Dye-sensitized solar cells using purified squid ink nanoparticles coated on TiO₂ nanotubes/nanoparticles

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Purified squid ink was used as a natural dye in TiO₂ nanocomposite films for the fabrication of dye-sensitized solar cells (DSSCs). The squid ink extract was purified by the reaction over a proteolytic enzyme and coated onto composites of TiO₂ nanotubes/nanoparticles. The resulting cells were compared with reference DSSCs in which N719 was used as a standard dye. Analysis revealed that the sub-500-nm eumelanine-based spherical nanoparticles were well adsorbed on the surface of the TiO₂ nanotubes/nanoparticles, and the cells demonstrated efficiencies of 0.72 and 0.86 %, respectively. The mechanisms over photosensitization induced by the purified ink particles are elucidated.

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1. Introduction

Solar electricity is a steadily growing energy technology, and solar cells have generated markets in a variety of applications, such as consumer electronics, small-scale distributed power systems, and megawatt-scale power plants.1,2) Moreover, solar energy must be further developed as part of a fundamental renewable energy strategy to counter the effects of the ever increasing proliferation of global warming gases. Solar photovoltaic technology generates electric power by converting solar radiation into electricity using a semiconductor that exhibits a photovoltaic effect, and is a standard-bearer of renewable energy technology.2,3) Since its invention in 1991 by O’Regan and Grätzel, based on a nanocrystalline porous electrode,4) DSSCs have attracted tremendous attention as a promising alternative to silicon technology for the conversion of solar energy to electricity because of their high efficiency, low cost, environmental friendliness, and low angle dependency of incident light. Compared to a conventional solar cell, the manufacturing cost of DSSCs ranges from 1/3 to 1/5, so they are expected to be very cheap.5) Among oxide semiconductors,6) which have been used in photovoltaic technology, TiO₂ is preferable for solar energy conversion in DSSCs due to its superior photovoltaic conversion efficiency, low-cost, non-toxicity, and high chemical stability.7)

In commercial DSSCs, ruthenium(II)8) and (III) complexes9–11) have been used as efficient photosensitizers because they have wide absorption bands, long lifetimes, and long-term chemical stability, but suffer from the costly use of noble metals, complicated synthetic routes, and low yields. The use of natural extracts as photosensitizers is an attractive alternative to synthetic dyes because of their environmental friendliness, cost-effectiveness, and relative abundance. Extracts from fruits, flowers, leaves, and other natural products show diverse colors ranging from red to purple, with natural dyes that can be extracted through simple procedures.12–14) All of those commonly report that the conversion efficiency can further improved when the anchoring groups, such as, –COOH and –SO₃H, to be adsorbed onto the TiO₂ surface with a large electronic coupling.

The inks of squid and cuttlefish are used not only as food additives, but also as pigments. The major component of squid ink is eumelanin, which is also the primary pigment found in human skin and is a sepioid-colored macromolecule of 5,6-dihydroxindole-2-carboxylic acid and 5,6-dihydroxyindole.15) Recently, Ueno et al. have patented a method of extracting size-controlled ink particles from the ink of a squid16) and introduced that the ink particles can be used as a porosity enhancer of titania electrode.17) The squid ink particles also exhibit paramagnetic properties due to the presence of endogenous free radicals.18,19) The hydroxyl and carboxylic functional groups of eumelanin present the possibility that a purified extract of the squid ink pigment may induce strong interactions with the hydroxyl groups of a TiO₂ surface. The ink also has potential application as a nonpoisonous black ink for inkjet printers.20)

In this report, we suggest an optimized purification procedure for squid ink by enzyme-based isolation of the pigments, and

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propose a potential application in DSSCs. The conversion efficiencies of dye-sensitized TiO2 nanotube and nanoparticle composites are compared to that of reference DSSCs in which N719 was used as a standard dye.

2. Experimental

The purification of squid ink extract was performed by removing proteins from the extract by dissolution using an enzyme-based reaction. Protease (Wako Pure Chemical Industries, Ltd.) was used as the proteolytic enzyme;21) 0.1 g of protease was dispersed in 40 ml of distilled water at 45°C followed by the introduction of 0.1 g of squid ink. The dissolution reaction was performed for 10 h under 1000 rpm at 45°C in 100 ml of glass reactor. The resultant mixture was centrifuged at 4000–8000 rpm for 30 min, and the suspension was recovered for later use.

TiO2 nanotubes were synthesized using the method initially developed by Kasuga et al.,22),23) and TiO2 nanoparticles from a commercial source (Titanium IV oxide, Anatase form) were used, as shown in Figs. 1(a) and 1(b). The TiO2 nanotubes were synthesized with an inner diameter of 1 nm, an outside diameter of 3–5 nm, and a length of 100–200 nm. The diameter of the commercial TiO2 nanoparticles ranged from 85–200 nm. X-ray analysis indicated that both powders were in the pure anatase phase.24) These nanopowders were used in the preparation of TiO2 pastes;25) first, 6 g of TiO2 was soaked in 1 ml of acetic acid and mixed with 5 ml of water for 10 min or with 30 ml of ethanol for 20 min in a mortar, respectively. The TiO2 dispersions were transferred to a tall beaker with excess ethanol (100 ml) and stirred with a magnetic bar at 300 rpm. Anhydrous terpineol and a mixed solution with two kinds of ethyl cellulose powders; 5–15 mPa s at 5 vol % in toluene:ethanol/80:20 and 30–50 mPa s at 5 vol % in toluene:ethanol/80:20 (Sigma-Aldrich Co.), were added followed by stirring and sonication. The contents of the dispersion were concentrated by evaporation of the ethanol.

The product was coated on a conducting F-doped tin oxide (FTO)-coated glass via the doctor-blade method to form working electrodes. For the desired thickness of about 12.7 μm, the doctor-blade procedure was repeated four times, and then the electrodes were dried for 10 min at 120°C to evaporate their volatile components. Electrodes coated with the TiO2 paste were heated under a 5 ml/min air flow at 450°C for 30 min to remove the organic load and improve the interconnection of the particles. Then, the TiO2-coated electrode was soaked in a 100 ml of aqueous solution containing the purified extract of 0.036 g of squid ink for 12 h to adsorb the squid ink nanoparticles on the TiO2 surface of the electrode. As for a standard dye, 0.036 g of N719 in a 100 ml of solvent mixture of acetonitrile:tert-butanol/50:50 was applied under the same adsorption condition.

Counter electrodes were prepared by placing a drop of solution consisting of 0.0517 g of sodium hexachloroplatinate(IV) (Nacalai Tesque, Inc.) and 1 ml of DI water on the surface of an FTO substrate, drying in air, and annealing at 400°C for 30 min. Finally, the two electrodes were attached with their coated surfaces facing inward, using a 50-μm Surlyn sheet [Dyesol Ltd., Australia] as a spacer, and then sealed by heating at 120°C for 10 min to form a DSSC. The active area of the cells was 0.25 cm². Then, the electrolyte solution was introduced into the space between the electrodes by capillary action.

The photocurrent–voltage characteristics of the DSSCs were measured using a digital source meter (Keithley model 2400) by applying an external potential bias to the cell under illumination by light with an energy of 150 mW/cm² (Solar simulator, Pecell Technologies, Inc., Japan). The light intensity of the illumination source was calibrated using a standard silicon photodiode.

The overall phases of the raw materials and synthesized TiO2 powders were analyzed using an X-ray diffractometer (XRD, Science products, RINT-2500PC). The surface morphology and microstructure of the samples were investigated by field emis-
sion scanning electron microscopy (FE-SEM, Japan Electronic Products, JSM-6700F), and high-resolution transmission electron microscopy (HR-TEM, Japan Electronic Products, JEM-2000FX). Optical spectra of the electrode films were recorded by UV visible spectroscopy (UV Vis; V630, Jasco).

3. Results and discussion

Figures 1(c) and 1(d) show SEM and TEM images of squid ink particles, obtained after purification by enzyme-based reaction. The size of the ink particles ranged from 100–500 nm, confirming the isolation of nano-dimensional ink particles. This implies that any other protein-containing substrates were successfully decomposed by the protease enzyme into minimal molecular units, including amino acids, which were easily separated in water during the subsequent purification step.

Figure 2 shows the UV visible light absorbance of the squid ink, which was compared to a commercial dye, N719. Although eumelanin is the most widely studied of all melanins because it comprises the prime pigment of human skin and is responsible for its dark coloration, its broad absorption spectrum is unavoidable; the adsorption peak nearly covers the entire UV–vis region from 300–800 nm with steady decrease. This is different from the absorption spectrum of N719, which has strong absorption peaks at 300–320, 400, and 500 nm. Among much scientific discussion of this, Mofsinger et al. suggests that aggregation of eumelanin motivates photogeneration of reactive oxygen species upon UV illumination, and which results in the smoothly decreasing absorption spectrum. The “chemical disorder model” suggested by Meredith et al. explains that melanin consists of many chemically distinct species, and the broad spectrum is created by the superposition of the spectra of these species. The absorption spectrum of eumelanin is similar to that of an amorphous semiconductor, this feature supports the model of eumelanin as a strongly heterogeneous and disordered polymer.

Figure 3 shows SEM and TEM images of ink particles on the surface of a) TiO2 nanoparticles and b) TiO2 nanotubes. Figure 4 shows photocurrent density–voltage (J–V) performance curves of DSSCs based on single-layered electrodes with TiO2 nanoparticles and nanotubes, which were coated with N719 or squid ink. The overall cell efficiency is the most important factor representing solar cell performance, and is defined as the ratio of output energy to the incident solar energy. The overall energy conversion η can be estimated as:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

(1)

where $V_{oc}$ is the open circuit voltage, $J_{sc}$ is the short circuit current density, $P_{in}$ is the intensity of the incident light, and $FF$ is the fill factor:

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}}$$

(2)

where $J_{max} \times V_{max}$ is the maximum power of the cell.
The transfer pathway seemed to be well developed between TiO$_2$ nanoparticles and nanotubes. In Fig. 3, squid ink sensitized TiO$_2$ nanoparticles had a higher efficiency than squid ink sensitized TiO$_2$ nanotubes. For DSSCs of squid-ink-coated TiO$_2$ nanoparticles, because the electron transport time in TiO$_2$ nanoparticles is longer than in nanotubes, which results in the electron transport time in TiO$_2$ nanoparticles rather than nanotubes. The purified squid ink particles that are partially localized on the surface of TiO$_2$ without monolayer adsorption (Fig. 3), which is considered to be induced by insufficient amount of squid inks during adsorption procedure. It is therefore required to perform downsizing squid ink particles during enzyme-based purification and to optimize adsorption techniques in order to induce the mono-dispersed coating of the pigments as further researches. However, the results do offer the new possibility of utilizing not only pigments extracted from squid ink, but also various other pigments from fish as natural photosensitizing dyes in DSSCs based on the purification technique presented herein.

### Table 1. Efficiency variation of TiO$_2$ nanoparticles and nanotubes sensitized with either N719 or squid ink

|                | TiO$_2$ nanoparticles | TiO$_2$ nanotubes |
|----------------|-----------------------|------------------|
| $V_{oc}$ [V]   | squid ink N719        | squid ink N719   |
| $J_{sc}$ [mA/cm$^2$] | 1.66               | 1.40             |
| Fill factor    | 0.71                  | 0.70             |
| Efficiency [%] | 0.86                  | 0.72             |

In terms of DSSC efficiency, the TiO$_2$ nanoparticle-based cells had a higher efficiency than the corresponding TiO$_2$ nanotube-based cells. In general, the electron flow and the interfacial charge recombination between TiO$_2$ nanotubes are superior to TiO$_2$ nanoparticles, because the electron transport time in TiO$_2$ nanoparticles is longer than in nanotubes, which results in the scattering of free electrons to random direction.$^{9,30}$ Moreover, the 2-D TiO$_2$ nanowire reportedly plays a bridge-like role, in what is called an “electron expressway” in the DSSC. As a result, TiO$_2$ nanotubes are the most promising candidate nanostructure for improving the strong light scattering effects and high surface-to-volume ratio.$^{9,31}$ These effects may be accentuated when the length of the nanotubes is longer than the diameter of the nanoparticles. Furthermore, the electron mobility will be greatly enhanced when the longitudinal direction of the nanotubes are perpendicularly ordered to the substrate.$^{31}$ However, this research showed the opposite result. This is because of the use of TiO$_2$ nanoparticles 85–200 nm in diameter, which is similar to the length of the TiO$_2$ nanotubes (100–200 nm), so that the charge transfer pathway seemed to be well developed between TiO$_2$ nanoparticles rather than nanotubes.

4. Conclusions

An extract of squid ink was purified by a proteolytic enzyme, coated on anatase-phase TiO$_2$ nanotubes and nanoparticles, and applied as a natural dye in DSSCs. Proteolytic enzyme purification enabled the recovery of sub-500-nm squid ink particles containing the eumelanin-base pigment. SEM and TEM analysis indicated that the ink nanoparticles were adsorbed on the surface of TiO$_2$, and successfully sensitized the TiO$_2$, resulting in a light-to-electric energy conversion efficiency of the DSSCs cells. Eumelanin, which comprises the main component of the ink pigment, was regarded to motivate the strong interaction with the TiO$_2$ surface and photosensitization. Light-to-electric energy conversion efficiencies of 0.72 and 0.86% were achieved from DSSCs using a combination of TiO$_2$ nanoparticles/squid ink and TiO$_2$ nanoparticles/squid ink, respectively. The higher efficiency of DSSCs based on a combination of squid ink and TiO$_2$ nanoparticles with a diameter longer than the length of the corresponding nanotubes. The range of particle size as well as homogeneous coating of squid inks should be further optimized to improve the final energy conversion efficiency, while the purification and novel utilization of pigments from fish extracts will expand the potential of DSSCs using natural dyes for photosensitization.

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