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Synthesis of $[Ru_3(\mu_3\text{-NPh})(Br)(CO)_9]^-$ on self-assembled monolayers of di(3-aminopropyl)viologen/ITO surfaces and its application to photoelectrochemical cells

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ABSTRACT

Triruthenium carbonyl clusters $\{[Ru_3(Br)(CO)_{11}]^-$ (denoted as Ru-1), $[Ru_3(\mu_2\text{-Br})(CO)_{10}]^-$ (denoted as Ru-2), and $[Ru_3(\mu_3\text{-NPh})(Br)(CO)_9]^-$ (denoted as Ru-3)$\}$ were synthesized on di(3-aminopropyl)viologen (DAPV)/indium tin oxide (ITO) using a surface reaction in a ruthenium (III) carbonyl $[Ru_3(CO)_{12}]$ solution, and were applied to photoelectrochemical cells (PECs) at the molecular level. The formation of DAPV on ITO was realized in the form of self-assembled monolayers. $Ru_3(CO)_{12}$ then easily reacted with the Br^- of DAPV, and a mixture of Ru-1 and Ru-2 was formed on DAPV/ITO. Furthermore, Ru-3 was successfully anchored on DAPV/ITO by adding nitrosobenzene in order to react with Ru-2 on DAPV/ITO. The photocurrents of (Ru-1 and Ru-2)/DAPV/ITO and Ru-3/DAPV/ITO in PECs at the molecular level were $6.3\,nA\,cm^{-2}$ and $8.6\,nA\,cm^{-2}$, respectively. The quantum yield of Ru-3/DAPV/ITO was ~0.8%. Time-resolved photoluminescence spectroscopy and emission spectroscopy were recorded to bring out the photoinduced charge transfer process from ruthenium clusters to DAPV.

1. Introduction

Design and manipulation of electrode surfaces is an important subject in the field of not only fundamental research, but also a wide range of applications [1–4]. To prepare useful electrode surfaces, researchers have utilized numerous methods including chemical bath deposition [5], chemical vapor deposition [6], atomic layer deposition [7], electro-deposition [8], etc. In addition to these methods, self-assembled monolayers (SAMs) have attracted a great deal of attention due to prospects for applications and fundamental research [9–12]. SAMs have many advantages such as exceptional stability, a highly packed and ordered nature, good insulating power and other unique properties, which use perspective scaffolds for a wide range of applications [9,10]. SAMs can be used in sensors [17–20], light-emitting devices [21] and other nanoscale devices [22–27].

To exploit nanoscale devices based on SAMs, researchers have been using donor–acceptor dyad composites on SAMs surfaces [13–16]. Not surprisingly, the donor–acceptor dyads on the electrode surface have been used to assemble photoelectrochemical cells (PECs) [13–16], to tailor light-emitting diodes [22], and to optoelectronic devices [27]. Organometallics compounds are commonly used as a sensitizer material in donor–acceptor dyad composites [18,27,28], and have many unique properties in the presence of *d*-orbitals, such as a high extinction coefficient, tailorability in photoresponse to the broad solar spectrum and easy tunability of light absorption capability [27–29]. For example, Cho et al. reported the formation of (60) fullerene metal clusters-porphyrin dyad SAMs on an indium tin oxide (ITO) for PECs at the molecular level [28]. They also provided direct spectroscopic evidence for the formation of [diazabicyclooctane-Zn porphyrin]$^{\bullet +}$ in a photoinduced electron transfer process of Zn porphyrin-C_{60}/ITO. Recently, we reported the formation of organometallic ruthenium (Ru) cluster compounds on viologen modified single walled carbon nanotubes (V-SWNTs) for optoelectronic photoinduced charge transfer systems and PECs at the molecular level [27]. Following the formation/installation of viologen on SWNTs, ruthenium (III) carbonyl $[Ru_3(CO)_{12}]$ was easily reacted with the

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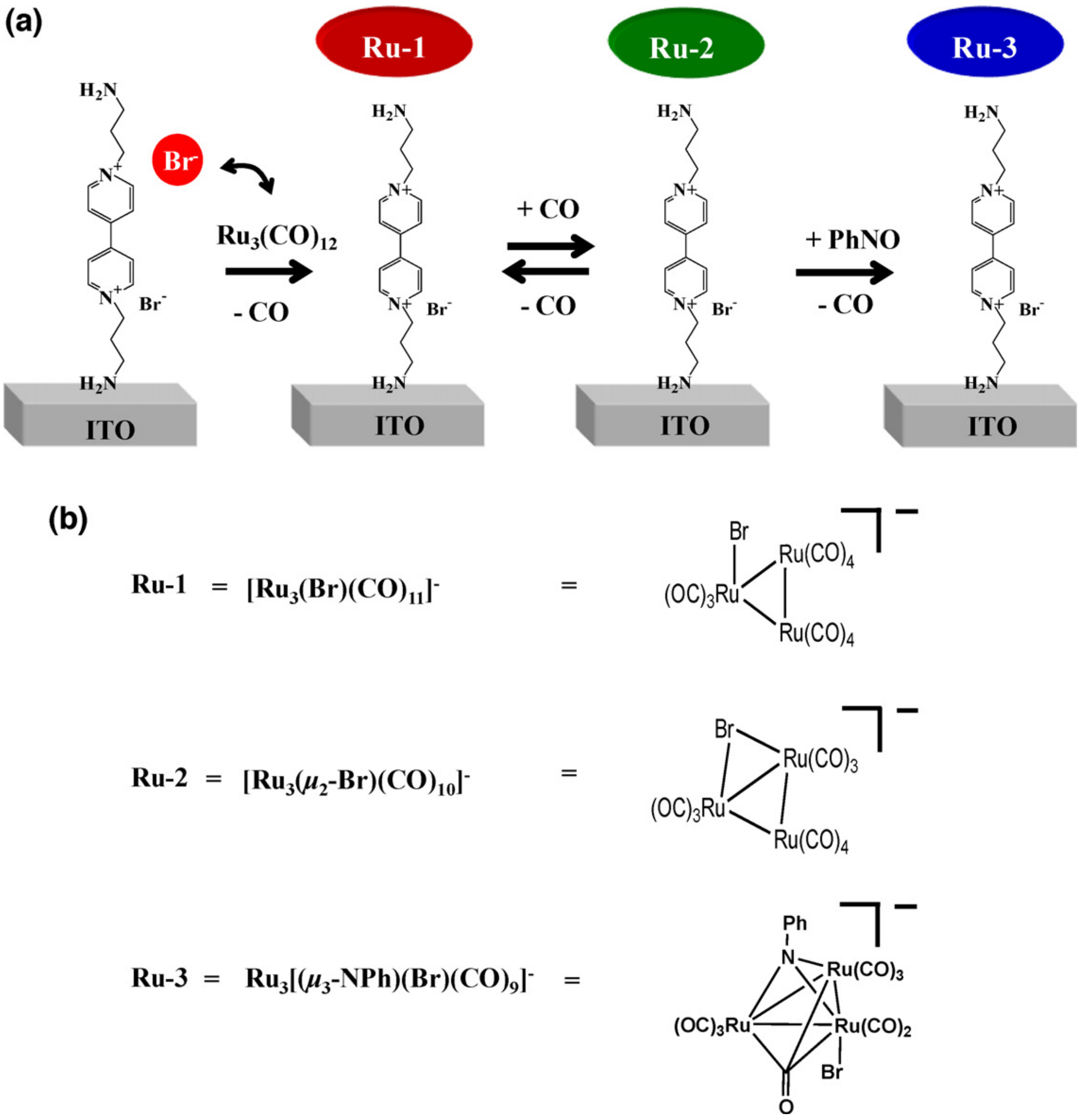

Fig. 1. Scheme of (a) the synthesis of Ru clusters on DAPV/ITO and (b) the chemical structural configurations of Ru clusters.

Br^- of viologen, leading to a mixture of $[Ru_3(Br)(CO)_{11}]^-$ (denoted hereafter as Ru-1) and $[Ru_3(\mu_2\text{-Br})(CO)_{10}]^-$ (denoted as Ru-2). $[Ru_3(\mu_3\text{-NPh})(Br)(CO)_9]^-$ (denoted as Ru-3) was then synthesized on V-SWNTs by adding nitrosobenzene (PhNO). Under illumination, the current of linear I–V curves of Ru-3/V-SWNT films decrease for the same voltage due to the effect of photoinduced charge transfer. Furthermore, the PECs at the molecular level were applied with a good quantum yield ($\Phi = 1.3\%$). However, although organometallics are a well developed research field, the preparation of highly purified organometallic compounds and the formation of organometallic clusters on SAMs surfaces are difficult to fabricate [27–29]. Therefore, it is necessary that a facile methodology is developed to directly form organometallic compounds on electrode surfaces. This has been the motivation of our work presented here.

With the aid of previous research on SAMs [17–28] and organometallic compounds [27], we describe a facile methodology to form Ru cluster compounds on SAMs for PECs at the molecular level. Organometallic ruthenium cluster compounds (Ru-1, Ru-2 and Ru-3) were successfully anchored on self-assembled di(3-aminopropyl)viologen (DAPV) monolayers/ITO using a surface reaction in a $Ru_3(CO)_{12}$ solution, and were applied to PECs at the molecular level. Furthermore, emission spectroscopy and time-resolved photoluminescence spectroscopy were used to demonstrate the photoinduced charge transfer process from Ru clusters to viologen.

2. Experimental details

2.1. Materials

$Ru_3(CO)_{12}$ was purchased from Strem Chemicals Inc. and PhNO was obtained from Aldrich and both were used as received. The DAPV was prepared as reported [12,18]. ITO (10 Ω cm) glass was purchased from Samsung Corning Co. (Korea).

2.2. Preparation of self-assembled DAPV monolayers on ITO

The ITO electrodes were washed with acetone, ethanol and deionized (18.2 MΩ cm) water in an ultrasonication bath for 15 min each, and were finally washed with *i*-propanol. SAMs of DAPV were obtained on an ITO surface using the previously reported method [12,18]. The SAMs of DAPV on ITO were prepared by immersing the