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COMMUNICATION

Efficient Photochemical Production of Hydrogen in Aqueous Solution by Simply Incorporating a Water-insoluble Hydrogenase Mimic into Hydrogel†Tianjun Yu^a, Yi Zeng^a, Jinping Chen^a, Xiaohui Zhang^a, Guoqiang Yang^{*b}, Yi Li^{*a}⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

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A composite catalyst Hy-pyr/PVP constructed by incorporating a hydrophobic [Fe-Fe]-hydrogenase mimic (Hy-pyr) into self-crosslinked polyvinylpyrrolidone (PVP) hydrogel has been successfully applied to photocatalytic production of hydrogen in aqueous solution with high catalytic activity and efficiency. The present study provides a general, simple and efficient strategy for the application of water-insoluble catalysts in aqueous solution by using the PVP hydrogel.

Converting solar energy into fuel is one of the most promising strategies to meet long term sustainable energy needs.¹⁻³ Of various approaches, the photocatalytic evolution of hydrogen from water is at the forefront.⁴⁻⁸ The photochemical production of hydrogen by mimicking natural photosynthesis is considered to be one of the most attractive and potentially useful approaches.⁹⁻¹² However, the development of energy-efficient, cost-effective and clean processes for hydrogen production by using sunlight remains a great challenge.

To construct artificial photosynthesis system for hydrogen production, it is essential to develop catalysts with high efficiency and low cost. Hydrogenases are a class of metalloenzymes evolved by nature, which catalyze the interconversion of protons and hydrogen efficiently and rely on metals abundant on earth such as iron and/or nickel.¹³⁻¹⁶ The resolving of the biological structures and the understanding of the active sites of hydrogenases have inspired chemists to develop artificial molecular catalysts to mimic natural hydrogenases for energy conversion.¹⁷⁻²⁹ Of these studies, a series of [2Fe2S] complexes have been synthesized to mimic the active sites of natural diiron

hydrogenases and result in a significant development in the catalytic reduction of protons.³⁰⁻⁴² Although various kinds of diiron hydrogenase mimics have been constructed rapidly, most of them can only be applied in organic solvents or a mixture of organic solvents and water because of the inherent insolubility of the majority of hydrogenase mimics in water.⁴³⁻⁴⁵ To accomplish hydrogen production in aqueous solution, many efforts have been devoted to improve the hydrophilicity of diiron hydrogenase mimics either by covalent or non-covalent methods. Over the past decade, only a handful of water-soluble hydrogenase mimics have been synthesized by covalently introducing hydrophilic groups to the hydrogenase mimics or attaching mimics of the active sites to a protein matrix.⁴⁶⁻⁵⁰ Although some of them have been successfully applied to hydrogen production systems, covalent synthesis processes for water-soluble diiron hydrogenase mimics are costly due to labor, time, and energy-consumption. In comparison with the covalent method, the non-covalent methods exhibit merits such as tunability, simplicity and convenience, for application of hydrophobic hydrogenase mimics in water. The employment of supramolecular architectures such as surfactant micelle,⁵¹ cyclodextrin,⁵² metal-organic framework (MOF),⁵³ and molecular sieve⁵⁴ has allowed the application of hydrophobic hydrogenase mimics in water, which opens an opportunity to circumvent the challenge. Following this line of thought, the introduction of hydrophilicity to a substrate by noncovalent strategy would conceivably benefit the hydrogen production catalyzed by hydrophobic hydrogenase mimics in water.

Chemical inert hydrogels have received much attention in a diverse range of applications due to their tunable dimensions, large surface area, and stable interior network structure.^{55, 56} The polyvinylpyrrolidone (PVP) is a widely used polymer, which can form a chemical inert hydrogel by self-crosslinking. The high affinity of the PVP hydrogel for both organic molecules and water facilitates the dispersion of hydrophobic substrates in water and the infiltration of water. Recently, Yang's group found that the PVP hydrogel could be developed to a common platform to detect the components in water with water-insoluble probes.⁵⁷ Inspired by these probing applications of the PVP hydrogel, we attempt to take advantage of the amphipathicity of the PVP hydrogel to achieve hydrogen production catalyzed by a

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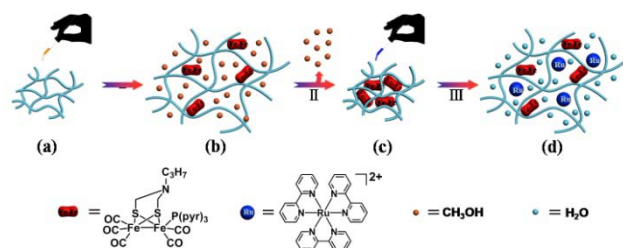
[†]Electronic Supplementary Information (ESI) available: Synthetic details and additional experimental data. See DOI: 10.1039/b000000x/

hydrophobic catalyst in water.

In the present work, a mimic of the active-site of diiron hydrogenase was incorporated into a UV-induced self-crosslinked PVP hydrogel noncovalently as an artificial hydrogenase, which was successfully applied to a hydrogen production system in water, demonstrating excellent catalytic activity and efficiency. This study provides a general, simple and efficient strategy for the application of water-insoluble hydrogenase mimics in water.

The PVP hydrogel was prepared by crosslinking PVP with an average molecular weight of 1,300,000 upon the UV irradiation according to the method reported in the literature.⁵⁸ The construction of a composite catalyst (Hy-pyr/PVP) by immobilization of the mimic of the active-site of diiron hydrogenase (Hy-pyr) into the PVP hydrogel and the preparation of the corresponding photocatalytic hydrogen production system are shown in Scheme 1. Hy-pyr/PVP was prepared by adding a methanol solution of Hy-pyr (5 μ M, 2 mL) into fine PVP xerogel particles (100 mg) (Scheme 1-I). After all the liquid was sucked up and the system became a gel, the gel was evaporated to dryness, giving the dry Hy-pyr/PVP (Scheme 1-II). The dry Hy-pyr/PVP was characterized by FTIR and UV/Vis spectroscopy (Figure S1 and Figure S2). Three prominent bands of the CO stretching vibration at 2054, 2002, and 1983 cm^{-1} attributed to Hy-pyr are observed in the FTIR spectrum of the dry Hy-pyr/PVP. The hypsochromic shift of the second peak (from 2010 cm^{-1} of Hy-pyr to 2002 cm^{-1} of Hy-pyr/PVP) suggests that the hydrogenase mimic is immobilized on PVP. The PVP hydrogel is transparent and shows little absorption of visible light, which avoids the energy loss of light during irradiation. Hy-pyr/PVP is reddish and its aqueous dispersion displays a main absorption band centered at 352 nm and a shoulder absorption band at around 490 nm, which are assigned to Hy-pyr. The main absorption band (352 nm) of the aqueous dispersion of Hy-pyr/PVP shows a hypsochromic shift of 6 nm in comparison with that of Hy-pyr in CH_3CN (346 nm, Figure S3). No absorption of Hy-pyr was observed in aqueous solution because Hy-pyr cannot dissolve in water. The dry Hy-pyr/PVP catalyst can be stored in a refrigerator for more than half year without any deterioration (Figure S4).

The photocatalytic evolution of hydrogen by Hy-pyr/PVP in



Scheme 1. Schematic illustration of construction of hydrogen production system fabricated with Hy-pyr/PVP and $\text{Ru}(\text{bpy})_3^{2+}$. (I) Preparation of the composite catalyst Hy-pyr/PVP by adding a methanol solution of Hy-pyr into a PVP xerogel. (II) Obtainment of the dry Hy-pyr/PVP by removing the solvent under reduced pressure. (III) Establishment of the photocatalytic hydrogen production system by adding the aqueous solution of the Ru photosensitizer and the electron donor reagent (not present) into the dry Hy-pyr/PVP.

aqueous solution was examined by using water soluble $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (bpy = 2,2'-bipyridine) as the photosensitizer (PS), and ascorbic acid (H_2A) as the proton source and the sacrificial electron donor. The photocatalytic system was constructed by adding an aqueous solution containing both $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and H_2A into the dry Hy-pyr/PVP (Scheme 1-III), which was stirred for 30 min to allow the PVP hydrogel fully swelling. Irradiation of the catalytic system with visible light ($400 \text{ nm} < \lambda < 780 \text{ nm}$) resulted in the immediate production of hydrogen, which was quantified by gas chromatography and the turnover numbers (TONs) were calculated based on the amount of H_2 molecules generated versus the number of artificial hydrogenase molecules. Control experiments indicated that no hydrogen production was observed in the absence of any of the catalyst, the photosensitizer and the sacrificial agent, validating that all of them are essential for the photocatalytic evolution of hydrogen. The performance of the photocatalytic system was dramatically affected by the reaction conditions, such as the concentrations of the photosensitizer and H_2A as well as the irradiation intensity and the pH value of the system. An optimization of the reaction conditions was conducted to improve the efficiency of the photochemical production of hydrogen.

To optimize the reaction conditions for this novel catalytic system, light-induced hydrogen production was conducted by varying one condition while keeping all the other conditions identical. The pH value of the catalytic system was adjusted by adding an aqueous solution of sodium hydroxide (0.1 M) or hydrochloric acid (0.1 M) prior to irradiation. To optimize the pH value for this novel photocatalytic system, the concentrations of Hy-pyr, $\text{Ru}(\text{bpy})_3\text{Cl}_2$, and H_2A were confirmed to be ca. 1 μ M, 0.5 mM, and 0.2 M, respectively, and the photocatalytic processes were conducted upon irradiation with visible light from a xenon lamp (200 mW/cm^2). The performance of the photocatalytic system are dramatically affected by the pH value as shown in Figure 1a. Hydrogen was generated in all four photocatalytic systems with the pH values of 3, 4, 5, and 6, respectively. The maximum turnover number and the corresponding turnover frequency were achieved at the pH value of 4, manifesting that the optimal pH value was 4. Neither higher nor lower pH values benefit the photocatalytic process. The hydrogen production involving the proton reduction is restrained at the higher pH values because of the lower concentration of H^+ . The bad photocatalytic performance at the lower pH values can be rationalized to the decreased ability of H_2A as a sacrificial electron donor, which is crucial to the reduction of the excited $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^+$. This conclusion is supported by the quenching experiment of $\text{Ru}(\text{bpy})_3^{2+}$ by H_2A at different pH values. The quenching efficiency increases dramatically with increasing the pH value, indicative of a weakened reduction ability of H_2A for $\text{Ru}(\text{bpy})_3^{2+}$ at lower pH values (Figure S5).

The effects of the concentration of PS and H_2A on the efficiencies of photochemical production of hydrogen were further investigated and the results are shown in Figures 1b and 1c, respectively. In the range of experimental concentrations, the more $\text{Ru}(\text{bpy})_3^{2+}$ or H_2A is added, the better the performance of the hydrogen production is observed. The increased amounts of $\text{Ru}(\text{bpy})_3^{2+}$ and H_2A make the photocatalytic system absorb more photons during the irradiation and produce more reduced

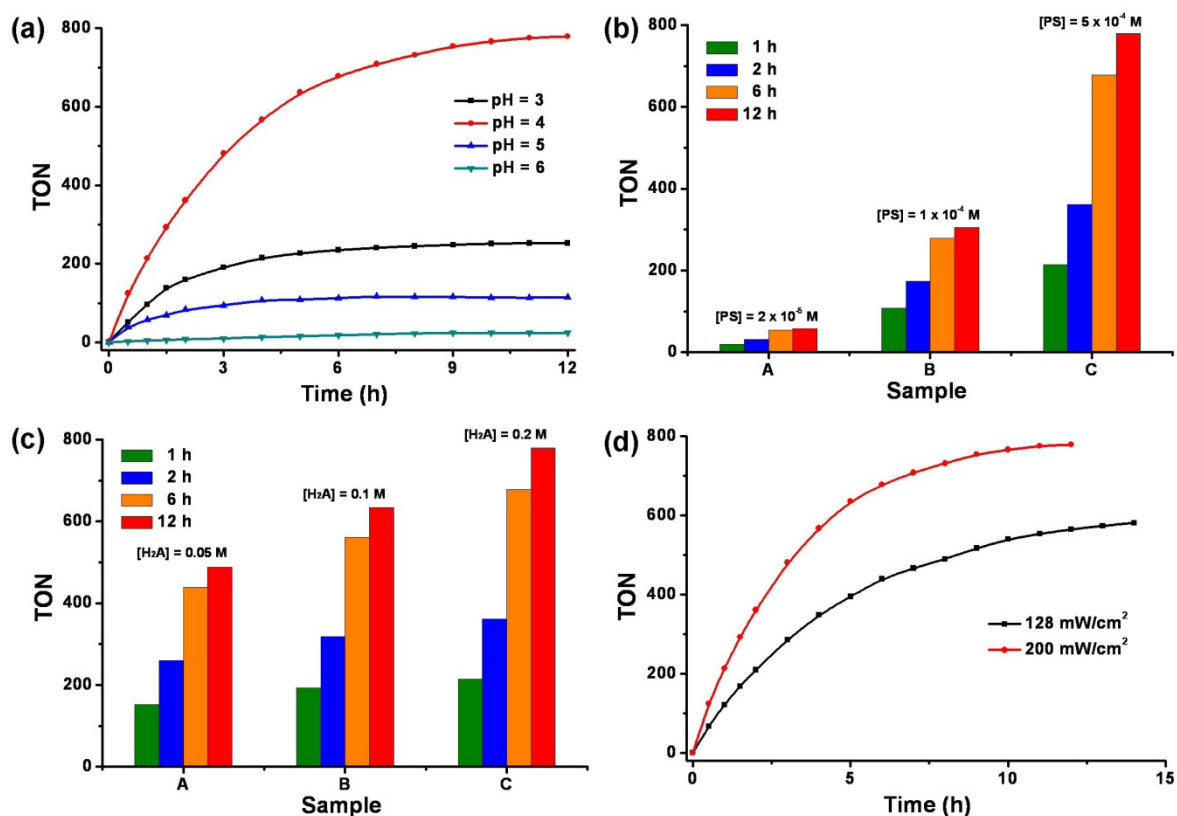


Figure 1. Influence of the pH value (a), the concentrations of PS (b), H_2A (c), and the illumination intensity (d) on the evolution of hydrogen catalyzed by Hy-pyr/PVP in aqueous solution. Other conditions ($[\text{Ru}(\text{bpy})_3\text{Cl}_2] = 0.5 \text{ mM}$, $[\text{Hy-pyr}] = 1 \text{ }\mu\text{M}$, $[\text{H}_2\text{A}] = 0.2 \text{ M}$, $\text{pH} = 4$, $[\text{PVP hydrogel}] = 10 \text{ mg/mL}$) are kept identical except the varying condition monitored.

5 photosensitizers, respectively, thus advancing the photocatalysis. The performance of the photocatalytic system was also affected by the illumination intensity. When the illumination intensity was decreased from 200 to 128 mW/cm^2 , the initial turnover frequency (TOF) of hydrogen production calculated based on Hy-pyr under the initial first 1 h irradiation decreased from 214 to 122 h^{-1} , and the TON also reduced by about 25% (Figure 1d). The intense illumination provides more photons to the catalytic system per unit time, resulting in a higher initial TOF for the catalytic system. The weaker illumination lowers the catalytic rate and prolonging irradiation time is needed to produce same amount of hydrogen as the intense illumination does. However, the catalyst and the photosensitizer decompose gradually during working. Prolonging the irradiation time does not benefit the catalytic output, resulting in lower TON compared with that under the intense illumination.

The best photocatalytic performance of Hy-pyr/PVP is depicted in Figure 1a ($\text{pH} = 4$) under the optimal conditions. Hydrogen was generated rapidly in this photocatalytic system during the first few hours of irradiation and the initial TOF calculated based on Hy-pyr under the initial first 1 h irradiation is up to 214 h^{-1} . The evolution of hydrogen slowed down gradually with prolonging irradiation time, and reached a maximum plateau after about 12 h irradiations. The maximum TON of 780 is observed.

Control experiment demonstrates that the photocatalytic production of hydrogen of the Hy-pyr/PVP catalytic system involves a photosensitizing mechanism. To clarify whether the

excited photosensitizer delivers an electron to the catalyst by direct oxidative quenching or after reduction by the sacrificial agent, the free energy change (ΔG) of the electron transfer process was estimated. The estimation results indicate that the Hy-pyr/PVP catalytic system can only conduct through a reductive quenching mechanism because the direct electron transfer from the excited photosensitizer to Hy-pyr is thermodynamically unfavorable (Table S1). The photocatalytic process begins with excitation of $\text{Ru}(\text{bpy})_3^{2+}$ followed by the reduction, and then the reduced product $\text{Ru}(\text{bpy})_3^+$ delivers an electron to the catalyst, which accords to the mechanism reported by Sun's⁵⁹ and Ott's³⁷ groups. The photoinduced electron transfer process in the Hy-pyr/PVP catalytic system is further evidenced by the flash photolysis experiments. Pulsed-laser photolysis of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was carried out in deaerated aqueous solution in the presence of PVP hydrogel by using 450 nm excitation light. Both transient absorption spectra of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in the presence and absence of sacrificial agent H_2A (0.2 M) at the pH value of 4 show a strong transient absorption band with a maximum at 360 nm (Figures 2a and 2b), which is assigned to the excited state $^*\text{Ru}(\text{bpy})_3^{2+}$ according to the literature.³⁷ The transient absorption spectrum of $^*\text{Ru}(\text{bpy})_3^{2+}$ almost comes back to the baseline at 1.6 μs after the excitation pulse in the absence of H_2A , indicating that $^*\text{Ru}(\text{bpy})_3^{2+}$ converts back to $\text{Ru}(\text{bpy})_3^{2+}$; however, the transient absorption spectrum of $^*\text{Ru}(\text{bpy})_3^{2+}$ cannot come back to the baseline during the same or even longer time range in the

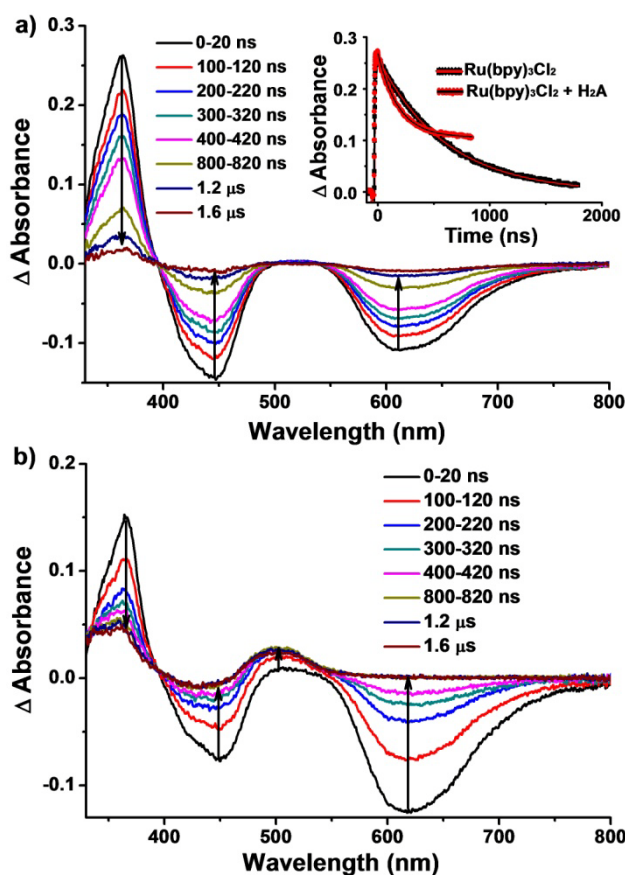


Figure 2. Transient absorption spectra obtained in the time range of 0-1.6 μ s following laser photolysis of deaerated aqueous solutions containing $\text{Ru}(\text{bpy})_3^{2+}$ (5×10^{-5} M) and the PVP hydrogel (10 mg/mL) in the absence (a) and presence (b) of H_2A (0.2 M) at pH=4. Inset: kinetic traces at 360 nm in the absence and presence of H_2A .

presence of H_2A , indicating the formation of new species. The formation of a new transient absorption band with maximum at 505 nm is observed accompanying with the decay of $^*\text{Ru}(\text{bpy})_3^{2+}$, which can be attributed to the formation of the reduced photosensitizer $\text{Ru}(\text{bpy})_3^+$.³⁷ Analysis of the kinetic traces at 360 nm gives the lifetimes of $^*\text{Ru}(\text{bpy})_3^{2+}$ in the absence and presence of H_2A to be 604 and 183 ns, respectively (inset of Figure 2a). The shortened lifetime of $^*\text{Ru}(\text{bpy})_3^{2+}$ in the presence of H_2A can be ascribed to the electron transfer from H_2A to $^*\text{Ru}(\text{bpy})_3^{2+}$. Further addition of Hy-pyr/PVP into the system causes no effect on the lifetime of $^*\text{Ru}(\text{bpy})_3^{2+}$ (Figure S7), demonstrating that the photocatalytic production of hydrogen of the Hy-pyr/PVP catalytic system proceeds via a reductive quenching mechanism.

The transient absorption spectra of deaerated aqueous solutions containing $\text{Ru}(\text{bpy})_3^{2+}$, H_2A and the PVP hydrogel in the absence and presence of Hy-pyr for the longer time range show clearly the decay of $\text{Ru}(\text{bpy})_3^+$ (Figure 3, Figure S8). The kinetic trace at 505 nm in the absence of Hy-pyr can be fitted well with a double exponential process, giving two lifetimes of 44 μ s (50%) and 163 μ s (50%). The shorter lifetime can be assigned to the $\text{Ru}(\text{bpy})_3^+$ located at the bulky aqueous phase because it is

similar to that of $\text{Ru}(\text{bpy})_3^+$ in the absence of the PVP hydrogel (Figure S9), and the longer lifetime can be assigned to the $\text{Ru}(\text{bpy})_3^+$ located at the hydrophilic interior of the PVP hydrogel, which are further validated by the transient absorption measurements in the presence of Hy-pyr. In the presence of Hy-pyr, the shorter lifetime of $\text{Ru}(\text{bpy})_3^+$ exhibits no change, while the longer one is shortened from 163 to 88 μ s, which must be caused by the electron transfer from $\text{Ru}(\text{bpy})_3^+$ to Hy-pyr. Generally, the electron transfer process requires strong donor-acceptor orbital overlap, therefore, the longer lifetime species of $\text{Ru}(\text{bpy})_3^+$ located at the hydrophilic interior of the PVP hydrogel closes to Hy-pyr embedded in the PVP hydrogel, which facilitates the electron transfer process from $\text{Ru}(\text{bpy})_3^+$ to Hy-pyr. The $\text{Ru}(\text{bpy})_3^+$ located at the aqueous phase cannot reach Hy-pyr embedded in the PVP hydrogel, resulting in no occurrence of the electron transfer process between them, consequently, giving the invariable shorter lifetime of $\text{Ru}(\text{bpy})_3^+$. The electron transfer

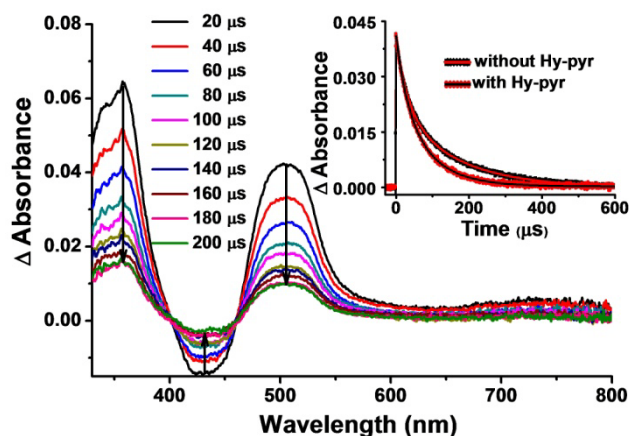


Figure 3. Transient absorption spectra obtained in the time range of 20-200 μ s following the laser flash photolysis of a deaerated aqueous solution containing $\text{Ru}(\text{bpy})_3^{2+}$ (5×10^{-5} M), H_2A (0.2 M) and the PVP hydrogel (10 mg/mL) at pH = 4, $\lambda_{\text{ex}} = 450$ nm. Inset: kinetic traces at 505 nm in the absence and presence of Hy-pyr (1×10^{-4} M).

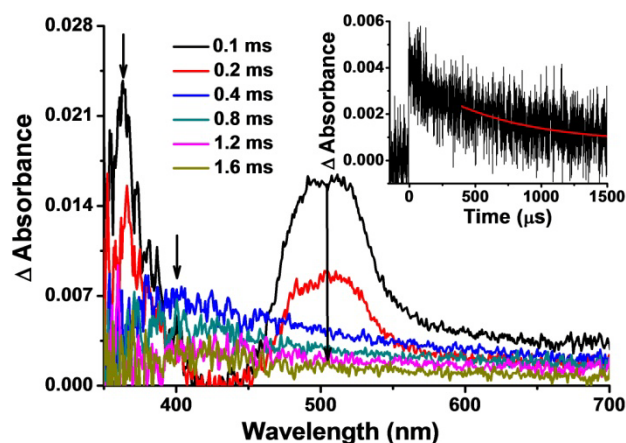


Figure 4. Transient absorption spectra obtained in the time range of 0.1 – 1.6 ms following the laser flash photolysis of a deaerated aqueous solution containing $\text{Ru}(\text{bpy})_3^{2+}$ (5×10^{-5} M), H_2A (0.2 M)

and Hy-pyr/PVP ([Hy-pyr] = 1×10^{-4} M, [PVP hydrogel] = 10 mg/mL) at pH = 4, λ_{ex} = 450 nm. Inset: kinetic trace at 400 nm.

from Ru(bpy)₃⁺ to Hy-pyr produces the reduced hydrogenase mimic Fe⁰Fe^I with the observed rate constant (k_{ET}) and efficiency (Φ_{ET}) of $5.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and 0.45, respectively, at the experiment conditions. The formation of the reduced hydrogenase mimic Fe⁰Fe^I was confirmed by the transient absorption spectroscopy. Pulse laser photolysis of a deaerated aqueous solution containing Ru(bpy)₃²⁺ (5×10^{-5} M), H₂A (0.2 M) and Hy-pyr/PVP ([Hy-pyr] = 1×10^{-4} M, [PVP hydrogel] = 10 mg/mL) at the pH value of 4 is shown in Figure 4 and Figure S8. The transient absorption spectra obtained in the time range of 20–200 μs after the excitation pulse only show absorption band at 505 nm assigned to Ru(bpy)₃⁺, which decays along with time. At the time window of 400 μs , the transient absorption band at 505 nm disappears, whereas a transient absorption band with maximum at 400 nm appears, which can be assigned to the Fe⁰Fe^I species by reference to the transient absorption of Fe⁰Fe^I reported in the literature.⁵⁹ The Fe⁰Fe^I species forms once the electron transfer occurs, but it can only be observed after Ru(bpy)₃⁺ fades away, because the intense transient absorption of Ru(bpy)₃⁺ interferes the observation for the formation of the Fe⁰Fe^I species at the time windows of 0–200 μs . The kinetic trace at 400 nm after 400 μs of the excitation pulse can be fitted well monoexponentially, giving the lifetime of the charge separation state Fe⁰Fe^I to be 664 μs . The lifetime of the charge separation state Fe⁰Fe^I observed in the present work is much longer than those of simple hydrogenase mimics reported in the literatures,^{43, 48} which may be rationalized to the stabilization effect of the PVP hydrogel. Effective charge separation has been considered to be a key factor in both natural photosynthesis and artificial photochemical conversion,⁴³ thus, application of the PVP hydrogel in photocatalytic hydrogen production systems may advance the catalytic performance. A second electron is needed to transfer to the diiron core to produce hydrogen, unfortunately, the intermediates after the second electron transfer is spectroscopically uncharacterized. Understanding the precise mechanism of the further reduction of the diiron core for hydrogenase mimics still remains a great challenge.

In summary, photochemical production of hydrogen in aqueous solution catalyzed by a water-insoluble hydrogenase mimic has been accomplished by simply immobilization of the hydrogenase mimic into the PVP hydrogel. The amphipathic character of the PVP hydrogel provides a scaffold to hold the catalyst and the photosensitizer together and facilitates the intermolecular electron transfer process, thus advancing photocatalysis. The present study provides a general, simple and efficient strategy for the application of hydrophobic artificial catalysts in aqueous solution by using the PVP hydrogel, which can reduce the substantial synthetic efforts for water solubility and avoids using of organic solvents.

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