Plasmon-enhanced light-driven water oxidation by a dye-sensitized photoanode

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Dye-sensitized photoelectrosynthesis cells (DSPECs) provide a flexible approach for solar water splitting based on the integration of molecular light absorption and catalysis on oxide electrodes. Recent advances in this area, including the use of core/shell oxide interfacial structures and surface stabilization by atomic layer deposition, have led to improved charge-separation lifetimes and the ability to obtain substantially improved photocurrent densities. Here, we investigate the introduction of Ag nanoparticles into the core/shell structure and report that they greatly enhance light-driven water oxidation at a DSPEC photoanode. Under 1-sun illumination, Ag nanoparticle electrodes achieved high photocurrent densities, surpassing 2 mA cm⁻² with an incident photon-to-current efficiency of 31.8% under 450-nm illumination. The approach that we have taken involves incorporation of cubic silver NPs onto a FTO/SnO₂/TiO₂ core–shell mesoporous surface. Silver has proven to be an optimal metal for supporting strong surface plasmons in visible wavelengths due to its low dielectric function, and therefore high quality factor (>10), over this range of the spectrum (15). To protect the Ag NPs from degradation by exposure to solution (16), the Ag NPs were deposited on the SnO₂ surface before forming the TiO₂ shell by atomic layer deposition.

Our experiments show that incorporating Ag NPs significantly enhances the performance of the DSPEC photoanode in comparison with a similarly prepared photoanode without the Ag NPs. The improved performance entailed higher photocurrent densities, above 2 mA cm⁻² under 1-sun irradiation, without any loss in the faradaic efficiencies for O₂ generation (~95%). An improved incident photon-to-current efficiency (IPCE) of 31.8% at 450 nm compared with 16.3% of photoanode without Ag NPs was observed for the Ag NP surface.

Results and Discussion

Photoanode Preparation and Characterization. Mesoporous FTO/SnO₂/TiO₂ core–shell electrodes used in this study were prepared as

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described elsewhere (4). Fig. S1 shows the image of 3.0-nm TiO$_2$ shell coating Ag particles. Different mesoporous layer thicknesses of 2.2, 4.1, and 8.1 μm were investigated. The effect of oxide layer thickness on the performance of the interface is shown in Fig. S2. As the 4.1-μm electrode gave the highest photocurrent response, the majority of experiments in this study were carried out with ~4-μm mesoporous electrodes.

The deposition of polyvinylpyrrolidone (PVP)-coated Ag NPs on the SnO$_2$ film was accomplished by an electrostatic interaction mechanism (9, 17). Briefly, this involved a short dip treatment of the FTO/SnO$_2$ electrode in piranha solution (3:1 H$_2$SO$_4$:H$_2$O$_2$), rinsing with deionized water, and then an overnight soak of the electrode in an ethanol solution with 0.05 wt % Ag NPs. After soaking in the Ag NP solution, the electrodes were air dried and underwent atomic layer deposition (ALD) to deposit the TiO$_2$ shell. This gave the complete FTO/SnO$_2$/AgNP/TiO$_2$ core/shell surface. The as-prepared electrodes were immersed in methanol solution containing 2 mM [Ru(4,4′-PO$_3$H$_2$-bpy)(4,4′-bpy)$_2$]$^{2+}$ (RuP$^{2+}$; bpy = 2,2′-bipyridine). After surface adsorption of the RuP$^{2+}$ chromophore, the water oxidation catalyst [Ru(bda)(4-O(CH$_2$)$_3$PO$_3$H$_2$)-pyr)$_2$] (WOC; pyr = pyridine; bda = 2,2′-bipyridine-6,6′-dicarboxylate) was incorporated onto the surface during a second soaking step in methanol solution containing 1 mM of the complex. Previous work demonstrated that the loading of the RuP$^{2+}$ chromophore on the surface does not preclude the adsorption of the catalyst containing the –(CH$_2$)$_3$-PO$_3$H$_2$ axial anchoring group (18).

Fig. 1 illustrates the fully assembled electrode interface, FTO/SnO$_2$/AgNP/TiO$_2$–RuP$^{2+}$/WOC. As shown previously by UV-visible measurements, these conditions result in a surface layer consisting of 2:1 chromophore:catalyst ratio (18).

Fig. 2 shows SEM images of the fully prepared FTO/SnO$_2$/AgNP/TiO$_2$–RuP$^{2+}$/WOC surface. The 100-nm cubic Ag NPs deposit on the outer surface of the oxide layer, and, as they are larger than the pore openings in the film, it is unlikely that they penetrate within the interior of the film. The 100-nm cubic Ag NPs are randomly dispersed across the top of the oxide layer with both isolated particles and clusters of particles observed. Based on the SEM images, the procedure for depositing the Ag NPs does result in a relatively even distribution across the entire surface.

As mentioned above, treatment of the surface by ALD simultaneously forms a TiO$_2$ coating on the Ag NPs and forms the SnO$_2$/TiO$_2$ core/shell surface in the underlying oxide film. The TiO$_2$ coating prevents direct contact of the Ag surface with solution (9, 19). The thickness of the TiO$_2$ surface layer was controlled by varying the number of deposition cycles with each cycle estimated to add 0.06 nm in thickness (20). As summarized in Fig. S3, different
thicknesses of the TiO$_2$ layer (3.0, 4.5, and 6.0 nm) were explored with the best photocurrent response observed with the 3.0-nm coating. Unless otherwise noted, all samples were prepared with a 3.0-nm TiO$_2$ shell coating by ALD.

Photochemical Studies. Photocurrent vs. time measurements for FTO/SnO$_2$/AgNP/TiO$_2$–RuP$^{2+}$/WOC and FTO/SnO$_2$/TiO$_2$–RuP$^{2+}$/WOC electrodes in pH 4.65 acetate buffer (0.1 M HAc/Ac$^-$) with 0.4 M NaClO$_4$ as supporting electrolyte were performed under a 0.2 V vs. Ag/AgCl bias with a Pt mesh counter electrode (Fig. 3). All measurements were performed with 100-mW cm$^{-2}$ white light (1 sun) irradiation with a 400-nm cutoff filter to avoid direct bandgap excitation of the oxide. The effect of Ag NPs on the photocurrent is apparent in Fig. 3A with nearly a doubling in the current during illumination with the Ag NPs as compared without. In Fig. 3B, the overall form of the current–voltage response with or without the Ag NPs is similar but with higher currents from the electrode with added NPs. Importantly, the point of zero current occurs at a similar voltage in both samples, indicating that charging effects of the metal NPs do not contribute to the improved current response (8).

The localized surface plasmon of the Ag NP extends only tens of nanometers from the particle surface and therefore only assemblies (Fig. 4). (A) IPCE plots for FTO/SnO$_2$/TiO$_2$–RuP$^{2+}$/WOC and FTO/SnO$_2$/AgNP/TiO$_2$–RuP$^{2+}$/WOC. (B) The difference in IPCE (ΔIPCE = IPCE with Ag NP minus IPCE without Ag NP) between the two electrodes.

Fig. 4. (A) IPCE plots for FTO/SnO$_2$/TiO$_2$–RuP$^{2+}$/WOC and FTO/SnO$_2$/AgNP/TiO$_2$–RuP$^{2+}$/WOC. (B) The difference in IPCE (ΔIPCE = IPCE with Ag NP minus IPCE without Ag NP) between the two electrodes.

Fig. 5. Nanosecond TA difference spectra recorded following excitation at 532 nm for (A) FTO/SnO$_2$/TiO$_2$–RuP$^{2+}$ and (B) FTO/SnO$_2$/AgNP/TiO$_2$–RuP$^{2+}$ electrodes. The data in A and B were recorded in 0.1 M HAc/Ac$^-$ buffer with 0.4 M NaClO$_4$ under an applied bias of 0.2 V vs. Ag/AgCl at room temperature. (C) Single-wavelength TA traces at 460 nm for FTO/SnO$_2$/AgNP/TiO$_2$–RuP$^{2+}$ (black) and FTO/SnO$_2$/TiO$_2$–RuP$^{2+}$ (red) recorded in 0.1 M HAc/Ac$^-$ with 0.4 M NaClO$_4$. 

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at the top of the film, near the Ag NP layer, likely contribute to the improved photocurrent generation (15, 21). Consistent with the localized effect of the plasmon, lower photocurrents were obtained with increasing thickness of the TiO₂ layer applied by ALD. Fig. S3 shows the current response with varying TiO₂ shell thicknesses of 3, 4.5, and 6 nm. The best performance was achieved with a 3-nm TiO₂ coating. Samples prepared with varying thicknesses of the TiO₂ shell, but without the inclusion of Ag NPs, showed little difference in the maximum photocurrent density (Fig. S4).

To assess possible photocurrent generation from the Ag NPs alone, Fig. S5 shows photocurrent measurements for FTO/SnO₂/AgNP/TiO₂/WOC with no surface-bound chromophore. Without the chromophore, a modest photocurrent of 60 μA cm⁻² is produced. This indicates that the enhanced photocurrent observed with FTO/SnO₂/AgNP/TiO₂–RuP²⁺/WOC is not a result of direct light absorption and sensitization by the Ag NPs. Similar to improvements observed in the performance of DSSCs by the incorporation of Au and Ag NPs, the localized surface plasmon of the Ag NPs improves the rate of excitation of RuP²⁺ chromophores near the NP and leads to higher sustained photocurrents compared with the DSPEC without the Ag NPs (8, 10, 11).

Optical characterization of FTO/SnO₂/AgNP/TiO₂–RuP²⁺/WOC and FTO/SnO₂/TiO₂–RuP²⁺/WOC electrodes including transmittance, reflectance, and absorptance measurements is shown in Fig. S6. It is notable that the plasmon absorbance of the Ag NP overlaps with the λ_max = 450 nm metal-to-ligand charge-transfer (MLCT) absorption band for RuP²⁺ as shown in Fig. S7. This spectral overlap between the chromophore and plasmon resonance of the Ag NP is essential to realizing the improved solar energy conversion of the interface. The IPCE measurements in Fig. 4 highlight the improved light harvesting with the incorporation of the Ag NPs. The IPCE of FTO/SnO₂/AgNP/TiO₂–RuP²⁺/WOC reaches 31.8% at 450 nm, a nearly 100% increase over the IPCE for FTO/SnO₂/TiO₂–RuP²⁺/ WOC (16.3%) at this same wavelength. The difference spectrum comparing the IPCE with the Ag NPs minus the IPCE without the Ag NPs is shown in Fig. 4B. From these data, improved light harvesting of the surface with the Ag NPs occurs over wavelengths corresponding to the MLCT excitation of RuP²⁺. This reiterates that the increased photocurrents are a result of improved light capture by the chromophore through interaction with the surface plasmon of the Ag NP as opposed to a direct effect of the Ag NP. The IPCE value for FTO/SnO₂/AgNP/TiO₂–RuP²⁺/WOC represents one of the highest yet observed for a RuP²⁺-based DSPEC at 450 nm (4, 22, 25).

Light-Driven Water Oxidation. A collector-generator method (24) was used to investigate light-driven O₂ production as shown in Fig. S8. These studies revealed essentially the same faradaic efficiency for O₂ production by FTO/SnO₂/TiO₂–RuP²⁺/WOC and FTO/SnO₂/AgNP/TiO₂–RuP²⁺/WOC electrodes (96% and 94%, respectively). During 15-min illumination periods, the photocurrent of both FTO/SnO₂/TiO₂–RuP²⁺/WOC and FTO/SnO₂/AgNP/ TiO₂–RuP²⁺/WOC decreased to half of their initial values. This result is consistent with previous observations using similar chromophore/catalyst interfaces, and the presence of the Ag NP does not appear to influence the surface stability of the film (4). The high faradaic efficiency for O₂ generation with or without the Ag NPs indicates that the presence of the metal NPs does not affect the functional identity of the catalyst. The substantially higher photocurrents with added Ag NPs are consistent with a plasmon enhancement of chromophores near the NPs, which likely enables higher turnover frequencies of nearby catalysts enabling the higher current densities.

Transient Absorption Studies. The results of transient absorption (TA) measurements were used to investigate interfacial electron transfer dynamics. The TA measurements were performed under an applied bias of 0.2 V vs. Ag/AgCl at pH 4.65 in 0.1 M acetate buffer 0.4 M in NaClO₄. Difference spectra for FTO/SnO₂/TiO₂–RuP²⁺ and FTO/SnO₂/AgNP/TiO₂–RuP²⁺ from 350 to 700 nm following excitation at 532 nm are shown in Fig. 5A and B. In both Fig. 5A and B, the spectra are consistent with excitation followed by rapid, <10-ns injection to give the oxidized chromophore, –RuP³⁺. With or without the presence of the Ag NPs, rapid loss of the characteristic MLCT absorption at λ_max = 450 nm evidences the loss of ground state and formation of the oxidized dye.

The bleaching recovery traces shown in Fig. 5C reveal similar lifetimes for photooxidized RuP³⁺ in the presence or absence of the Ag NPs, 25 and 16 μs, respectively, as measured by the time required for half of the absorption feature to decay to zero. Based on the similar lifetime data, the presence of the Ag NPs does not appear to affect either the sensitization of the oxide by RuP²⁺ or the recombination of injected electrons to the oxidized RuP³⁺. While not offering direct evidence, taken in concert with the decrease in transmittance (Fig. S6D) and increase in absorbance (Fig. S6D), these observations do support the conclusion that the Ag NPs contribute to the improved performance by plasmon-enhanced light absorption of the RuP²⁺ sensitizer.

Conclusion. Our results are consistent with localized surface plasmon-enhanced light harvesting by including Ag NPs in the DSPEC photoanode surface. From the photocurrent and TA measurements, photoinduced electron injection and back-electron transfer are unaffected by the presence of the Ag NPs. However, the introduction of the Ag NPs leads to a nearly twofold increase in the photocurrent generated by the interface under identical conditions. Our results are important in understanding and extending the plasmonic enhancement of molecular light absorption to DSPEC water oxidation applications. The Ag NPs show no detrimental effect on the DSPEC device stability or faradaic efficiency for light-driven water oxidation. The addition of Ag NPs enhances light absorption of the MLCT RuP²⁺ dye and leads to an increase in the IPCE with a maximum of 31.8% at 450 nm. The plasmonic DSPEC produces a photocurrent density above 2 mA cm⁻² after 30 s of illumination with 1 sun simulated solar light. At the microscopic level, the impact of the plasmonic effect is extraordinary. Additional improvements in light collection maybe possible by varying the surface architectures to integrate a greater population of immobilized RuP²⁺ sensitizers in close proximity to the Ag NPs.

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