

Efficient photocurrent generation by SnO₂ electrode modified electrophoretically with composite clusters of porphyrin-modified silica microparticle and fullerene†

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A silica microparticle has been successfully employed as a nanoscaffold to self-organize porphyrin and C₆₀ molecules on a nanostructured SnO₂ electrode which exhibits efficient photocurrent generation.

Much effort has been devoted to the development of organic solar cells including dye-sensitized¹ and bulk heterojunction² ones in relevance to environmental and energy problems.³ Supramolecular self-assembly of donor (D) and acceptor (A) molecules on electrodes is a potential approach for realizing the both efficient charge separation and subsequent electron and hole transportation in the films on the electrodes. Recently, we have successfully constructed a novel type of supramolecular organic solar cells (dye-sensitized bulk heterojunction type),⁴ which possesses both characters of the organic solar cells. Namely, porphyrins are three-dimensionally organized using dendrimers,⁵ oligomers,⁶ and nanoparticles^{7,8} (first step). These porphyrin molecular assemblies form supramolecular complexes with C₆₀ molecules in toluene due to the π - π interaction (second step)⁷ and they are associated to grow larger composite clusters in acetonitrile-toluene mixed solvent due to the lyophobic interaction (third step). Then, the large composite clusters can be assembled as three-dimensional D-A arrays onto nanostructured SnO₂ electrodes to afford the SnO₂ electrodes modified with the composite clusters of the porphyrin and C₆₀ molecules using an electrophoretic deposition method (fourth step).⁹ In particular, the bottom-up step-by-step self-assembled film of the composite clusters using gold nanoparticles exhibited efficient photocurrent generation relative to the other systems. However, further improvement has been hampered by the fact that the porphyrin excited singlet state is strongly quenched by the gold surface *via* energy transfer (EN).¹⁰ Thus, small particles as a scaffold of porphyrin molecules without EN quenching are required to improve photocurrent generation efficiency in the

composite cluster systems with C₆₀. To the best of our knowledge, no silica small particles covalently functionalized with chromophores have been self-assembled with acceptor molecules on electrodes leading to efficient photocurrent generation.¹¹

We report herein novel photoelectrochemical devices composed of porphyrin-modified silica microparticle and fullerene clusters, which are electrophoretically deposited on nanostructured SnO₂ electrode. The expensive gold core is successfully replaced by low-cost silica microparticle, which suppresses the undesirable EN quenching. Thus, the photocurrent generation efficiency of the porphyrin-modified silica microparticle and C₆₀ composite system is expected to be enhanced compared with a reference system with porphyrin-modified gold nanoparticle and C₆₀ composite.

Activated porphyrin **1** (Fig. 1)¹² was coupled to (aminopropyl)silylated silica microparticle **2** (Fuji Silicia Chemical) by refluxing for 24 h in toluene to give porphyrin-modified silica microparticle **3**. Activated porphyrin **1** also reacted with 1-butylamine to afford porphyrin reference **4**.¹² The structure of

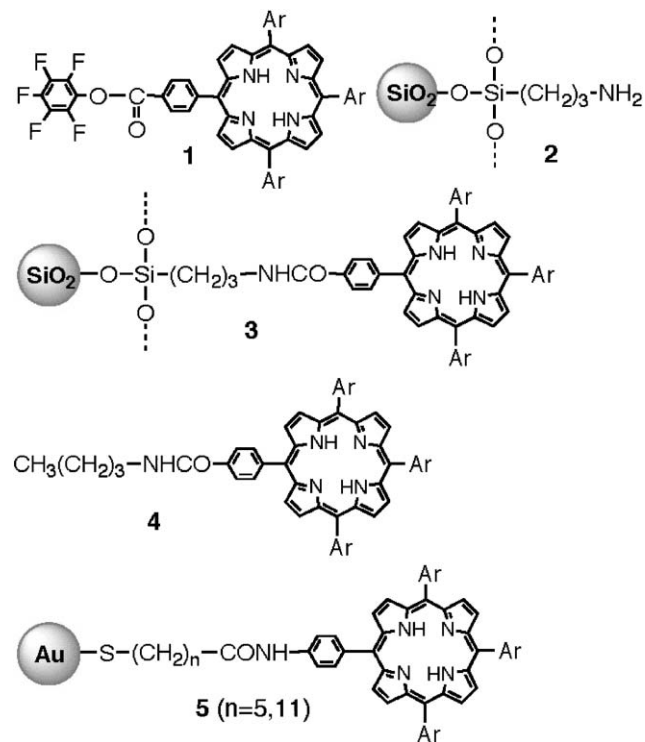


Fig. 1 Molecular structures used in this study (Ar = 3,5-(*t*-Bu)₂C₆H₃).

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† Electronic supplementary information (ESI) available: Optical microscopic image of **3** (S1), IR spectrum of **3** (S2), diffuse reflectance absorption spectrum of **3** (S3), absorption spectra of ITO/SnO₂/(**3** + C₆₀)_m (S4) and SEM images of ITO/SnO₂/(**3** + C₆₀)_m electrodes (S5). See DOI: 10.1039/b513707a

3 was characterized by elemental analysis, optical microscopy and diffuse reflectance absorption and IR spectroscopies. Optical microscopic images of **3** reveal purple–red-colored spheres with an average size of 5 μm , whereas that of **2** exhibits similar non-stained spheres (ESI, S1†). The peak frequency for CONH group in the IR spectrum of **3** reveals a characteristic value (1670 cm^{-1}) for the formation of amide linkage between the porphyrin and the surface of the silica microparticle (ESI, S2†). These results support that porphyrin molecules are covalently immobilized on the silica microparticle. The λ_{max} value of the Soret band of **3** in the diffuse reflectance absorption spectrum is slightly red-shifted (2 nm) relative to absorption spectrum of **4** in CHCl_3 (ESI, S3†). This indicates that the porphyrin environment of **3** is moderately perturbed on the surface. The average distance between the porphyrin moieties of **3** is estimated as 1.6 nm, based on the elemental analysis for **3** (C: 13.9%; H: 1.78%; N: 1.64%) and actual surface area ($224\text{ m}^2\text{ g}^{-1}$) and the density of amino group ($3.0\text{ }\mu\text{mol m}^{-2}$) for **2**. The estimated distance between the two adjacent porphyrins in **3** is long enough for the two porphyrins to accommodate C_{60} with a size of $\sim 1\text{ nm}$ (*vide infra*).⁷

The porphyrin-modified microparticle **3** was suspended in toluene containing C_{60} and they were associated to grow large clusters in an acetonitrile–toluene mixed solvent (denoted as $(\mathbf{3} + \text{C}_{60})_m$). Herein, the concentration of one porphyrin unit in these composite clusters is kept constant in the experiments: $[\text{H}_2\text{P}] = 0.17\text{ mM}$ in acetonitrile–toluene (2:1), whereas the concentration of C_{60} (0–0.5 mM) is varied in acetonitrile–toluene (2:1). This procedure allows us to achieve the complex formation between **3** and C_{60} and the larger association at the same time. Then the clusters were attached to nanostructured SnO_2 electrodes by the electrophoretic deposition method (300 V, 2 min) to give the working electrode modified with the composite clusters (denoted as $\text{ITO}/\text{SnO}_2/(\mathbf{3} + \text{C}_{60})_m$). The light-collecting property of $\text{ITO}/\text{SnO}_2/(\mathbf{3} + \text{C}_{60})_m$ is found to be intensive in the visible and near-IR region (ESI, S4†). SEM images of $\text{ITO}/\text{SnO}_2/(\mathbf{3} + \text{C}_{60})_m$ and $\text{ITO}/\text{SnO}_2/(\mathbf{3})_m$ electrodes reveal close packing of spherical particles with a size of 5 μm on the surface (ESI, S5†). The rough surface of the particles for $\text{ITO}/\text{SnO}_2/(\mathbf{3} + \text{C}_{60})_m$ relative to the smooth surface of the particles for $\text{ITO}/\text{SnO}_2/(\mathbf{3})_m$ demonstrates the formation of the composite clusters of **3** with C_{60} molecules which are deposited successfully onto the ITO/SnO_2 electrode.

Photoelectrochemical measurements were performed with a standard three-electrode system consisting of the working electrode, a Pt wire electrode and an I^-/I_3^- reference electrode in 0.5 M LiI and 0.01 M I_2 in acetonitrile. We examined the effect of C_{60} concentration on the incident photon-to-photocurrent generation efficiency (IPCE) of $\text{ITO}/\text{SnO}_2/(\mathbf{3} + \text{C}_{60})_m$ system under the same conditions (+0.05 V vs. SCE, $\lambda_{\text{max}} = 420\text{ nm}$ ($125\text{ }\mu\text{W cm}^{-2}$)). The action spectra largely agree with the absorption spectra on ITO/SnO_2 . The IPCE value initially increases and exhibits 17% as a maximum at 420 nm and finally decreases with increasing the C_{60} concentration (Fig. 2).¹³ The maximum IPCE value (17%) is four times as large as that (4%) of photoelectrochemical device ($\text{ITO}/\text{SnO}_2/(\mathbf{5}(n = 5) + \text{C}_{60})_m$) comprising of the composite clusters of C_{60} and porphyrin-modified gold nanoparticle whose spacer between the gold surface and the porphyrin is similar to **3**.^{7,14,15} These results clearly demonstrate that the replacement of gold core by silica particle in the porphyrin-modified particles is responsible for the

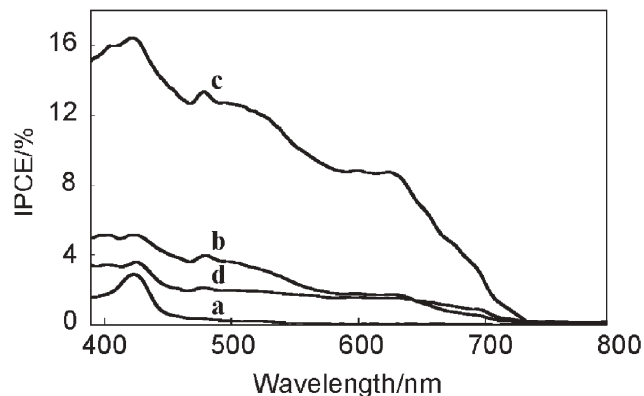


Fig. 2 Photocurrent action spectra of $\text{ITO}/\text{SnO}_2/(\mathbf{3} + \text{C}_{60})_m$ system ($[\text{C}_{60}] = 0\text{ mM}$ (a), 0.17 mM (b), 0.33 mM (c), 0.50 mM (d) in acetonitrile–toluene (2:1). Applied potential: +0.05 V vs. SCE. Electrolyte: 0.5 M LiI, 0.01 M I_2 , $[\text{H}_2\text{P}] = 0.17\text{ mM}$).

enhancement of photocurrent generation efficiency due to the suppression of undesirable EN quenching of the porphyrin excited singlet state by the core in the present system. Photocurrent generation in the present system is initiated by photoinduced charge separation from the porphyrin excited singlet state (${}^1\text{H}_2\text{P}^*/\text{H}_2\text{P}^+ = -1.1\text{ V vs. NHE}$)^{4–8} to C_{60} ($\text{C}_{60}/\text{C}_{60}^- = -0.2\text{ V vs. NHE}$)^{4–8} in the porphyrin– C_{60} complex rather than direct electron injection to conduction band of SnO_2 (0 V vs. NHE)^{4–8} system. While the reduced C_{60} injects electrons into the SnO_2 nanocrystallites, the oxidized porphyrin ($\text{H}_2\text{P}/\text{H}_2\text{P}^+ = 0.8\text{ V vs. NHE}$)^{4–8} undergoes electron transfer reduction with the iodide ($\text{I}_3^-/\text{I}^- = 0.5\text{ V vs. NHE}$)^{4–8} in the electrolyte system.

In conclusion, we have successfully constructed a photoelectrochemical device comprising of porphyrin-modified silica microparticle and C_{60} composites for the first time. Remarkable enhancement of the photocurrent generation was achieved in the present system compared with reference system where gold core was used as a scaffold of porphyrins instead of silica particle. Further improvement of the photocurrent generation efficiency is possible by reducing the size of silica particle (*i.e.*, silica nanoparticles) where the relative volume of electron and hole transporting pathways in the blend film would be enhanced relative to the present system.

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- 13 With increasing relative ratio of C₆₀ vs. porphyrin in ITO/SnO₂/(**3** + C₆₀)_m device, an electron produced by photoinduced charge separation between the porphyrin and C₆₀ is relayed through the excess of C₆₀ molecules to reach the conduction band (CB) of the SnO₂ electrode via electron hopping mechanism.⁸ On the other hand, hole migration through the porphyrins becomes inefficient with increasing the relative ratio. Thus, the C₆₀-porphyrin ratio would have large impact on the optimal photoelectrochemical conditions. Similar dependence of the IPCE value on the relative ratio was reported in ITO/SnO₂/(**5**(n = 11) + C₆₀)_m device.⁸
- 14 The shortest center-to-center distance of two porphyrins which can accommodate C₆₀ between the rings is estimated as 1.28 nm,⁷ which is slightly longer than the estimated distance between two porphyrins in **5**(n = 5) (1.15 nm).⁷ The larger IPCE value of ITO/SnO₂/(**3** + C₆₀)_m device may result from the favorable complexation between the porphyrin and C₆₀ in **3** relative to **5**(n = 5), which leads to the efficient quenching of ¹H₂P* by C₆₀ in the complex rather than the EN quenching of ¹H₂P* by the gold surface.
- 15 The maximum IPCE value (17%) is similar to that (16%) of photoelectrochemical device (ITO/SnO₂/(**5**(n = 11) + C₆₀)_m)⁸ comprising of the composite clusters of C₆₀ and porphyrin-modified gold nanoparticle whose spacer between the gold surface and the porphyrin is much longer than that of **3**.