Very Important Paper

Immobilization of Molecular Catalysts for Enhanced Redox Catalysis

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DOI: 10.1002/cctc.201701786
1. Introduction

The immobilization of homogeneous catalysts on various insoluble supports such as a siliceous material makes the immobilized catalyst insoluble in the reaction solution, providing great advantages for the easy separation of the catalyst from the reaction mixture, the fast isolation of the reaction products, and catalyst recovery and recycling by simple filtration.\[1\]–\[6\] The immobilization of homogeneous catalysts also allows insoluble catalysts, which would otherwise be aggregated, to be well dispersed in the reaction medium such as water, resulting in the significant enhancement in the catalytic activity. The use of water as solvent with immobilized catalysts also call attention to the importance of the requirements of green chemistry.\[21\]–\[26\] In general, the supported catalyst may be more sterically hindered and hence less accessible to substrates as compared to its non-supported counterpart, while the selectivity may be enhanced by the steric effect. Catalyst instability in the homogeneous phase is mainly caused by bimolecular deactivation pathways, which are prevented by immobilization of the catalyst to isolate the catalytic reactive sites.\[1\]–\[6\]

Excellent examples of immobilization of catalysts are well recognized in enzymes in which the catalytically active centers are isolated and immobilized by protein environments to avoid the bimolecular deactivation. In photosystems I and II (PSI and PSII), the efficient charge-separation processes in the photosynthetic reaction centers are made possible by the isolation and immobilization of the components in the protein environments.\[27\]–\[33\] Otherwise, bimolecular back electron transfer would occur rapidly by diffusion of each positively and negatively charged species to fail to achieve long lifetimes of the charge-separated (CS) states for solar energy conversion. A variety of electron donor-acceptor ensembles connected by covalent and non-covalent bonds have so far been designed and synthesized to model the light-harvesting and charge-separation functions in photosynthetic reaction centers (RCs) of PSI and PSII.\[34\]–\[52\] When the lifetimes of CS states of the model compounds for photosynthetic reaction center are as comparably long as those in the photosynthetic reaction center in frozen media, fast bimolecular back electron transfer between the charge-separated molecules by diffusion in solution has indeed been observed to shorten the apparent lifetimes of the CS states.\[53\]–\[55\] Immobilization of photosynthetic reaction center model compounds, which prevents the bimolecular deactivation, is required for development of photonic devices, such as photovoltaic devices.

Catalytic intermediates, such as metal-superoxo (M-O\(\text{O}^{-}\)), metal-peroxo (M-O\(\text{O}^{2-}\)) species, in redox enzymes are prone to be deactivated by bimolecular reactions,\[56\]–\[60\] which can be avoided by immobilization of catalysts. This Review is intended to focus on immobilization of the photosynthetic reaction center model compounds as well as redox enzyme model metal complexes to develop molecular photonic devices such as photovoltaic devices as well as efficient heterogeneous catalysts.

2. Immobilization of Photosynthetic Reaction Centers and Model Compounds

2.1. Photocurrent generation of RCs

There is much interest how the high photovoltaic efficiency of natural photosynthetic reaction centers (RCs) can be adopted in development of photovoltaic devices in which photocurrent is generated by use of RCs incorporated in solar cells or immobilized on functionalized metal electrodes.\[61\]–\[65\] Immobilization of RCs from Rba. sphaeroides was performed by simply depositing a high concentration solution of RCs (10 \(\mu\)L) on the clean bare Au electrode surface and incubating for one hour at 4\(^\circ\)C.\[66\] The photocurrent generation was observed by use of RCs immobilized on the Au electrode in a potassium phosphate solution (10 mm, pH 8) with Q-0 (100 \(\mu\)M) and cyt-c.
(20 μm), which act as redox mediators (referred to cyt-c/Q-0) as shown in Figure 1a. The photoaction spectrum of RCs immobilized on a bare Au electrode (shown as black squares in Figure 1b, when the light was turned on) agrees well with the absorption spectrum of the RCs in solution (red line in Figure 1b). The much higher photocurrent was generated using adhered *Rba. sphaeroides* RC-LH1 complex with cyt-c and Q-0 in the buffer solution under irradiation with the light intensity of 450 mWcm⁻² at 870 nm to attain a current density of around 25 μAcm⁻², whereas photocurrent generation by RCs reported in most studies was limited to a few hundred nA cm⁻² with red light illumination at a few tens of W cm⁻².

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PSI molecules together with cyt-c, which was used as a wiring agent, were immobilized on a mesoporous indium tin oxide electrode (ITO) to develop a photobiocathode as shown in Figure 2. The photoaction spectrum normalized to the peak under irradiation agrees well with the absorption spectrum of PSI in solution, which also corresponds to the absorption spectrum measured for a ITO-PSI-cyt-c electrode prepared by six spin coating steps (Figure 3a). The photocurrent intensity increased linearly with an increase in the thickness of the ITO to reach 150 μA cm⁻². The incident light-to-current efficiency, that is external quantum efficiency (EQE), exhibits a maximum value of 11% at a low light intensity, whereas the internal quantum efficiency (IQE) shows a peak value of 30% as shown in Figure 3b, where the ITO structure exhibits an inverse opal mesoporous structure with nanoparticle surface roughness. Cyt-c is bound to the surface to make the electrical connection of PSI to the ITO electrode surface. Photoexcitation of μITO electrode results in electron transfer from the base ITO electrode composed of sintered ITO nano-

![Figure 1. (a) Immobilization of RCs to a bare Au electrode and photocurrent generation in a cyt-c/Q-0 buffer solution. (b) Action spectrum of the photocurrent generation from RCs adhered to a bare Au electrode as compared to the absorption spectrum of RCs in solution (solid red line). Reprinted with permission from Ref. [66]. Copyright 2011, American Chemical Society.](image-url)
particles (ITO NPs) to cyt-c, which then reduces PSI. The electron photogenerated in PSI is transferred to $O_2$ to produce the superoxide ion ($O_2^{-}$) as shown in Figure 2.\[73\]

PSII from the thermophilic cyanobacterium Thermosynechococcus elongatus was immobilized with a redox polymer matrix on inverse opal mesoporous ITO (IO-ITO) electrodes to achieve high amount loading of PSII with the polymer (Figure 4a).\[74\]

The energy level diagram of photocurrent generation of two redox polymers ($P_{Phen}$ and $P_{Os}$) in Figure 5, employed as electron conducting matrices for PSII in IO-ITO electrodes is shown in Figure 4b. The photoaction spectra of the reference electrodes, such as IO-ITO, IO-ITO/$P_{Os}$, and IO-ITO/$P_{Phen}$ also agreed with the absorption spectra of the respective polymers, confirming no significant contribution from the polymers to the photocurrent generation.\[74\]

The photocurrent density increased with an increase in the thickness of the IO-ITO/$P_{Os}$ electrode to reach $381 \pm 31 \mu A cm^{-2}$ that corresponds to EQE of $6.9 \pm 0.9$% for 40 μm thick electrodes. This value was obtained by use of the maximum PSII loading. Addition of 2,6-dichloro-1,4-benzoquinone (DCBQ) employed as a model compound of the terminal electron acceptor plastoquinone B ($Q_b$) resulted in a further 1.35-fold increase in the photocurrent density to reach $513 \pm 29 \mu A cm^{-2}$ that corresponds to EQE of $9.3 \pm 1.2$%.\[74\]

The high photocurrent density enabled the quantification of $O_2$ evolution with a Faradaic efficiency of $85 \pm 9$%.\[24\] The maximum TOF$_{PSII}$ of 4.0 $s^{-1}$ was obtained with use of 20 μm thick IO-ITO/$P_{Os}$-PSII electrodes, which increased further by the addition of DCBQ, to $6.7 \pm 0.7 s^{-1}$, which is the highest value ever reported for PSI electrodes.\[24,74–77\]

RCs usually become unstable in a non-cellular environment and the unfeasible scalability of electrode materials has precluded the practical application of RCs. A highly stable and scalable RC electrode was reported by directly immobilizing RCs isolated from cultures of *Rb. sphaeroides* 2.4.1 on a flexible and transparent mercapto reduced graphene oxide (mRGO) electrode.\[78\]

RCs immobilized on a mRGO film were proven to be robust to retain the photoactivity after 20 week storage under dark and even after 24 h continuous photoirradiation at room temperature in the air.\[78\]

2.2. Photocurrent generation of RC model compounds

Photocurrent generation was observed by immobilization of RC model compounds on an Au electrode by use of mixed self-assembly monolayers (SAMs) composed of energy donor and acceptor molecules (Figure 7).\[79\] SAMs formed from bis(-

**Figure 2.** Schematic drawing of a μITO electrode with integrated PSI and cyt-c. The light blue arrows shows the direction of electron transfer in μITO. The dark blue arrows show electron transfer in μITO, the yellow arrows display electron transfer between proteins, and the red arrows indicate the intramolecular electron-transfer cascade in PSI. Reprinted with permission from Ref. [73]. Copyright 2016, Royal Society of Chemistry.

**Figure 3.** (a) Photoaction spectrum of a $6 \times \mu$ITO-PSI-cyt-c electrode (black opened circles) obtained by use of six spin coating steps, under photoirradiation with use of monochromatic light at $<10$ mW cm$^{-2}$ in an aerobic phosphate buffer solution (5.0 mM at pH 7) in comparison to the absorption spectra of PSI in a phosphate buffer solution (5.0 mM at pH 7; red line) and a $6 \times \mu$ITO-PSI-cyt-c (blue line). All the spectra were normalized to the absorption band at 680 nm.\[72\] (b) Plots of external (EQE) and internal (IQE) quantum efficiencies of a $6 \times \mu$ITO-PSI-cyt-c electrode vs. power density of the light source. Reprinted with permission from Ref. [73]. Copyright 2016, Royal Society of Chemistry.
pyrene) disulfide (1) as an energy donor and bis(porphyrin) disulfide (2) as an energy acceptor on the Au electrode exhibited efficient energy transfer from the singlet excited state (S\textsubscript{ExS}) of the pyrene moiety to the porphyrin moiety (P), which was monitored by the decrease in the fluorescence lifetime\textsuperscript{[79, 80]}.

Energy transfer from the S\textsubscript{ExS} of the boron-dipyrrin moiety (1B\textsuperscript{*}) to the P\textsubscript{m} moiety also occurred in mixed SAMs of boron-dipyrrin thiol (3) as an energy donor and porphyrin alkanethiol (4) as an energy acceptor as detected by steady-state fluorescence measurements\textsuperscript{[79]}.

Then, a RC model compound, ferrocene-porphyrin-fullerene triad thiol (5: Fc-P-C\textsubscript{60} triad thiol), was immobilized on the Au electrode by use of mixed SAMs with 3 as a light-harvesting unit\textsuperscript{[79]}.

Photoinduced electron transfer from the S\textsubscript{ExS} of the porphyrin moiety (P\textsuperscript{*}) to the C\textsubscript{60} moiety occurs, followed by the subsequent electron transfer (charge shift) from the ferrocene moiety (Fc) to the resulting porphyrin radical cation (P\textsuperscript{+}) to yield the final charge separated (CS) state (Fc\textsuperscript{+}-P-C\textsubscript{60}·) which has a CS lifetime of 8.4 ms\textsuperscript{[81]}. Electron transfer from the C\textsubscript{60} moiety to the methyl viologen (MV\textsuperscript{2+}) and/or O\textsubscript{2} occurs, whereas an electron is injected from the Au electrode.
to the Fc⁺ moiety to regenerate Fc-P-C₅⁺ leading to the cathodic photocurrent generation as shown in Scheme 1.[79]

Figure 8 shows the photoaction spectrum of the mixed SAMs of 3 and 5 with a molar ratio of 50:50 on the Au electrodes in a three electrode system, denoted as Au/3,5(50:50)/MV²⁺/Pt cell in an O₂-saturated Na₂SO₄ (0.10 M) solution containing MV²⁺ (30 mM). Input power and applied potential are 380 µW cm⁻² and −200 mV vs. Ag/AgCl, respectively. Reprinted from Ref. [79]. Copyright 2001, American Chemical Society.

Figure 8. Photoaction spectra (solid lines) of the Au/3,5(50:50)/MV²⁺/Pt cell (○) and the Au/3/MV²⁺/Pt cell (●), and the visible absorption spectrum (dashed line) of a mixed SAM of 3 and 5 on the Au electrode, 3,5(50:50)/Au, from a CH₃Cl solution with a molar ratio of 50:50 in an O₂-saturated Na₂SO₄ (0.10 M) solution containing MV²⁺ (30 mM). Input power and applied potential are 380 µW cm⁻² and −200 mV vs. Ag/AgCl, respectively. Reprinted with permission from Ref. [79]. Copyright 2001, American Chemical Society.

2.3. Solar cells with RC model compounds

High performance dye-sensitized solar cells (DSSCs) have so far been mainly fabricated by use of ruthenium polypyridine complexes and zinc porphyrins as the light-harvesting and charge-separation components, respectively, affording the highest power conversion efficiency (PCE ≈ 13.0%) under photoirradiation of simulated sunlight (1 Sun = AM 1.5G) at 100 mW cm⁻².[82–85] Metal-free organic electron donor-acceptor linked compounds have recently emerged as the near-infrared photosensitizing dyes, exhibiting over 80% external quantum efficiency (EQE) in a broad spectral range, and a high power conversion efficiency (PCE = 13.0%) under photoirradiation of simulated sunlight (AM 1.5G) at 100 mW cm⁻².[86–88]

A higher PCE of 14.3% with the maximum incident photon-to-current conversion efficiency (IPCE) of 91% has been attained by use of a photosensitizer, i.e., carbazole/alkyl-functionalized oligothiophene/alkoxysilyl-anchor dye (ADEKA-1 in Figure 9a),[89] as well as the co-sensitizer (LEG415 in Figure 9b),[90] and [Co(phen)₃]²⁺/2⁻ (phen: 1,10-phenanthrolsine) as the redox electrolyte couple under photoirradiation of simulated sunlight (AM 1.5G) at a 100 mW cm⁻² intensity (Figure 10).[91] The higher PCE value (14.7%) was attained under simulated sunlight at a 50 mW cm⁻² intensity.[91] A better...
photovoltaic performance is observed at the lower light intensity for DSSCs (vide infra).

By combining the donor-π-acceptor (D-A) dye coded D35 (see Figure 11 for structure) with the benzothiadazole-based D-A-π-A sensitizer XY1 (see Figure 11 for structure), an EQE of 90% was achieved in the visible region between 400 and 650 nm. When these sensitizers (D35 and XY1) were combined with the copper redox shuttle between [Cu(tmbly)]_{2}^{2+} and [Cu(tmbly)]_{2}^{+} (Figure 11), the highest PCE (28.9%) was attained under indoor conditions with weak light intensity at 1000 lux, where lux is the unit of light luminance. Such high PCE of 28.9% is sufficient to ensure the autonomous operation of a wide range of electronic devices in indoor environments with a reasonable size of the photovoltaic cell. On the other hand, the photovoltaic cells exhibited their high performance over a large domain of light intensities and spectral distributions to afford PCE of 11.3% under irradiation of simulated sunlight (AM 1.5G) at 100 mW cm^{-2}.

Perovskite solar cells (PSCs) have recently emerged as next-generation solar cells since the first use of perovskites as light absorption materials by Miyasaka et al., being composed of a layering of fluorine-doped tin oxide (FTO), an electron-transporting layer (ETL), perovskites, a hole-transporting layer (HTL), and a counter electrode. Electron donor-acceptor (D-A) type conducting polymers used in HTL of PSCs afford high hole mobility (μ_{h}) to attain high PCE up to 22.1%.

2.4. Redox photocatalysis of RC model compounds

Photoexcitation of 9-mesityl-10-methylacridinium cation (Acr^{+}Mes) composed of an electron donor (mesityl) and acceptor (acridinium) moieties resulted in formation of the triplet electron-transfer (ET) state (Acr^{+}Mes^{+}) via intersystem crossing to afford an extremely long lifetime (no decay at 77 K) in frozen media. The X-ray single crystal structure of Acr^{+}Mes has revealed that donor (Mes) moiety is orthogonal to the acceptor (Acr^{+}) moiety when the HOMO and LUMO are completely localized on the donor and acceptor moieties, respectively. However, at room temperature in solution, the
ET state decays via diffusion-limited intermolecular back electron transfer from the Acr⁺ moiety in one Acr⁺-Mes⁺⁺ molecule to the Mes⁺⁺ moiety in another Acr⁺-Mes⁺⁺ molecules.\cite{112,114} Acr⁺-Mes has merited increasing attention as an excellent organic photocatalyst for various organic transformations via a wide range of electron-transfer reactions, because the Mes⁺⁺ moiety in Acr⁺-Mes⁺⁺ has high oxidizing ability ($E_{\text{red}} = 2.06$ V vs. SCE) whereas the Acr⁺ moiety in Acr⁺-Mes⁺⁺ has high reducing ability ($E_{\text{red}} = -0.57$ V vs. SCE).\cite{115-119}

When Acr⁺-Mes was immobilized by cation exchange in nanosized tubular mesoporous silica-alumina (tAlMCM-41) to form a nanocomposite (Acr⁺-Mes@tAlMCM-41), the bimolecular decay of the ET state (i.e., Acr⁺-Mes⁺⁺) was prevented completely to afford the long lifetime of 2 s due to intramolecular back electron transfer from the Acr⁺ moiety to the Mes⁺⁺ moiety in the ET state (i.e., Acr⁺-Mes⁺⁺) in MeCN at 298 K as depicted in Figure 13 (part D).\cite{140} The lifetime of solvent-free Acr⁺-Mes⁺⁺@tAlMCM-41 became as long as 10 s even at high temperatures (373 K).\cite{114} The longer lifetime of solvent-free Acr⁺-Mes⁺⁺@tAlMCM-41 results from the smaller solvent reorganization energy ($\lambda$) inside mesoporous silica-alumina as compared in an MeCN solution, because the smaller the $\lambda$ value of electron transfer, the slower becomes the rate of back electron transfer in the Marcus inverted region, where the driving force of back electron transfer is much larger than the $\lambda$ value of electron transfer.\cite{142} The size of Acr⁺-Mes was too large to be incorporated into a supereage of zeolite Y by cation exchange, whereas 3-mesityl-1-methylquinolinium cation (Qu⁺-Mes) was immobilized inside a supereage of zeolite Y (Qu⁺-Mes) by cation exchange, because the size of Qu⁺-Mes was small enough to be incorporated into the zeolite supereage, exhibiting long-lived charge separation upon photoexcitation.\cite{114} The photocatalytic activity and stability of 9-mesityl-10-methylacridinium ion (Acr⁺-Mes) was improved by immobilization of Acr⁺-Mes on spherical AlMCM-41 (sAlMCM-41) together with [Cu(II)(tmpa)]²⁺ (tmpa = tris(2-pyridylmethyl)amine), which acts as an O₂ reduction catalyst.\cite{144-146} in O₂-saturated MeCN.\cite{140} The photocatalytic oxygenation of p-xylene to p-tolualdehyde with Acr⁺-Mes/[Cu(II)(tmpa)]²⁺@sAlMCM-41 reached ca. 100% yield after 4 h photoradiation as depicted in Figure 14, where the conversion with use of the homogeneous photocatalyst (Acr⁺-Mes) in O₂-saturated MeCN containing trifluoroacetic acid (TFA) was limited below 40%.\cite{140}

The photocatalytic cycle of oxygenation of p-xylene by O₂ with Acr⁺-Mes/[Cu(II)(tmpa)]²⁺@sAlMCM-41 is shown in

![Figure 12](image12.png)

**Figure 12.** (a) X-ray crystal structure, (b) HOMO and (c) LUMO of 9-mesityl-10-methylacridinium ion (Acr⁺-Mes). Reprinted with permission from Ref. [112]. Copyright 2004, American Chemical Society.

![Figure 13](image13.png)

**Figure 13.** (A) ESR spectrum of Acr⁺-Mes@tAlMCM-41 in acetonitrile (MeCN) observed under visible light illumination for 120 s by use of a high-pressure Hg lamp with a UV cut-off filter ($\lambda > 390$ nm). (B) ESR spectrum of Acr⁺-Mes generated by the electron-transfer reduction of the ET state (Acr⁺-Mes⁺⁺) of Acr⁺-Mes (0.50 mM) by 1-benzyl-1,4-dihydronicotinamide (BNAH: 2.5 mM) in MeCN. (C) ESR spectrum of mesitylene radical cation produced by the photoinduced electron-transfer oxidation of mesitylene (75 mM) with Hg(CF₂COO)₂ (20 mM) in CF₂COOH (TFA) at 298 K. (D) Decay time profile of intensity of the ESR signal due to Acr⁺-Mes⁺⁺@tAlMCM-41 in MeCN at 298 K upon cutting off the light. Reprinted with permission from Ref. [140]. "Copyright 2012, National Academy of Sciences.

![Figure 14](image14.png)

**Figure 14.** Time profiles of conversion of p-xylene in the photocatalytic oxidation of p-xylene (30 mM) with O₂ by use of 1.3 x 10⁻⁵ mol Acr⁺-Mes [a] with TFA (1.3 x 10⁻⁵ mol) and 12 mg of Acr⁺-Mes/[Cu(II)(tmpa)]²⁺@sAlMCM-41 [b] in O₂-saturated CD₃CN (2.0 mL). Reprinted with permission from Ref. [140]. Copyright 2012, National Academy of Sciences.

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of Acr$^+$ moiety in Acr$^+$-Mes to produce the singlet ET state, which undergoes intersystem crossing to the triplet ET state, 1(Acr$^+$-Mes$^*$). Because the Mes$^+$ moiety in 1(Acr$^+$-Mes$^*$) has the strong oxidizing ability ($E_{\text{red}}$ vs. SCE = 2.06 V), electron transfer from p-xylene ($E_{\text{red}}$ vs. SCE = 1.93 V) to the Mes$^+$ moiety in Acr$^+$-Mes$^*$ occurs efficiently to produce p-xylene radical cation that undergoes deprotonation to produce p-methylbenzyl radical.\(^{[146]}\) The carbon centered p-methylbenzyl radical reacts rapidly with O$_2$ to give p-methylbenzylperoxyl radical. The bimolecular disproportionation of p-methylbenzylperoxyl radical yields p-methylbenzyl alcohol, p-tolualdehyde and O$_2$.\(^{[146]}\) p-Methylbenzyl alcohol is further oxidized by O$_2$ via photocatalysis of Acr$^+$-Mes@AlMCM-41 to form p-tolualdehyde selectively as the final oxidized product of p-xylene.\(^{[146]}\) It should be noted that further oxidation of p-tolualdehyde occurred because the $E_{\text{red}}$ value of p-tolualdehyde ($E_{\text{red}}$ vs. SCE > 2.4 V) is higher than the $E_{\text{red}}$ value of the Mes$^+$ moiety of Acr$^+$-Mes$^*$ ($E_{\text{red}}$ vs. SCE = 2.06 V).\(^{[146]}\) The enhanced catalytic activity and stability of Acr$^+$-Mes/[Cu(tmpa)]$^{2+}$@-AlMCM-41 as compared to Acr$^+$-Mes result from the efficient redox catalysis of [Cu(tmpa)]$^{2+}$ for the two-electron/two-proton reduction of O$_2$ to H$_2$O$_2$ via the copper-superoxo and copper-peroxo intermediates.\(^{[144-147]}\)

Among the reaction media, H$_2$O is the most frequently used solvent owing to its abundance and environmentally benign properties. However, organic photocatalysts are normally insoluble in H$_2$O. Immobilization of 2-phenyl-1-naphthylquinolinium ion (QuPh$^+$-NA)\(^{[146]}\) on sAlMCM-41 by cation exchange enabled to use the composite material (QuPh$^+$-NA@sAlMCM-41) as an efficient photocatalyst in aqueous media, because photoexcitation of QuPh$^+$-NA results in formation of the ET state that acts as a strong oxidant ($E_{\text{red}}$ = 1.87 V vs. SCE), as well as a strong reductant ($E_{\text{ox}}$ = -0.90 V vs. SCE).\(^{[149]}\) Scheme 3 depicts the photocatalytic cycle for H$_2$O$_2$ production by the two-electron/two-proton reduction of O$_2$ by oxalate by use of QuPh$^+$-NA@sAlMCM-41 as a heterogeneous photocatalyst in H$_2$O.\(^{[149]}\) The rate of photocatalytic H$_2$O$_2$ formation was maximized at pH 4.5, which is close to the pK$_a$ of oxalic acid (4.27) and the pK$_a$ of HO$_2^-$ (4.9), because (COO$^-$)$_2$ acts as an effective electron donor and the protonation of O$_2^-$ is required for the disproportionation of HO$_2^-$ to produce H$_2$O$_2$.\(^{[148]}\) The maximum quantum yield of the H$_2$O$_2$ production in water without any organic solvent was determined to be 10%, which is about the same as that obtained in the homogeneous photocatalytic reaction in an organic solvent.\(^{[150]}\)

An organic photocatalyst (QuPh$^+$-NA) was immobilized by cation exchange in sAlMCM-41, where metal ions were also incorporated.\(^{[151]}\) Incorporated metal ions were reduced and converted to an H$_2$-evolution nanocatalyst in situ under photoirradiation.\(^{[151]}\) Acr$^+$-Mes, QuPh$^+$-NA and porphyrins were reported to act as efficient organic photocatalysts for H$_2$ evolution with dihydronicotinamide adenine dinucleotide (NADH) by use of metal nanoparticles as catalysts.\(^{[152-159]}\) However, no H$_2$ evolution occurred under visible light illumination ($\lambda > 340$ nm) of a phthalate buffer dispersion containing QuPh$^+$-NA@sAlMCM-41 as a photocatalyst, sodium oxalate as an electron donor and PtNPs as an H$_2$-evolution catalyst (Figure 15 a).\(^{[151]}\)

When K$_2$PtCl$_6$ (0.050 mm) was added to the reaction solution instead of PtNPs as a precursor of H$_2$-evolution catalyst, H$_2$ was evolved continuously as shown in Figure 15 a (c).\(^{[151]}\) After the H$_2$ evolution ceased, the QuPh$^+$-NA@sAlMCM-41 particles were separated by centrifugation from the reaction solution and the particles were washed with water twice.\(^{[151]}\) The reusability of the washed QuPh$^+$-NA@sAlMCM-41 together with the photodeposited PtNPs catalyst resulted in more efficient H$_2$ evolution compared to that before washing. This indicates that PtNPs deposited on QuPh$^+$-NA@sAlMCM-41 under photoirradiation act as a more efficient H$_2$-evolution catalyst. More efficient H$_2$ evolution in the second cycle compared to the first cycle was also observed when NADH (1.0 mm) was used instead of oxalate as an electron donor (Figure 15 b).\(^{[151]}\) Not only precious PtNPs but also earth-abundant CuNPs acted as an H$_2$-evolution catalyst in the photocatalytic H$_2$ evolution with use of an organic photocatalyst.\(^{[151,160]}\) In situ generation of PtNPs from K$_2$PtCl$_6$ was also reported for photocatalytic H$_2$ evolution with
composite catalysts of QuPh+·NA and carbon quantum dots and those of amorphous carbon and graphitic carbon nitride (g-C3N4) by use of NADH or triethanolamine (TEOA) used as a sacrificial electron donor.[161, 162]

Self-assembly of monodispersed SiO2 nanoparticles with the size of 20–30 nm resulted in formation of a densely packed monolithic structure containing discrete mesopores (2–6 nm) among the particles by convective flow through evaporation.[163] The mesopores can immobilize Rhodamine B, zinc porphyrins, and also even entire enzymes.[163–165] The uniform mesoporous structure of SiO2 nanoparticles is suited for incorporation of PtNPs without agglomeration during the catalytic reaction.[166] Al+4-doped SiO2 nanoparticles with the size of 20–30 nm (Al-SiO2 NPs) were prepared by surface aluminization of SiO2 NPs with NaAlO2 in an aqueous dispersion.[166] An aqueous suspension of PtNPs capped with PVP and an MeCN solution of QuPh+·NA were added successively to the aqueous dispersion of Al-SiO2 NPs and placed on an ultrasound sonicator for 30 min to afford the composite catalyst (PtNPs/QuPh+·NA/Al-SiO2 NPs).[166] In this case, each PtNP is surrounded by multiple QuPh+·NA cationic molecules and the surfaces of the Al-SiO2 NPs are covered with QuPh+·NA molecules as shown in Figure 16.[166] Such a mesoporous structure allows PtNPs to accept many electrons from QuPh+·NA molecules that are produced by the reduction of the photogenerated ET state of QuPh+·NA (QuPh+·NA−) by NADH, leading to efficient photocatalytic H2 evolution as shown in Figure 17, where the catalyst can be recycled several times.[166] In contrast to the case of the composite catalyst (PtNPs/QuPh+·NA/Al-SiO2 NPs), H2 evolution was hardly observed for the photocatalytic reaction system with use of the conventional mesoporous silica-alumina containing QuPh+·NA with PtNPs instead of PtNPs/QuPh+·NA/Al-SiO2 NPs under the same reaction conditions (Figure 17, blue square). The size of the PtNPs (∼2 nm) was too large to interact QuPh+·NA molecules immobilized inside the cylindrical mesopores, resulting in no photocatalytic H2 evolution.[166]

Metal-free graphene-organic dye aerogels also improved the photocatalytic activity of the dye aerogels, which were spatially and uniformly distributed inside the interconnected porous and conductive framework of graphene.[167] Such a bulk aerogel manifests excellent recyclability by simple replenishment of organic dyes, such as fluorescein, Eosin Y, and rose bengal, which ensures the long-term photocatalytic activity of the 3D aerogel.[167]
3. Immobilization of Metal Complexes

3.1. Enhanced redox catalysis

An early attempt to enhance redox catalysis of metal complexes by immobilization was reported by using [Fe(TPP)Cl] (TPP<sup>2</sup> = tetraphenylporphyrin dianion) that was readily converted inactive μ-oxo-dimer ([Fe(TPP)]<sup>2+</sup>) during the oxygenation of cyclohexene with NaBH<sub>4</sub>.<sup>168</sup> The heterogenized Fe<sup>II</sup> or Mn<sup>II</sup> porphyrin supported on SiO<sub>2</sub> activates O<sub>2</sub> with use of excess amounts of NaBH<sub>4</sub> and cyclohexene without generation of catalytically inactive [Fe(TPP)]<sup>2+</sup>O, affording cyclohexanol and cyclohex-2-ene-1-ol in a 4:1 ratio. This ratio is the same as that obtained in the Mn(TPP)Cl-catalyzed cytochrome P450 type oxidation of cyclohexene with NaBH<sub>4</sub> used as a reductant in a homogeneous solution.<sup>168</sup>

A recent example of biomimetic heterogeneous catalyst was reported by immobilization of meso-tetrakis(4-carboxyphenyl)porphyrinatoiron(III) chloride (Fe(TCPP)Cl) on multiwalled carbon nanotubes (MWCNTs).<sup>169</sup> The immobilization of Fe(TCPP)Cl was performed by using a covalent bond between Fe-porphyrin and MWCNTs formed by esterification of the hydroxyl groups of the MWCNTs with carboxylic acid groups of the porphyrin in the presence of 2-(1H-benzotriazole-1-yl)-1,3,3-tetramethylammonium tetrafluoroborate (TBTU) and N,N'-diisopropylamine (DIPEA) (Figure 18).<sup>169, 170</sup> The anchored Fe(TCPP)Cl catalyst was thermally stable up to ca. 350 °C, showing high thermal stability.<sup>169</sup> Oxidation of sulfides and phenols with urea hydrogen peroxide (UHP) in water was efficiently enhanced with excellent selectivity with [Fe(TCPP)Cl]<sup>2+</sup> on MWCNTs.<sup>169</sup>

[Fe(TPP)Cl] was also immobilized on the activated multiwalled carbon nanotube (AMWCNT) with use of hydroxyl functionality to afford Fe(TPP)Cl-AMWCNT, which acted as an efficient catalyst for epoxidation of olefins and oxidation of saturated hydrocarbons to the related ketones and also oxidation of sulfides to the sulfones with excellent selectivity.<sup>171</sup>

Immobilization of a cobalt(II) chlorin complex [Co(Ch)]<sup>2+</sup> on multi-walled carbon nanotubes (MWCNTs) also resulted in significant improvement of the catalytic activity and selectivity for the photocatalytic CO<sub>2</sub> reduction with triethyleneglycol (TEA) in competition with the proton reduction to H<sub>2</sub> by use of [Ru(μ-Me<sub>2</sub>phen)]<sup>2+</sup> (Me<sub>2</sub>phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst in MeCN containing H<sub>2</sub>O (v/v 5%) to yield CO and H<sub>2</sub> with a 2.4 to 1.0 ratio with a TON of 710.<sup>172</sup> The π-π interaction between MWCNTs and Co<sup>2+</sup>(Ch) provided a hydrophobic environment suitable for binding CO<sub>2</sub> instead of proton, resulting in the selective reduction of CO<sub>2</sub> to CO rather than the reduction of proton to H<sub>2</sub>.<sup>173–176</sup>

When [(tpa)Mn]<sup>2+</sup> @AI-MCM-41 catalyzed selective hydroxylation of benzene with H<sub>2</sub>O, to produce phenol selectively without further oxidation at ambient temperature as shown in Figure 19.<sup>177</sup> In contrast, no benzene oxidation occurred by use of Mn<sup>2+</sup> @AI-MCM-41, [(tpa)Mn<sub>2</sub>(μ-O)]<sup>3+</sup> @AI-MCM-41, or [(tpa)Mn]<sup>2+</sup><sup>3+</sup> under the same reaction conditions. It was reported that the oxidation of Mn<sup>2+</sup> complexes with H<sub>2</sub>O, in solution resulted in formation of the dimeric bis(μ-oxo)dimanganese(III,IV) ([Mn<sup>III</sup>(μ-O)<sub>2</sub>Mn<sup>III</sup>]<sup>2+</sup>) complexes.<sup>178, 179</sup> The formation of the bis-μ-oxo manganese dimer ([tpa]Mn<sub>2</sub>(μ-O)<sub>2</sub>]<sup>2+</sup>) was prevented, when [(tpa)Mn]<sup>2+</sup> was immobilized on a solid support. No oxidation of phenol occurred at 298 K, because the strong acid sites of AI-MCM-41<sup>180, 181</sup> captured phenol to prevent further oxidation.<sup>177</sup> Inhibition of phenol oxidation in the presence of a strong acid was also reported in a homogeneous hydroxylation of benzene.<sup>182</sup>

The kinetic study combined with the ESR detection of the intermediate indicated that the catalytic hydroxylation of benzene occurred via the Mn<sup>2+</sup>-oxo species generated by the reaction of [(tpa)Mn]<sup>2+</sup> with H<sub>2</sub>O inside AI-MCM-41 ([tpa]Mn<sup>2+</sup>(O)<sub>2</sub>]@AI-MCM-41), as illustrated in Scheme 4.<sup>177</sup>

The immobilized [(tpa)Mn]<sup>2+</sup> @AI-MCM-41 catalyzed the hydroxylation of electron deficient nitrobenzene as well with H<sub>2</sub>O, at a higher temperature (323 K) to produce o-nitrophenol selectively.<sup>177</sup> This regioselectivity is suggested to result from a cooperative interaction of [(tpa)Mn<sup>2+</sup>(O)]<sup>2+</sup> with the ortho-
proton and the NO₂ group as reported for the selective hydroxylation of nitrobenzene to o-nitrophenol with use of H₃PV₂Mo₁₀O₄₀ polyoxometalate.[183] Alkanes can also be hydroxylated by H₂O₂ by use of [(tpa)MnIV]²⁺@Al-MCM-41 in MeCN even at 298 K.[177]

A copper(II) complex with tmpa (tris(2-pyridylmethyl)amine) ligand ([Cu²⁺(tmpa)]²⁺) catalyzed hydroxylation of benzene to produce phenol that was further oxidized to produce p-benzoquinone in acetonitrile as shown in Figure 20a.[184] Immobilization of [Cu²⁺(tmpa)]²⁺ on Al-MCM-41 resulted in significant improvement of the selectivity to produce only phenol without further oxidation to p-benzoquinone (Figure 20b), because of the strong acid sites of Al-MCM-41.[180,181] which can capture phenol to prevent further oxidation (vide supra).[177,184] The TON reached 4320 after 118 h, demonstrating a high durability of [Cu²⁺(tmpa)]²⁺@Al-MCM-41.[184]

An [Fe³⁺(biuret-amide)] complex was also immobilized on mesoporous SiO₂NPs (mesoporous silica nanoparticles; MSNs) via CuI-catalyzed azide-alkyne click chemistry.[185] The azide functionalized SiO₂NP was prepared by one-pot co-condensation of tetraethyl orthosilicate (TEOS) with 3-azidopropyl triethoxysilane (AzPTES) in the molar ratio of 99:1 as shown in Scheme 5.[185] The Fe-MSN hybrid catalyst acted as an efficient peroxidase mimic, being successfully utilized for the quantitative determination of H₂O₂ and glucose via a one-pot colorimetric assay.[185] The catalytic activity of Fe-MSN was ca. 1000 times higher than that of natural HRP and 100 times higher than those of most HRP mimics based on metal/metal oxide NPs reported to date.[186]

Immobilization of a tricopper complex [Cu/Cu/Cu(7-N-Etppz)]³⁺ (CuEtpp; 7-N-Etppz = 3,30-(1,4-diazepane-1,4-diyl)bis[1-(4-ethyl-piperazine-1-yl)propan-2-ol]) (Figure 21) on mesoporous silica nanoparticles also resulted in significant improvement of the catalytic activity and TONs with higher chemical yields, offering the most proficient catalyst for the selective conversion of methane into methanol at room temperature,[187] as compared with other heterogeneous catalysts.[188–196] When [Cu/Cu/Cu(7-N-Etppz)]³⁺ was employed as a homogeneous catalyst for oxidation of methane with 20 equiv of H₂O₂ at room temperature, the maximum TON was only 6.5.[197] In contrast, the TON increased to 166.5 for oxidation of methane with
200 equiv of H₂O₂ by use of immobilized catalyst (CuEt₃-p@AlMSN₃₀-ex) as shown in Figure 22, where the catalyst can be reused. However, there is a small loss in the catalyst activity after each 3 h run. The TONs calculated based on the remaining tricopper-complex content agree to one another (Figure 22b). Thus, the immobilized [Cu/Cu/Cu(7-N-Etppz)]⁺ is quite robust in the oxidation process.⁹

3.3. Photoredox catalysis

A cyano-bridged polynuclear FeⅡ and RuⅡ complex was immobilized on sAl-MCM-41 to afford the hybrid photocatalyst, [Fe(H₂O)₃]₂[Ru(CN)₆]@sAl-MCM-41, as shown in Figure 23. The [Fe(H₂O)₃]₂[Ru(CN)₆] complex acted as an efficient catalyst for the thermal benzene hydroxylation with H₂O₂ in MeCN, where the TON of production phenol reached 393 after 60 h. The TON increased to 2500 after 114 h by immobilization of [Fe(H₂O)₃]₂[Ru(CN)₆] on Al-MCM-41. [Ru(bpy)₃]²⁺ also acted as a water oxidation catalyst by use of [Ru(bpy)₃]²⁺ as a photocatalyst and Na₂S₂O₈ as a sacrificial electron acceptor. The evolved oxygen came from water as evidenced by ¹⁸O-isotope labeling experiments. Thus, photoirradiation of an O₂-saturated MeCN solution containing [Fe(H₂O)₃]₂[Ru(CN)₆]@sAl-MCM-41 and Sc³⁺ ion resulted in production of H₂O₂ from H₂O and O₂. The overall photocatalytic mechanism is shown in Scheme 6.⁹

![Figure 21](image1.png)

Figure 21. Space-filling (left) and ball-and-stick (right) models of the optimized structure of [Cu/Cu/Cu(7-N-Etppz)]⁺ to exhibit the funnel-like opening or cleft at the bottom for CH₄ to access the “hot” oxene group [Cu (brown), H (white), C (gray), N (blue), and O (red)]. Reprinted with permission from Ref. [187]. Copyright 2016, Royal Society of Chemistry.

![Figure 22](image2.png)

Figure 22. (a) Time courses of TONs of methanol produced by the methane oxidation with 200 equiv of H₂O₂ by use of CuEt₃-p@AlMSN₃₀-ex for three repeated cycles (TONs = mols of produced methanol per mol of the tricopper complex, Cu₃[7-N-Etppz], immobilized on the MSNs) at room temperature. (b) Time courses of TONs of methanol produced in the three cycles re-calculated based on the amount of remaining CuEt₃-p@AlMSN₃₀-ex content determined by ICP-MS and C/N elemental analysis before the reaction. Reprinted with permission from Ref. [187]. Copyright 2016, Royal Society of Chemistry.

![Figure 23](image3.png)

Figure 23. Partial structure of a cyano-bridged complex containing FeⅡ and RuⅡ ([Fe(H₂O)₃]₂[Ru(CN)₆]). Three water molecules (in average) bind to FeⅡ ions to afford the octahedral coordination structure. Reprinted with permission from Ref. [198]. Copyright 2016, American Chemical Society.

![Scheme 6](image4.png)

Scheme 6. Photocatalytic cycle for phenol production from benzene and O₂ with [Fe(H₂O)₃]₂[Ru(CN)₆]@sAl-MCM-41. Reprinted with permission from Ref. [198]. Copyright 2016, American Chemical Society.
Photoexcitation of [Fe(H₂O)₆]³⁺[Ru(CN)₆]³⁻ resulted in electron transfer from the excited state of [Fe(H₂O)₆]³⁺[Ru(CN)₆]³⁻ to O₂ in the presence of Sc³⁺ to produce [Fe(H₂O)₆]³⁺[Ru²⁺(CN)₆]²⁻ and the O₂·⁻-Sc³⁺ complex.¹⁹⁰ The reduction potential of [Ru²⁺(CN)₆]³⁻ moiety in the presence of iron ions has been reported as Eₒ₂/²⁻ = 1.24 V vs. SHE,¹⁹⁰ which is higher than the standard electrode potential (1.06 V vs. SHE) for water oxidation to evolve oxygen at pH 2.8. Thus, the Fe³⁺ moiety was oxidized by [Ru²⁺(CN)₆]³⁻ to afford the high-valent iron species, which is responsible for the water oxidation.¹⁹⁰ The O₂·⁻-Sc³⁺ complex disproporinates in the presence of H₂O to produce H₂O₂.²⁰⁰–²⁰² Then, the catalytichydroxylation of benzene with H₂O₂ occurs by use of [Fe(H₂O)₆]³⁺[Ru²⁺(CN)₆]²⁻ as the hydroxylation catalyst to produce phenol (Scheme 6).¹⁹⁰

4. Conclusion
Immobilization of RCs from PSI and PSII and RC model compounds on various electrodes has enabled photocurrent generation, leading to development of solar cells. Immobilization of a simple RC model compound, 9-mesityl-10-methylacridinium ion (Acr⁺-Mes), composed of an electron donor (mesityl) and acceptor (acridinium) moieties, on nanosized tubular mesoporous silica-alumina (tAlMCM-41) to form a composite (Acr⁺-Mes@tAlMCM-41). Photoexcitation of Acr⁺-Mes@tAlMCM-41 results in formation of the triplet electron-transfer (ET) state (Acr⁺-Mes⁺*), which has the long lifetime of 2 s by preventing intermolecular back electron transfer between two Acr⁺-Mes⁺* molecules.¹⁴⁰ The photocatalytic activity and stability of Acr⁺-Mes for selective oxidation of p-xylene with O₂ was much improved by immobilization of both Acr⁺-Mes and [Cu(Imova)]⁺⁺ that acts as an O₂ reduction catalyst,¹⁴⁴–¹⁴⁶ in spherical AlMCM-41 (sAlMCM-41) in O₂-saturated MeCN.¹⁴⁷ Nanocomposites composed of both an organic photocatalyst (QuPh⁺-NA) and metal salts immobilized on sAlMCM-41 act as effective photocatalyst for H₂ evolution in the presence of electron donors such as NADH, when metal ions were reduced and converted into an H₂-evolution nanocatalyst in situ under photolirradiation.¹⁵¹ Immobilization of metal complexes on heterogeneous supports enhanced both the reactivity and selectivity of catalysts for selective benzene hydroxylation to phenol when no further oxidation of phenol occurred because of strong interaction of the acid sites of heterogeneous supports and phenol. Nanocomposites composed of both organic RC mimics and metal complexes described in this Review may provide more reactive and selective photoredox catalysts for methane oxidation to methanol and CO₂ reduction to methanol, which remain big challenge to accomplish.

Acknowledgements
The authors appreciate significant contributions of their collaborators and co-workers cited in the listed references, and support by a SENTAN project (to S.F.) from Japan Science and Technology Agency, a grant for scientific research from Japan Society for the Promotion of Science (No. 16H02268 to S.F.), the NRF of Korea through CRI (NRF-2012R1A1A3A2048842 to W.N.), GRL (NRF-2010-00353 to W.N.), and also Basic Science Research Program (2017R1D1A1B03029982 to Y.M.L. and 2017R1D1A1B03032615 to S.F.).

Conflict of interest
The authors declare no conflict of interest.

Keywords: immobilization · metal complex catalyst · organic photocatalyst · reaction center models · redox catalysis


