Preparation of platinum nanoparticles using iron(II) as reductant and photosensitized H₂ generation on an iron storage protein scaffold†

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The quest for efficient solar-to-fuel conversion has led to the development of numerous homogeneous and heterogeneous systems for photochemical stimulation of 2H⁺ + 2e⁻ → H₂. Many such systems consist of a photosensitizer, an H₂-evolving catalyst (HEC), and sacrificial electron donor often with an electron relay between photosensitizer and HEC. Colloidal platinum remains a popular HEC. We report here a novel, simple, and high yield synthesis of Pt nanoparticles (Pt NPs) associated with human heavy chain ferritin (Hfn). The formation of the Pt NPs capitalizes on Hfn’s native catalysis of autoxidation of Fe(II)(aq) (ferroxidase activity). Fe(II) reduces Pt(II) to Pt(0) and the rapid ferroxidase reaction produces FeO(OH), which associates with and stabilizes the incipient Pt NPs. This Pt/Fe–Hfn efficiently catalyzes photosensitized H₂ production when combined with Eosin Y (EY) as photosensitizer and triethanolamine (TEOA) as sacrificial electron donor. With white light irradiation turnover numbers of 300H₂ per Pt, 250H₂ per EY were achieved. A quantum yield of 18% for H₂ production was obtained with 550 nm irradiation. The fluorescence emission of EY is quenched by TEOA but not by Pt/Fe–Hfn. We propose that the photosensitized H₂ production from aqueous TEOA, EY, Pt/Fe-Hfn solution occurs via a reductive quenching pathway in which both the singlet and triplet excited states of EY are reduced by TEOA to the anion radical, EY⁻, which in turn transfers electrons to the Pt/Fe–Hfn HEC. Hfn is known to be a remarkably versatile scaffold for incorporation and stabilization of noble metal and semiconductor nanoparticles. Since both EY and Hfn are amenable to scale-up, we envision further refinements to and applications of this photosensitized H₂-generating system.

Introduction

The quest for efficient solar-to-fuel conversion has led to the development of numerous homogeneous and heterogeneous systems for photochemical stimulation of 2H⁺ + 2e⁻ → H₂. These systems are typically modular, consisting of a redox active photosensitizer (PS), sacrificial electron donor (SED), H₂ evolving catalyst (HEC), and often an electron relay (typically methyl viologen (MV²⁺)) between PS and HEC. Although intensive efforts have been devoted to development of HECs using earth-abundant elements, colloidal platinum continues to be used due to its ease of synthesis, stability, catalytic efficiency, and versatility.⁵⁺⁻¹²

The three most commonly used visible light-absorbing PSs for H₂ generation in aqueous solutions have been transition metal–polypyridyl complexes,¹³⁻¹⁵ porphyrins,¹⁶ and xanthene dyes.¹⁷⁻¹⁹ Among these PSs, xanthene dyes are the most amenable to scale-up and usually give higher H₂ quantum yields than either metal–polypyridyl complexes or porphyrin-type. Photosensitized H₂ generation from a combination of the inexpensive xanthene dye, Eosin Y (2,4,5,7-tetrabromo-fluorescein, EY), triethanolamine (TEOA) as SED, polymer-coated Pt NPs as HEC, and MV²⁺ as an electron relay was reported as long ago as 1983.³⁰ Deposition of colloidal Pt on surfaces or within films that are presumed to facilitate photosensitized electron transfer reactions of EY function relatively efficiently for H₂ generation without an added electron relay.¹¹,¹⁹,²¹⁻²³ Depending on the system, the photochemistry has been reported to occur by either oxidative or reductive quenching of ³EY*, via the cation radical, EY⁺⁺, or the anion radical, EY⁻⁻, respectively.²⁴,²⁵ Oxidative quenching is likely to predominate in the presence of a large excess of an electron relay molecule. More recently, TEOA has been reported to reductively quench the singlet excited state, ¹EY*, in a concentration-dependent fashion.²⁶

Various cage-like proteins have been shown to enclose catalytically active noble metal nanoparticles (NPs), including Pt in aqueous solution.²⁷ The iron storage protein, ferritin, has proven to be remarkably versatile in this regard.²⁸,²⁹ The ~8 nm
hollow cavity of ferritins, represented by that of human ‘heavy chain’ ferritin (Hfn) in Fig. 1, can store up to an average of ~3000 irons per 24-mer as either amorphous ferric oxyhydroxide (FeO(OH)) or the mineralized form, ferrihydrite. Ferritins incorporate iron by catalyzing the autoxidation of Fe(II)(aq), referred to as ferroxidase activity. In the absence of iron, Pt NPs have been shown to form within the ferritin cavity upon borohydride reduction of either tetrachloroplatinate(II) or hexachloroplatinate(III). We have found only one report of the use of ferritin 24-mer-encapsulated Pt NPs for photo-sensitized H2 generation. That system used tris(2,2’-bipyridine)ruthenium(II)chloride as PS and MV2+ as electron relay. A bacterial homolog called bacterioferritin can bind a zinc(II)-hydride reduction of Pt(II) or Pt(IV) salts. Previous reports of Pt NPs incorporated into ferritins furnishes an explanation for the differing sizes. The Pt/Fe-Hfn showed individual 24-mer-sized protein shells containing multiple small (~1 nm) electron dense Pt NPs lining the inner walls of the shell but also coating the outer surface (inset to Pt/Fe-Hfn panel of Fig. 3). Given our method of preparation and iron content of the Pt/Fe-Hfn, we presume voids between Pt NPs within the 24-mer contain much less electron dense colloidal or mineralized FeO(OH). The larger hydrodynamic diameter of Pt/Fe-Hfn could indicate formation of dimers of 24-mers, consistent with dimers observed by TEM (inset to the Fig. 3 Pt/Fe-Hfn panel).

**Effects of Pt/Fe-Hfn on EY spectroscopic properties**

The UV-vis absorption spectrum of 72 μM EY in 0.3 M TEOA pH 9 (Fig. 4) shows the features expected for the photochemically active dianionic form (λmax 304, 343, and 517 nm), and these features are unperturbed by the presence of Pt/Fe-Hfn. Since binding to proteins normally shifts the absorption maxima of EY, this lack of perturbation indicates no stable interaction between EY and the Pt/Fe-Hfn protein particles under our conditions.

TEOA is known to dynamically quench the luminescence of photoexcited EY in anaerobic aqueous solutions. We investigated whether Pt/Fe-Hfn had any effect on this quenching. 1EY* shows a characteristic fluorescence emission spectrum with λmax at ~540 nm in neutral to basic aqueous solution. Fig. 5 shows the expected quenching of EY fluorescence by TEOA but little or no quenching by Pt/Fe-Hfn. These observations indicate that reductive quenching of 1EY* can occur in our H2-generating system.

**Photosensitized generation of H2**

We optimized the TEOA, Pt, and EY concentrations starting from those reported by Wang et al. but omitting MV. Time courses for photosensitized H2 production using white light
irradiation are shown in Fig. 6. The six-hour turnover numbers (TONs) for Pt NP and Pt/Fe-Hfn (inset to Fig. 6) were similar to each other. As reported previously for polymer-coated Pt NPs, we found 72 μM EY to be optimal for photosensitized H₂ production. The leveling off of H₂ production by 6 h irradiation is most likely due to gradual debromination of EY, resulting ultimately in the completely debrominated form, fluorescein, which is typically a much less efficient PS. Fig. S1† shows that, in fact, substitution of fluorescein in place of EY leads to a relatively low level of photosensitized H₂ generation. Omission of any single component (EY, TEOA, Pt-Hfn or Pt/Fe-Hfn) resulted in no photosensitized H₂ generation. The time course for photosensitized H₂ production of Pt/Fe-Hfn under the same conditions but irradiated using a 550 ± 25 nm filter is shown in Fig. S2,† and these data were used to determine the quantum yield. The 6 h H₂ quantum yield for Pt/Fe-Hfn using chemical actinometry was 18%.

When Fe-Hfn was substituted in place of Pt/Fe-Hfn at an iron concentration of ~230 μM in 0.3 M TEOA pH 9 and 72 μM EY, less than 0.6 μmol H₂ was generated over 6 h irradiation. Attempts to load the pre-formed Pt-Hfn with iron by the aerobic multiple- aliquot ferrous ammonium sulfate procedure or single addition of ~1500 iron as ferrous ammonium sulfate per 24-mer to the anaerobic Pt-Hfn/EY/TEOA reaction solution immediately prior to irradiation gave less than half the 6 h yield of H₂ and TONs per Pt or EY compared to those shown in Fig. 6.
EY limits H₂ generation

We further tested that decomposition of EY and not the Fe/Pt-NP Hfn was the limiting factor in H₂ generation by adding more EY after 6 h of irradiation, where H₂ generation had leveled off in the initial reaction mixture (Fig. 6). As shown in Fig. 7, the additional EY prevented the 6 h levelling off of H₂ generation, the rate of which decreased again between 9 and 12 h, but with an increased overall H₂ yield.

Iron release

Fig. 9 shows that iron was gradually released upon white light irradiation of a Pt/Fe-Hfn solution under the same conditions as for photosensitized H₂ generation. Approximately 30% of initial iron content remained in the Pt/Fe-Hfn after 6 h of irradiation. This iron release presumably occurred upon photosensitized reduction of Fe(O)OH to Fe(II), as demonstrated in our previous work using Zn protoporphyrin IX as photosensitizer.⁴⁸ Assuming the iron is released as Fe(II), the ~300 mol H₂/mol Pt TON shown in Fig. 6 translates to ~2% of photogenerated reducing equivalents being devoted to iron reduction relative to H₂ production during 6 h irradiation.

Air tolerance

³EY* generates singlet O₂ from ground state triplet O₂ with quantum yield ~0.5 in aqueous solution.⁴⁵ Nevertheless, in the absence of quenchers EY undergoes relatively slow photodegradation in aerobic aqueous solutions.⁴¹ A more recent report shows that EY⁻⁻ produced from reductive quenching by TEOA can be quantitatively recycled back to EY via an oxidative photoreaction with O₂, which generates superoxide.⁴⁶ Despite the photoinduced generation of these reactive oxygen species, photosensitized H₂ generation by the TEOA, EY, Pt/Fe-Hfn system, showed some tolerance to air exposure. The time course for H₂ production upon white light irradiation of an air-saturated reaction mixture is shown in Fig. 8. H₂ production leveled off after 2 h at approximately one-third that from an equivalent anaerobic reaction mixture (Fig. 6). Fig. S3 and S4† show GC traces corresponding to the time course in Fig. 8. These traces clearly show the presence of O₂ in the headspace through at least 4 h of irradiation. A subsequent addition of another 72 μM of EY at 4 h irradiation time led to a restart of photosensitized H₂ production, consistent with degradation of EY being the limiting factor.
Ferroxidase activity and Pt NP formation

Previous preparations of Pt NPs within ferritins have typically used commercial horse spleen apoferritin (HSAF) and borohydride as reducing agent.\textsuperscript{32–34} HSAF consists of a combination of ‘heavy’ and ‘light’ protein subunits in the 24-mer. The Hfn used in this work contains only the ‘heavy’ chain subunits. The heavy chains contain ferroxidase centers (FCs), which are located in the protein shell. The FC in each of the 24 subunits binds two Fe(II) and catalyzes their autoxidation. The resulting Fe(III) in the FC migrates into the inner cavity of the protein shell, where it forms polynuclear FeO(OH) nucleation sites.\textsuperscript{31,47} The FC then binds two more Fe(II) and repeats the cycle. Additional Fe(II) can migrate through pores on the protein shell and are oxidatively incorporated onto the growing FeO(OH) surface. This process is diagrammed in Scheme 1.

Scheme 1 also diagrams likely pathways for formation and stabilization of the Pt NP in Pt/Fe-Hfn. Our results show that Pt NPs can be incorporated into Hfn in air-saturated solutions upon adding aliquots of Fe(II) salt to Hfn that had been preincubated with the Pt(II) salt. When we titrated the Pt(II) salt/Hfn solution with Fe(II) salt under anaerobic conditions, the resulting Pt(0) formed a bulk precipitate with little or no formation of Pt NPs associated with Hfn. This observation is consistent with a requirement for the ferroxidase reaction for formation of the Pt NPs. We suggest that the added iron serves as both reductant and Pt NP coating. Fe(II) reduces Pt(II) to Pt(0) and the rapid ferroxidase reaction produces FeO(OH), which associates with the incipient Pt NPs. This association would inhibit aggregation to form the larger Pt NPs obtained when using borohydride as reductant (Fig. 3, Pt-Hfn panel). Some Pt NPs also associate with the outer protein surface of the Pt/Fe-Hfn (inset to Fig. 3 Pt/Fe-Hfn panel). How these outer surface Pt NPs form and whether they are associated with FeO(OH) is not known. HSAF and light chain human ferritin were reported to show increased ferroxidase activity via incorporation of Pt NP via the Pt(II) salt/borohydride reduction procedure.\textsuperscript{34,48} Using our protocol, the Pt NPs form during addition of Fe(II) and are therefore less likely to significantly contribute to the ferroxidase activity.

FePt alloy NPs were reported to form at elevated temperature in a more heat stable ferritin using a mixture of ferrous ammonium sulfate, potassium tetrachloroplatinate and sodium borohydride as reducing agent.\textsuperscript{49} However, this report explicitly stated that this procedure was unsuccessful using Hfn. In any case our more oxidizing conditions at room temperature seem unlikely to result in formation of FePt mineral phases via reduction of the M(II) salts.

Photosensitization mechanism

While both oxidative and reductive quenching of $^3$EY$^\ast$ to EY$^\ast$ and EY$^\ast$–, respectively, are thermodynamically feasible,\textsuperscript{24,25} our results are more consistent with the reductive quenching pathway shown in Scheme 2. TEOA is an efficient reductive quencher of not only $^3$EY, but also the shorter-lived $^1$EY$^\ast$.\textsuperscript{26,43,44} Under conditions close to those used for the luminescence quenching results shown in Fig. 5, it has been estimated that TEOA reductively quenches about half of the photogenerated $^1$EY$^\ast$.\textsuperscript{44} Continuous irradiation, thus, likely generates a low steady state level of EY$^\ast$.\textsuperscript{44} EY is too large to penetrate the pores of the Hfn protein shell. However, reducing agents such as reduced flavins, which do not penetrate the Hfn protein shell, are known to reduce FeO(OH) to Fe$^{2+}$ inside the shell.\textsuperscript{20} We, therefore, propose that the highly reducing EY$^\ast$ transfers electrons to Pt NPs on the outer surface and inside the protein shell, both of which function as HEC. The pathway shown in Scheme 2 would also apply to the borohydride-prepared Pt-Hfn, in which the Pt NPs are located only inside the protein shell.
Comparisons with other TEOA/EY/Pt NP systems

Due to wide variations in solution volumes, heterogeneity, irradiation pathlengths and photon flux, comparing \( \text{H}_2 \) generation rates among various systems using EY as photosensitizer is not straightforward. However, the 18% quantum yield and separation rates among various systems using EY as photosensitizer required the presence of both Fe(II)(aq) and O\(_2\). We conclude that this requirement stems from the native ferroxidase activity of the Hfn. The FeO(OH) produced from this activity associates with and stabilizes the Pt NPs. Photosensitized \( \text{H}_2 \) production from aqueous TEOA, EY, Pt/Fe-Hfn solutions occurred with TON and quantum efficiency comparable to other systems using xanthene dye PSSs and does not require an added electron relay between PS and Pt NPs. We propose a reductive quenching pathway in which TEOA reduces \(^3\text{EY}^*\) and \(^3\text{EY}^*\) to \( \text{EY}^-\), which then transfers electrons to the Pt/Fe-Hfn. A small portion of the photogenerated reducing equivalents is diverted towards reduction of FeO(OH), whereas the vast majority are funneled into catalytic \( \text{H}_2 \) production on the Pt NPs.

Experimental

Reagents and general methods

All chemicals were purchased from either Sigma-Aldrich or Fisher Scientific at the highest grades available. Stock solutions of EY or fluorescein were prepared in DMSO. All aqueous solutions were prepared in water that had been passed through a Milli-Q ultrapurification system (Merk Millipore, Inc.) to achieve a resistivity of 18 M\( \Omega \). Solutions containing EY were stored in aluminum foil-covered containers and manipulated in low room light.

Potential advantages of the TEOA, EY, Pt/Fe-Hfn system

We have not found previous reports of Fe(II)(aq) used for preparation of Pt NPs. In our Hfn system ferrous ammonium sulfate functions as the reducing agent for tetrachloroplatinate and occurs in aerobic aqueous solutions near neutral pH. Hfn is quite durable, and its production is amenable to scale-up. Our photosensitized H\(_2\)-generating system also showed activity in air-saturated solution. This activity could be advantageous in Pt-containing ‘water splitting’ systems, which produce both \( \text{H}_2 \) and O\(_2\). Pt is known to catalyze the back reaction of \( \text{H}_2 \) with O\(_2\). The remarkably versatile ferritin scaffold can incorporate a variety of metal oxide and semiconductor NPs, can be adsorbed to electrochemically active surfaces, and is tolerant to a variety of modifications to the polypeptide chains.

We can, thus, envision further refinements to and applications of our photosensitized TEOA, EY, Pt/Fe-Hfn \( \text{H}_2\)-generating system.

Conclusions

We have described a novel method for producing and stabilizing small Pt NPs via reduction of a Pt(II) salt by Fe(II)(aq) in an iron storage protein scaffold. The formation of the Pt NPs required the presence of both Fe(II)(aq) and O\(_2\). We conclude that this requirement stems from the native ferroxidase activity of the Hfn. The FeO(OH) produced from this activity associates with and stabilizes the Pt NPs. Photosensitized \( \text{H}_2 \) production from aqueous TEOA, EY, Pt/Fe-Hfn solutions occurred with TON and quantum efficiency comparable to other systems using xanthene dye PSSs and does not require an added electron relay between PS and Pt NPs. We propose a reductive quenching pathway in which TEOA reduces \(^3\text{EY}^*\) and \(^3\text{EY}^*\) to \( \text{EY}^-\), which then transfers electrons to the Pt/Fe-Hfn. A small portion of the photogenerated reducing equivalents is diverted towards reduction of FeO(OH), whereas the vast majority are funneled into catalytic \( \text{H}_2 \) production on the Pt NPs.
containing ~2300 Fe/24-mer, as determined using the protein and iron analyses methods described below.

For preparations of Pt-containing Hfns a 100 mM aqueous stock solution of K₂PtCl₄ was prepared 12 hours prior to use. K₂PtCl₄ was added to 3.5 mL of 1 μM Hfn to achieve a Pt concentration of 1.6 mM. The Hfn/K₂PtCl₄ solution was incubated for 2 h. For preparation of Pt only loaded Hfn (Pt-Hfn) sodium borohydride was added from a freshly prepared aqueous solution to achieve 0.5 mol borohydride per mol K₂PtCl₄. The mixture was stirred for ~60 min, then centrifuged at 10,000 g for 5 min to remove an insoluble black precipitate. For preparation of Pt and iron-loaded Hfn (Pt/Fe-Hfn) an aliquot of an anaerobic aqueous stock solution of 0.02 M ferrous ammonium sulfate was added via syringe to 3.5 mL of an air-saturated 1.6 mM K₂PtCl₄/1 μM Hfn solution in a septum capped-vial to achieve 100 mol equivalents of added Fe(II) per Hfn 24-mer. The mixture was incubated at room temperature for 20 minutes and then centrifuged at 5500 g for 10 minutes to remove any precipitate. This process was repeated to achieve a mol ratio of ~1500 added iron per Hfn 24-mer (extensive precipitation and loss of protein occurred beyond this ratio). If used within a few days of preparation, after the final centrifugation the Pt-Hfn or Pt/Fe-Hfn solutions were exchanged into 0.3 M TEOA pH 9, solid EY, and DMSO were brought into the glovebox (Vacuum Atmospheres Co) for 8–12 h before use. Solutions for irradiation were prepared to contain Pt-Hfn or Pt/Fe-Hfn at a concentration of 60 μM Pt-Hfn or Pt/Fe-Hfn 24-mer in 0.3 M TEOA were placed in a HOYA 62 mm UV-IR multi-coated filter (Optical Filter Shop) covering the projector lens. The photon flux for H₂ quantum yield was determined by chemical actinometry using solutions of Reineke’s salt. For quantum yields solutions were irradiated identically to that described above but using a 550 ± 25 nm filter (Optical Filter Shop) covering the projector lens. The photon flux for H₂ quantum yield was determined by chemical actinometry using solutions of Reineke’s salt. The quantum yield percent was calculated as: [(2 × mol H₂ produced) ÷ mol incident photons] × 100.

Light-triggered iron release from Pt/Fe-Hfn

A 25 mL solution of Pt/Fe-Hfn (60 μM Pt) and 72 μM EY in 0.3 M TEOA pH 9 was prepared in the glovebox under a N₂ atmosphere. The solution was split equally into seven 6.5 mL vials containing a 100 μL aliquot, which contained the protein, were collected from the irradiation beam, and solutions were passed through desalting columns (Econo-Pac 10DG column, Bio-Rad); the first 3.0 mL of effluent, which contained the protein, were collected and prepared as described above to determine iron remaining with the protein by ICP-OES.

Conflicts of interest

There are no conflicts to declare.

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