In fact, Fujihira *et al* [4] have first fabricated D-A molecular systems on the electrode using the Langmuir-Blodgett (LB) method and have been successful for photocurrent generation. The LB method, however, is disadvantageous in terms of stability, uniformity, manipulation, and sophisticated instrumentation.

Self-assembled monolayers (SAMs) via gold-sulfer bond formation [5] are relatively new and superior to the LB films, since they can be prepared very easily without any expensive instruments and the molecules are chemically bound to the gold surface. We have reported, for the first time, fabrication of the SAM consisting of a D-A pair on the gold electrode and the photocurrent generation from this modified electrode in 1995. [6] Hereafter, various types of intra- and inter-molecular D-A monolayers and their photocurrent properties have been reported.[7, 8] In the meantime, self-assembling could be extended for transparent semiconductor electrodes such as an indium-tin-oxide (ITO) electrode.[9] In this article, we will describe recent progress on photoelectric conversion using SAMs and related multistructure assemblies especially focused on the researches of our group.

SELF-ASSEMBLED MONOLAYERS

A tris (2,2'-bipyridine) ruthenium (II) (Ru^{2+})-viologen (V^{2+}) couple is a well known D-A pair.[10] We have reported fabrication and photoelectrochemical properties of a series of SAMs containing Ru^{2+} (D) and V^{2+} (A), The earliest SAM of the Ru^{2+}-V^{2+} pair was a mixed SAM using **RuS** and **VS** (see Figure 1).[6] In the presence of triethanolamine (TEOA) as a sacrificial reagent, photocurrents were observed in the anodic
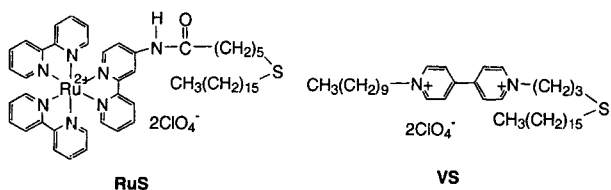
Figure 1. Molecular structures of ruthenium complex and viologen sulfides
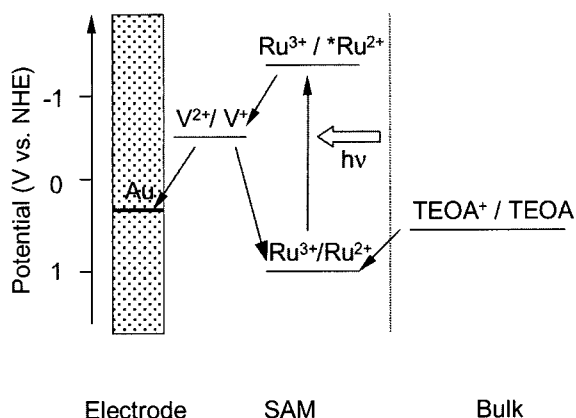
Figure 2. Photocurrent generation mechanism and electron flow.

Figure 3. Molecular structures of ruthenium complex-viologen linked thiols and ruthenium complex thiols.

direction and the photocurrent action spectrum overlapped well with the absorption spectrum of **RuS** in solution. These observations lead to the photocurrent mechanism and the electron flow as shown in Figure 2.

The intermolecular ET from the photoexcited Ru^{2+} ($*Ru^{2+}$) to V^{2+} generates a charge-separated state as Ru^{3+}-V^{+}. The oxidized complex, Ru^{3+}, is reduced by TEOA, so that the reverse ET is suppressed and the reduced viologen, V^{+}, gives an electron to the gold electrode, resulting anodic photocurrent generation.

Intramolecular ET seems to be superior to intermolecular ET in terms of photoelectric conversion efficiency because D and A can be appropriately aligned favorable to ET. From these view points, we have prepared linked thiol derivatives of Ru^{2+} and V^{2+} with different spacer-chain lengths between Ru^{2+}-V^{2+} and V^{2+}-S as shown in Figure 3.[11-14] The photocurrent mechanism is basically identical to Figure 2. Comparison of photocurrent intensities among RuCnVCmS and RuS has revealed that there seems to be an optimum distance between Ru^{2+} and V^{2+}, and that the distance between V^{2+} and S (connecting to electrode) is as short as possible.

In order to improve the efficiency of photoelectric conversion, suppression of reverse ET from V^{+} to Ru^{3+} is an important key. Early studies using organized viologen assemblies as electron accepting sites achieved highly-efficient CS states, based on electron migration among the viologen moieties. [10] From these viewpoints, photocurrents were compared with different molar ratios of Ru^{2+} and V^{2+} as Ru^{2+}:V^{2+} = 2:1,
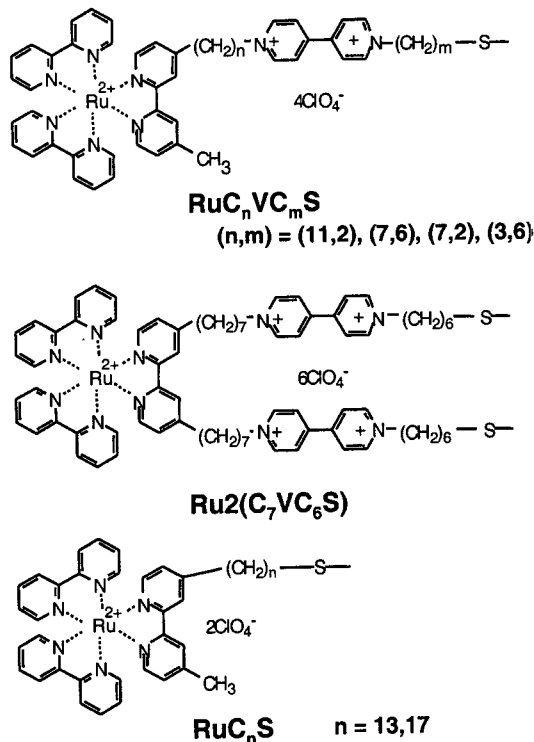
1:1, and 1:0, using the molecules shown in Figure 2. We also found that the photocurrent efficiency was in the order of Ru2 (C_7VC_6S) (2:1) > RuC_7VC_6S (1:1) >> $RuC_{17}S$ (1:0 for Ru^{2+}: V^{2+})[13, 14]. These findings support our prediction that the electron delocalization among the viologen moieties in the SAM is one of the keys for improving the photocurrent efficiency.

D-A PAIR MOLECULAR ASSEMBLIES

Although D-A linked molecules are certainly useful for highly-efficient photoelectric conversion, they need complicated and time-consuming synthetic procedures. In the practical point of view, fabrication of photoelectric conversion devices should be as simple as possible. In this section, we will show two examples of bottom-up approaches by the combined use of the self-assembling and the related methods.

The surface sol-gel method does not require any sophisticated synthetic procedures and is applicable to fabricate molecular layers of metal alkoxide-dye pairs.[15] We have applied this method for the fabrication of molecular films with D-A pairs by using the molecules shown in Figure 4. The method for the porphyrin(D)-fullerene(A) pair is schematically shown in Figure 5.[16] First, the SAM of $C_{60}S$ (step 1) and then the mixed SAM of $C_{60}S$ and **AcS** (step 2) were prepared on the ITO electrode. Then, the titanium oxide layer (some hydroxy groups were still remained) was superimposed on the modified
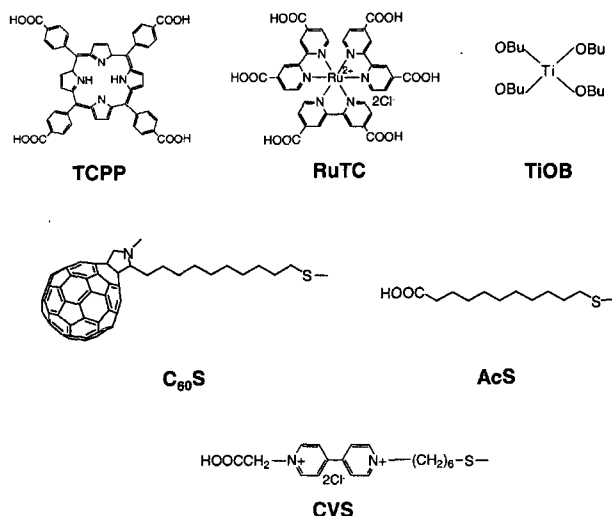
Figure 4. Molecular structures of donors and acceptors and some chemicals used for the combination of self-assembling and surface sol-gel methods.
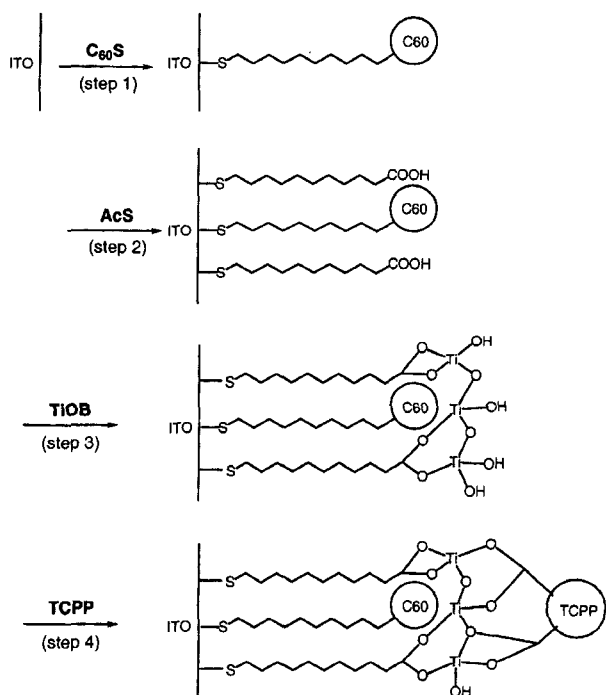

Figure 5. Schematic illustration for preparing porphyrin-fullerene assembly by the combination of self-assembling and surface sol-gel methods.

Figure 6. Schematic illustration for preparing porphyrin (or ruthenium complex)-viologen assembly by the combination of self-assembling and surface sol-gel methods.

Figure 7. Molecular structures for preparing porphyrin-fullerene multistructure assemblies by an electrostatic approach.

electrode by the surface sol-gel process (step 3) to implant OH groups at the outermost layer. Finally, the **TCPP** layer was similarly implanted, to give the porphyrin (D)-fullerene(A) multistructure assembly on the ITO electrode. The photocurrent was much larger in the presence of D and A as compound with the assembly of D or A alone. Similar assemblies also have been successful for the porphyrin(D)-viologen(A) and the ruthenium complex(D)-viologen(A) pairs,
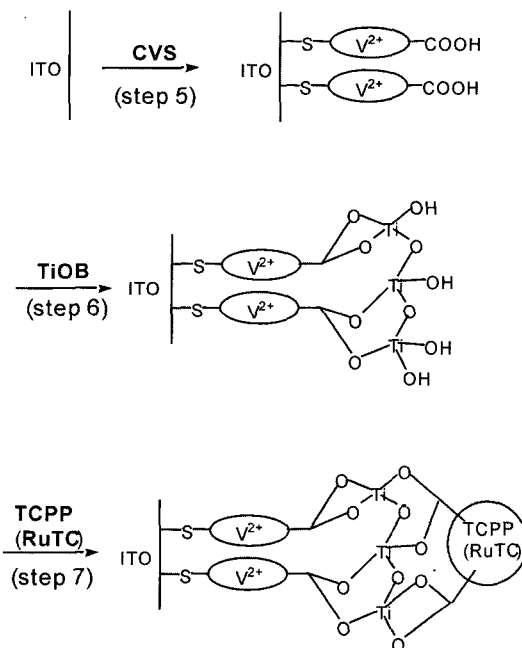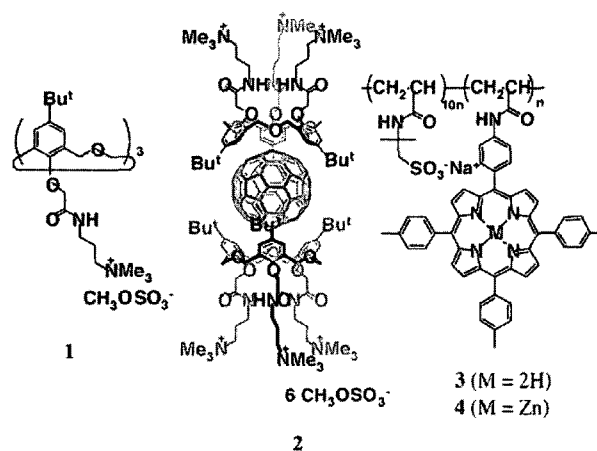
as shown in Figure 6.[17] In this case, the procedure has been further simplfied as compared with the case of Figure 5. The success owes to the use of the viologen derivative, **CVS**, having SH and OH groups (step 5). In this case, superimposition of TCPP multilayers has been achieved by repeating the steps 6 and 7.

An alternative method using the self-assembling and electrostatic interactions has been applied for the fabrication of porphyrin(D)-fullerene(A) assemblies as shown in Figure 7. [18] First, the SAM of 2-mercaptoethanesulfonate was prepared on the ITO electrode, to generate anionic charges (-SO_3^-) on the surface. Independently, a cationic 2:1 complex of

fullerene and calix [3] arene (1)[19] was prepared by electrostatic interactions. Then, a polyanion with the porphyrin moiety was subsequently superimposed by electrostatic interactions. Above-described approaches are experimentally simpler for fabricating D-A molecular assemblies, though the molar ratio of D and A cannot be precisely controlled.

GOLD NANOPARTICLE-DYE ASSEMBLIES

As described above, the self-assembling method is very fascinating in preparing monolayer assemblies on the electrode. Until recently, however, fabrication of SAMs have been restricted only to the planar electrode. Thus, the number of immobilized molecules has been limited. To overcome this limitation, build-up of thee-dimensional multistructure electrode using gold nanoparticles is one of the most promising approaches, as illustrated in Figure 8. In addition, localization of surface plasmon electric field at the near surfaces of gold nanoparticles may enhance the efficiency of photoexcitation located at the near surfaces of the gold nanoparticles, as has been verified for the planar electrode. [20] Quite recently, Lahav et al[21] reported multistructure assemblies consisting of gold nanoparticles and ionic dyes via electrostatic interactions. The self-assembling approach is superior to the electrostatic assembling approach in terms of the structural stability because of the formation of Au-S coordinative bonding. From these viewpoints, we have utilized the self-assembling method in fabricating gold nanoparticle-dye multistructures.

The first approach is alternate self-assembling of gold nanoparticles and a thiol dye (M) as illustrated in Figure 9. [22, 23] As to M, the ruthenium complex (RuS₃)[22] and the porphyrin (PoS₄)[23] were investigated. Thus, these systems operate only by the D unit. For example, 1,6-hexanedithiol was immobilized on the ITO electrode. Next, this electrode was immersed into the colloidal solution of AuP for self-assembling, and then was immersed into a dye (M) solution to self-assemble M on the surfaces of gold nanoparticles. By repeating these assembling processes, multi-structures of AuP and M were constructed on the surface of ITO electrode. Photocurrents increased with increasing assembling cycles and were remarkably larger than the two-dimensional monolayers
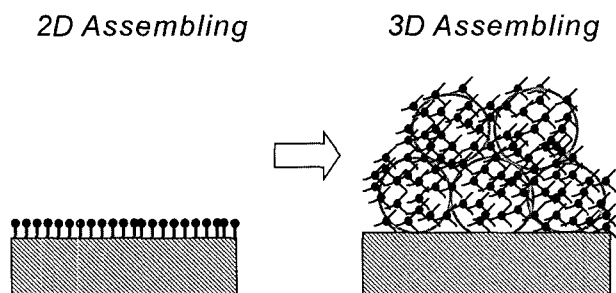
2D Assembling   3D Assembling

Figure 8. Comparison of two-(planar) and three-dimensional assemblies.

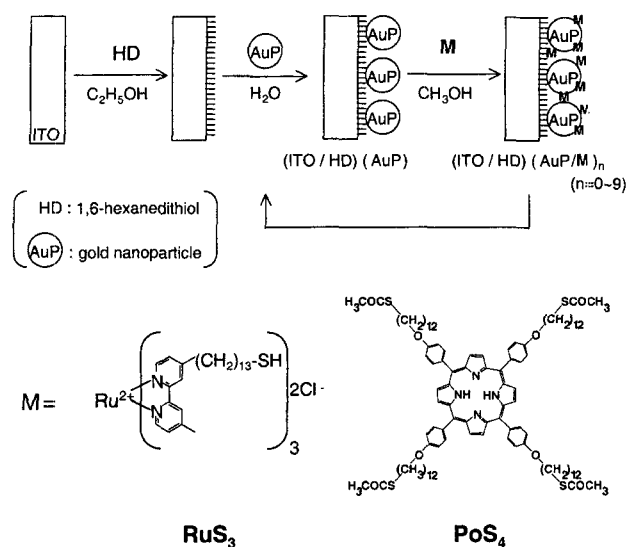Figure 9. Schematic illustration for alternate self-assembling of gold nanoparticle (AuP) and thiol dye (M), and molecular structures of RuS₃ and PoS₄.

of M. In this case, only D molecules have been preliminarily used to establish the practical usefulness of this assembling strategy.

In the case of alternate self-assembling method, the assembling processes are considerably time-consuming (typically a few days for each assembling). Thus, we have tried a more convenient method as follows.[24] First, the electrode is placed at the bottom of a glass vessel containing the colloidal solution of AuP. Then, an aqueous NaClO₄ solution was added, resulting precipitation (salting-out) of AuP on the electrode. Then, RuC₇VC₆S was self-assembled on the surfaces of AuP, giving three-dimensional multistructures only by two-steps. Typical SEM (scanning electron microscope) images of the above described multistructure are shown in Figure 10. Agglomerates of AuP are clearly seen on the electrode. In this approach, the photocurrent intensity per unit objective area was more than 15-fold larger than the two-dimensional monolayer electrode. Also, some contribution of localized surface plasmon electric field on the photocurrent enhancement is implied from the profile of the photocurrent action spectra. Particle-size effects on the photocurrents also have been found in the 18-220 nm diameter region.[25] An important key for the success of using AuP must be to optimize the three-dimensional nanoporous structure.

APPLICATIONS TO PHOTOCELLS

A number of research groups have been investigating strategies for improving the photoelectric conversion efficiency as well as practicality of organic photocells. We first applied the SAM of D-A linked thiol, RuC₇VC₆S, to a sandwich-type photoelectrochemical cell.[26] Figure 11 shows the schematic illustration of a photoelectrochemicall and the basic principle
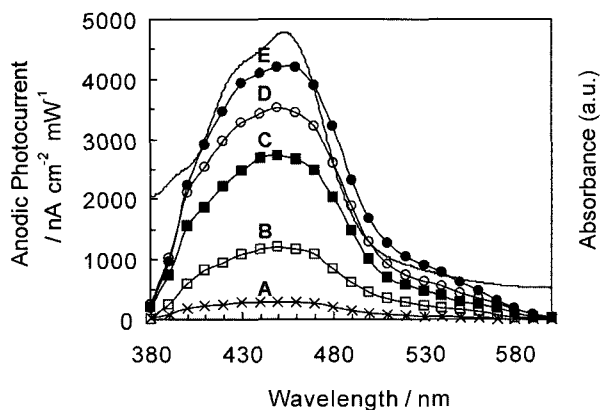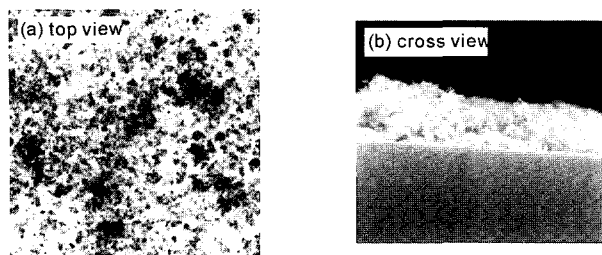
three-orders of magnitude lower. The open-circuit voltage, the short-circuit photocurrent, and the fill factor were 0.42 V, 1.9 μAcm^{-2}, and 0.21, respectively. Thus, the use of gold nanoparticle multistructures is fascinating for increasing the photocurrent intensity.

In the meantime, a double-driven photoelectrochemical cell in which both electrodes are modified with spin coated films of porphyrin (D) and/or fullerene (A) has been proposed as a new type of a solar cell.[27]

CONCLLUSION

By taking advantage of self-assembling properties in organic molecules, we have built up two- and three-dimensional molecular architectures, intended for organic photoelectric conversion devices.

Especially, the combination of self-assembling and surface sol-gel processes has made it possible to sequentially built up donor-acceptor layers on the electrode. Also, the use of gold nanoparticles has been successful for three-dimensional multistructures.

These bottom-up strategies must explore novel and practical nanoscale photoelectronic devices using organic molecules in the nearer future. The work is in progress along this line.

Figure 10. (a,b) SEM images of the RuC_7VC_6S-**AuP**/Au electrode prepared from salting-out of **AuP** from 30 ml of colloidal solution. (c) Photocurrent action spectra of RuC_7VC_6S/Au(planar) and RuC_7VC_6S-**AuP**/Au(B-E) electrodes prepared by using 10(**B**), 20 (**C**), 30(**D**), and 50(**E**) ml of colloidal solutions.

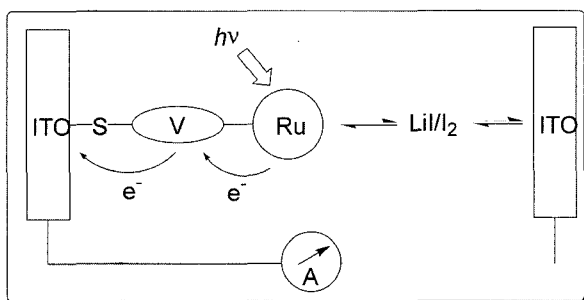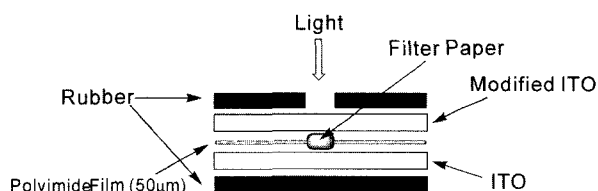**Figure 11.** Schematic illustration of a photocell using the SAM of RuC_7VC_6S and the basic principle of operation

of operation. It consists of the monolayer-modified ITO electrode, the ITO electrode, and the electrolyte solution of LiI and I_2. Thus, the cell is very thin and can be transparent. Because the surface area of the immobilized dye layer is much lower ($\sim10^{-3}$ times) than the Grätzel cell[3] using nano-porous TiO_2 film, the photocurrent intensity was roughly

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