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# Artificial Photosynthetic Assemblies Constructed by the Self-Assembly of Synthetic Building Blocks for Enhanced Photocatalytic Hydrogen Evolution

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**Abstract:** An artificial photosynthetic assemblies (APA) of hollow-rod structure was successfully constructed by using synthetic building blocks to mimic the structure and function of natural photosynthetic bacteria. The APA was formed by the self-assembly of incorporation of carbon nanoparticles as light harvesters into an enzyme-like polymer, **PEI-Co**, containing cobalt complexes as redox catalytic centres. The APA features a bacteria-like shape of ca. 2-3  $\mu$ m length rod and a hollow structure of positioning photosynthetic components at the surface. The

APA integrates key components, light harvester, redox catalyst, and proton relay group, of photosynthetic system in assemblies formed by polymeric framework. The APA system in aqueous solution converts proton to  $H_2$  under visible light irradiation with obvious advantages. It exhibits a 50-fold improvement on hydrogen production activity and have a broader pH response of photocatalytic  $H_2$  production compared with those of a non-assembled system.

#### 1. Introduction

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Self-assembly of synthetic building blocks to rebuild biomaterials and biomimics is of considerable interest to chemists.<sup>1-5</sup> In this sense, some morphological or functional mimics, such as artificial hierarchical structures,<sup>6</sup> enzymes,<sup>7-9</sup> and cells,<sup>10-12</sup> have been fabricated in recent years. An ideal biomimic should have both morphological and functional characteristics like those of the target. However, achievement of this goal remains a challenging task, and successful examples are rarely documented.

Natural photosynthetic bacteria (NPB) are single-cell organisms capable of converting organic acid to hydrogen (H<sub>2</sub>) *via* a photofermentation process under visible light irradiation.<sup>13, 14</sup> This property makes NPB useful in industrial and agricultural effluent treatment for obtaining H<sub>2</sub> as renewable energy. The photosynthetic H<sub>2</sub> evolution of NPB occurs in photosynthetic systems, which are located at the cell membrane to maximize light absorption.<sup>15, 16</sup> In a photosynthetic system, the protein-binding light-harvesting pigments and redox catalytic centres form microenvironments, in which several light harvesting pigments surround a redox catalytic centre.<sup>15, 16</sup> During photosynthesis, the pigments deliver excited electrons to a nearby redox reaction centre to generate a reduced species, which attracts protons and releases hydrogen. The

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appropriate location and arrangement of photosynthetic systems in NPB ensures maximum light absorption by the pigments and efficient photoinduced electron transfer (PET) and protonation.

Herein, we wish to report the successful construction of a kind of artificial photosynthetic assemblies (APA), which is self-assembled from synthetic components. The APA features a bacteria-like shape and structure and can produce H<sub>2</sub> under visible light irradiation. A synthetic enzyme **PEI-Co** (Scheme 1) was obtained by grafting the  $[Co(TPA)Cl_2]$  redox reaction centres onto branched polyethylenimine (PEI), and surface-functionalized carbon nanoparticles (CNPs) were synthesized. Photoluminescent carbon nanoparticles are a kind of emerging emissive materials with advantages of low cost, easy preparation, and free of toxic metals, which had been used in bioimaging, sensing, and light emitting devices.<sup>17-20</sup> However, the utilization of CNPs as a photosensitizer for solar fuels production is rare.<sup>21</sup> PEI-Co and CNPs can self-assemble in an aqueous solution to form uniform hollow rod-like CNPs@PEI-Co assemblies (APA) ca. 2-3 μm in length. In these assemblies, CNPs act as a light harvester located at the surface of the hollow rod structures formed by branched polymeric **PEI-Co**. The self-assembled APA have enhanced activity and broader pH response of the photocatalytic H<sub>2</sub> production compared with those of a non-assembled system.<sup>22-27</sup> The APA system efficiently produced H<sub>2</sub> within a pH range of 4.0-10.0; however, the non-assembled system was functional only within a pH range of 2.0-5.0; the APA system has 50-fold higher turnover number (TON) of H<sub>2</sub> production compared with that of the non-assembled system. At the optimal conditions, the APA system produced H<sub>2</sub> with a turnover number (TON, based on cobalt active sites in PEI-Co) up to 198 and an initial rate of 538 µmol g<sup>-1</sup> h<sup>-1</sup> (based on mass of CNPs@PEI-Co assemblies), these values exceed those of state-of-the-art homogeneous photocatalytic H<sub>2</sub> production systems using carbon dots and cobalt complexes.<sup>28-30</sup>

### 2. Results and discussion

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# 2.1 Synthesis and characterization of PEI-Co



**Scheme 1.** The synthetic routes and chemical structures of organic ligand *L1-L3*, complex *C1* and *PEI-Co* (NBS: N-bromosuccinimide, BPO: benzoyl peroxide, DPA: 2,2-dipicolylamine, PyBOP: benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate; details of the synthesis are given in Experimental section).

The **PEI-Co** was designed by grafting the carboxyl group modified cobalt complex **C1** onto branched PEI ( $M_w = 25$  k) by an amide bond (Scheme 1 and Experimental section).<sup>31</sup> The branched PEI was selected for three reasons. First, its branched polymeric structure can mimic protein environment.<sup>32, 33</sup> Second, the abundant amino groups of PEI act as a protons relay for efficient protonation of the catalytic centre.<sup>34-36</sup> Third, these positively charged amino groups function as binding sites to attract negatively charged CNPs to form assemblies. The successful



Figure 1. (a) UV-Vis absorption spectra of **PEI-Co** (0.10 mg mL<sup>-1</sup>,  $8.46 \times 10^{-6}$  M), PEI (0.10 mg mL<sup>-1</sup>), and C1 ( $5.29 \times 10^{-4}$  M in aqueous solution. (b) IR spectra of **PEI-Co**, PEI, and C1.

grafting of C1 onto PEI was characterized by UV-Vis and IR spectroscopy. The UV-Vis spectrum (Fig. 1a) of **PEI-Co** shows characteristic TPA-ligand absorption at 260 nm, which is also observed in the spectrum of C1. Broad weak absorption at 330 - 560 nm in C1 is assigned to LMCT absorption of cobalt core;<sup>37, 38</sup> this absorption was suppressed due to low concentration of C1 in **PEI-Co**. IR spectrum of **PEI-Co** (Fig. 1b) shows an amide signal at 1658 cm<sup>-1</sup>, which is different from the characteristic C=O signal at 1734 cm<sup>-1</sup> of the carboxyl group of C1.<sup>39</sup> The amount of C1 in **PEI-Co** was 8.46 × 10<sup>-5</sup> mmol mg<sup>-1</sup> as determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Another two samples with different C1 loading amount, **PEI-Co\*** of [Co] =  $2.88 \times 10^{-6}$  M and **PEI-Co\*\*\*** of [Co] =  $5.24 \times 10^{-5}$  M, were prepared for comparison experiments. The surface carboxyl groups-functionalized CNPs were prepared by hydrothermal treatment using poly-3-thiopheneacetic acid in NaOH aqueous solution as characterized and reported previously.<sup>40</sup> The CNPs used in this work were

nanoparticles with a diameter of 20-60 nm (SI, Fig. S1). The UV-Vis spectrum of the CNPs have a strong absorption in the range of 300-600 nm with a maximum at 415 nm (SI, Fig. S4).

#### 2.2 Self-assembly of APA

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The self-assembly of PEI-Co and CNPs was performed in water. We investigated the morphology of individual PEI-Co and CNPs by SEM and confocal laser scanning fluorescence microscopy. The SEM image (Fig. 2d) shows that PEI-Co uniformly forms ca. 2.0-3.0 µm long hollow rod structures. Mixing **PEI-Co** with CNPs results in CNPs incorporation into the **PEI-Co** assemblies to form the CNPs@PEI-Co assemblies. As shown in SEM image (Fig. 2e), the CNPs@PEI-Co assemblies maintain ca. 2.0-3.0 μm long rod structure; however, they have a nodular morphology different from that of PEI-Co, indicating the incorporation of CNPs into PEI-Co. The CNPs@PEI-Co assemblies are emissive under 405 nm laser excitation in the green confocal channel and merged images (Fig. 2b and 2c). Interestingly, the emission areas are concentrated on the edges of the rod-shaped assemblies, indicating that the CNPs locate at the surface of the hollow PEI-Co assemblies. The special structure of PEI-Co and CNPs@PEI-Co assemblies in water may be caused by the amphiphilic property of the branched **PEI-Co**. Namely, the positively charged amino groups (discussed below) and the organic -CH<sub>2</sub>CH<sub>2</sub>- framework in **PEI-Co** act as a hydrophilic and hydrophobic part, respectively. The positively charged amino groups in **PEI-Co** stay outside of the hollow structures; they act as binding sites to attract negatively charged CNPs on the surface of the hollow assemblies. This self-assembly process was continuously monitored by confocal microcopy and recorded as a video (SI). The whole process was recorded starting from the addition of CNPs into aqueous solution of **PEI-Co** to the formation of the emissive CNPs@PEI-Co assemblies (Fig. 2f-i). The non-fluorescent rod structures of PEI-Co move in solution prior to the addition of CNPs (SI, Fig. S5 and S6). After



**Figure 2.** (a)-(c) Confocal microscopy images of CNPs@**PEI-Co**, inset: enlarged view of the selected area (red line). (d) SEM image of **PEI-Co**. (e) SEM image of CNPs@**PEI-Co**. (f)-(i) Confocal microscopy images recorded after adding CNPs into aqueous solution of **PEI-Co**. (j)

Surface zeta-potentials of **PEI-Co** and CNPs in aqueous solution at different pH values. (k) Surface zeta-potentials of **PEI-Co**, CNPs, and CNPs@**PEI-Co** in aqueous solution at pH 8.4. (l) FTIR second derivative spectra of CNPs@**PEI-Co** at different pH values. (m) Schematic diagram of the self-assembly of **PEI-Co** and CNPs.

adding CNPs to the solution (Fig. 2f), no fluorescence was observed at the initial stage indicating that fluorescence of CNPs in its mono-dispersion state is unobservable under these conditions. However, a few emissive assemblies were formed after approximately one minute (Fig. 2g). This result indicates that CNPs are incorporated into the **PEI-Co** assemblies, and the fluorescence of CNPs can be observed after CNPs@**PEI-Co** formation. In the next recording time, additional fluorescent CNPs@**PEI-Co** assemblies can be observed in confocal images (Fig. 2h-i). Two synthetic building blocks, **PEI-Co** and CNPs, were successfully self-assembled into the CNPs@**PEI-Co** assemblies; in these assemblies, the light harvester CNPs and the redox catalytic cobalt complexes compose the photosynthetic systems confined in the microenvironment formed by the PEI framework and are located at the surface of the assemblies, which resembles the situation in NPB.<sup>15, 16</sup>

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To determine the driving force of this self-assembly, surface zeta-potential measurements were performed. The relationship between the surface zeta-potential ( $\xi$ ) and pH values of **PEI-Co** and CNPs in aqueous solution are shown in Fig. 2j. The  $\xi$  values of **PEI-Co** are positive in the pH range of 3.0-12.0, indicating that **PEI-Co** is positively charged on the surface.<sup>41</sup> Higher surface zeta-potentials were obtained in acidic solutions increasing from 4.35 mV at pH 9.2 to 24.7 mV at pH 3.0. This increase is due to the protonation of amino groups of **PEI-Co**. The CNPs containing surface carboxylic acid groups are negatively charged in aqueous solution; thus, higher  $\xi$  values were obtained in basic solutions. The  $\xi$  values increased from -14.97 mV at pH

5.4 to -52.63 mV at pH 12.4 because of deprotonation of the surface carboxylic acid groups of CNPs under the basic conditions.<sup>42</sup> Mixing **PEI-Co** solution (0.10 mg mL<sup>-1</sup>) with a  $\xi$  value of 13.4 mV and CNPs solution (0.14 mg mL<sup>-1</sup>) with a  $\xi$  value of -28.8 mV at an equal volume ratio results in a  $\xi$  value of -24.2 mV of the self-assembled CNPs@**PEI-Co** (Fig. 2k). Therefore, the driving force of the self-assembly can be attributed to electrostatic interactions between the positively charged **PEI-Co** and negatively charged CNPs.<sup>26, 43-45</sup> The electrostatic interaction in CNPs@**PEI-Co** was further confirmed by the second derivative spectra of the corresponding peaks of the FTIR spectra (Fig. 2l). The C=O stretching vibration peak of the carboxyl groups of CNPs is moved from 1656 cm<sup>-1</sup> assigned to -COOH at pH 5.25 to 1651 cm<sup>-1</sup> assigned to deprotonated -COO<sup>-</sup> at pH 9.72. Analogous changes in the N-H bending vibration peak in **PEI-Co** from 1583 cm<sup>-1</sup> of -NH<sub>3</sub><sup>+</sup> in an acidic solution to 1574 cm<sup>-1</sup> of -NH<sub>2</sub> in a basic solution were observed.<sup>46</sup>

#### 2.3 Photocatalytic H<sub>2</sub> production of APA

The photosynthetic H<sub>2</sub> evolution experiments of APA were carried out in an aqueous solution in the presence of sodium ascorbate (NaHA) as an electron donor. Typically, a standard sample containing **PEI-Co** (0.10 mg mL<sup>-1</sup>), CNPs (0.14 mg mL<sup>-1</sup>), and NaHA (0.02 M) in 5.00 mL water (pH 8.4) was irradiated under a blue LED lamp ( $\lambda_{max} = 450$  nm) for 10 hours. A standard sample produced 5.54 µmol H<sub>2</sub> with a TON of 131 based on the cobalt sites (Table 1). No H<sub>2</sub> was detected in the systems that were lacking **PEI-Co**, CNPs, NaHA, or light irradiation, indicating that all these components are necessary for H<sub>2</sub> production (Table 1). If PEI was used to replace **PEI-Co**, the system produced only a trace of H<sub>2</sub> under the same conditions (Table 1). This result demonstrates that the cobalt complex in **PEI-Co** functions as a catalytic centre for H<sub>2</sub> production.

Entry	Photosensitizer	Catalyst	Electron donor	$H_2$ / $\mu mol$	$H_2$ / µmol g <sup>-1</sup> h <sup>-1</sup>	TON (H <sub>2</sub> )
				total amount	based on APA mass	based on cobalt
1[b]	CNPs	PEI-Co	NaHA	5.54	461.7	131
2 <sup>[b]</sup>	CNPs	PEI-Co*	NaHA	1.78	148.3	124
3[b]	CNPs	PEI-Co**	NaHA	17.92	1493.5	68
4[c]	CNPs	PEI-Co	NaHA	0	0	0
5[d]	/	PEI-Co	NaHA	0	0	0
6[e]	CNPs	/	NaHA	0	0	0
7[f]	CNPs	PEI-Co	/	0	0	0
8[g]	CNPs	PEI	NaHA	Trace	Trace	Trace
9[h]	CNPs	C1	NaHA	0.11	9.2	2.6

**Table 1**. Control experiments of photocatalytic H<sub>2</sub> production<sup>[a]</sup>

[a] all samples were irradiated for 10 hours; [b] samples concentrations: [CNPs] = 0.14 mgmL<sup>-1</sup>,  $[PEI-Co] = 0.10 \text{ mg} \text{ mL}^{-1}$  ( $[Co] = 8.46 \times 10^{-6} \text{ M}$ ),  $[PEI-Co^*] = 0.10 \text{ mg} \text{ mL}^{-1}$  ( $[Co] = 2.88 \times 10^{-6} \text{ M}$ ),  $[PEI-Co^{**}] = 0.10 \text{ mg} \text{ mL}^{-1}$  ( $[Co] = 5.24 \times 10^{-5} \text{ M}$ ), [NaHA] = 0.02 M, total volume = 5.00 mL; [c] in dark; [d] in the absence of CNPs; [e] in the absence of PEI-Co; [f] in the absence of NaHA; [g] [PEI] = 0.10 \text{ mg} \text{ mL}^{-1}; [h] [C1] = 8.46 \times 10^{-6} \text{ M}.

However, if complex C1 was used to replace PEI-Co to compose a non-assembled system under the same conditions, the TON of H<sub>2</sub> production was only 2.6 (Table 1). The APA system improves H<sub>2</sub> production by over 50 times compared with that of a non-assembled system.

The H<sub>2</sub> production activity of the APA system is highly dependent on the concentrations of CNPs and **PEI-Co**. As shown in Fig. 3a, a decrease in the CNPs concentration from 0.14 mg mL<sup>-1</sup> (standard sample) to 0.035 mg mL<sup>-1</sup> decreased the TON of H<sub>2</sub> production from 131 to only 7. An increase in the CNPs concentration to 0.28 and 0.56 mg mL<sup>-1</sup> also resulted in a decrease in the TON to 35 and 16, respectively, due to the light filter effect at a higher CNPs concentration. A decrease in the **PEI-Co** concentration from 0.10 mg mL<sup>-1</sup> in the standard sample to



**Figure 3.** The photocatalytic  $H_2$  production by APA and reference systems in aqueous solutions, pH 8.4, [NaHA] = 0.02 M, total volume = 5.00 mL, initial pH 8.4, irradiation time = 10 hours, light source was a blue LED lamp ( $\lambda_{max} = 450 \text{ nm}$ ). (a) [**PEI-Co**] = 0.10 mg mL<sup>-1</sup>, [CNPs] = 0.035-0.56 mg mL<sup>-1</sup>. (b) [**PEI-Co**] = 0.025-0.40 mg mL<sup>-1</sup>, [CNPs] = 0.14 mg mL<sup>-1</sup>. [c] [CNPs] = 0.14 mg mL<sup>-1</sup>, [**PEI-Co**] = 0.10 mg mL<sup>-1</sup> ([Co] = 8.46×10<sup>-6</sup> M), [**PEI-Co**\*] = 0.10 mg mL<sup>-1</sup> ([Co] = 2.88×10<sup>-6</sup> M), [**PEI-Co**\*\*] = 0.10 mg mL<sup>-1</sup> ([Co] = 5.24×10<sup>-5</sup> M). [d] [**PEI-Co**] = 0.10 mg mL<sup>-1</sup>, [**C1**] = 8.46 × 10<sup>-6</sup> M, [CNPs] = 0.14 mg mL<sup>-1</sup>, at different initial pH. (e) [CNPs] = 0.14 mg mL<sup>-1</sup>, [**PEI-Co**] = 0.10 mg mL<sup>-1</sup> ([Co] = 8.46×10<sup>-6</sup> M), [NaHA] = 0.02 M.

0.025 mg mL<sup>-1</sup> (Fig. 3b) resulted in a decrease in the TON to 60 because of low concentration of the catalytic centres under these conditions. Interestingly, an increase in the **PEI-Co** concentration from 0.10 mg mL<sup>-1</sup> to 0.20 mg mL<sup>-1</sup> and 0.4 mg mL<sup>-1</sup> resulted in a decrease in the TON to 16 and 2 (Fig. 3b), respectively. This decrease is due to the formation of additional APA assemblies at a higher **PEI-Co** concentration; the local concentration of CNPs in each APA assembly decreases, thus leading to a decrease in TON. As shown in Fig. 3c, by decreasing the cobalt complex loading amount in PEI from  $5.24 \times 10^{-5}$  M in **PEI-Co**<sup>\*\*</sup> to  $2.88 \times 10^{-6}$  M in **PEI-Co**<sup>\*</sup>, the H<sub>2</sub> production amount decreased from 17.92 µmol to 1.78 µmol after 10 hours of irradiation (Table 1), indicating the cobalt complexes function as a real catalytic site for protons reduction. However, the maximum TON based on cobalt sites was obtained by a moderate cobalt loading sample **PEI-Co** (Table 1), indicating that **PEI-Co** has the highest utilization efficiency of the cobalt sites under the conditions employed.

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The APA system had H<sub>2</sub> production activity in a broad pH range from pH 4.0 to pH 10.1 (Fig. 3d); the highest TON of 131 was obtained at pH 8.4. However, the non-assembled system, physical mixture of complex **C1** and CNPs, produced H<sub>2</sub> only in acidic solutions with pH 2.2-5.5. The highest TON was 40 at pH 4.0. The amino groups of the PEI framework improve local protons concentration in the vicinity of the cobalt catalytic centres and function as proton sponge binding protons in water within a broad pH range and subsequently delivering protons to the catalytic cobalt centre during photocatalysis.<sup>34-36</sup>

Based on these results, a long-time photocatalysis test of the APA system by using **PEI-Co** was performed under the optimized conditions. The system maintained the H<sub>2</sub> production activity within the first 24 hours (Fig. 3e). After 34 hours of irradiation, a total of 8.36  $\mu$ mol H<sub>2</sub> with a TON of 198 was obtained. The highest H<sub>2</sub> production rate based on CNPs@**PEI-Co** mass is 538

 $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>. To the best of our knowledge, the APA system is the most efficient photocatalytic H<sub>2</sub> production system based on carbon dots/nanoparticles as a photosensitizer and cobalt complex as a catalyst reported so far. To reveal the cause of inactivation, we added fresh CNPs or **PEI-Co** into the inactivated samples for another 10 hours of irradiation. However, both samples produced only small amount of H<sub>2</sub> (SI, Table S1). Confocal observation of the solution from the inactivated sample showed that the rod-like structures of **PEI-Co** still exist, however, no obvious emissive assemblies can be observed from green confocal channel (SI, Fig. S5). The comparison of the UV-vis absorption spectra of the photocatalytic sample before and after 34 hours of irradiation demonstrated that the characteristic absorption of CNPs disappeared (SI, Fig. S7). These results indicate that both CNPs and cobalt complexes in **PEI-Co** decomposed during long-time photocatalysis.

#### 2.4 Photoinduced electron transfer

To gain an insight into the photocatalytic mechanism of the APA system, the photoinduced electron transfer (PET) process was investigated. Excitation of an aqueous solution of CNPs at 400 nm results in a maximal emission at 548 nm (Fig. 4a) with an average lifetime of 1.11 ns (SI, Fig. S8). This emission can be efficiently quenched by **PEI-Co** (Fig. 4a) with a quenching constant of  $3.69 \times 10^{13}$  M<sup>-1</sup> s<sup>-1</sup> (SI, Fig. S9). However, the quenching constant is decreased to  $1.32 \times 10^{13}$  M<sup>-1</sup> s<sup>-1</sup> by using **C1** to quench the aqueous solution of CNPs in the presence of PEI under the same conditions (SI, Fig. S10). Due to a negligible spectroscopic overlap of the absorption of **PEI-Co** with emission of CNPs (Fig. 4a), photoinduced energy transfer between these two components can be excluded. We therefore attributed this quenching to PET from excited CNPs to the cobalt complexes in **PEI-Co**. The free-energy change ( $\Delta G^0$ ) of the PET process was estimated. The oxidation potential (E<sub>ox</sub>) of CNPs and the reduction potential (E<sub>red</sub>) of

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**Figure 4.** (a) UV-Vis absorption of **PEI-Co** (0.10 mg mL<sup>-1</sup>) in aqueous solution, emission quenching spectra of CNPs (0.14 mg mL<sup>-1</sup>) by **PEI-Co** (2.12 × 10<sup>-6</sup> - 1.27 × 10<sup>-5</sup> M) in aqueous solution at 400 nm excitation wavelength. (b) Transient photocurrent response to on-off illumination, (c) linear sweep voltammetry, and (d) electrochemical impedance spectroscopy curves of CNPs and CNPs@**PEI-Co** modified electrodes in Na<sub>2</sub>SO<sub>4</sub> (0.1 M) aqueous solution under a Xe lamp ( $\lambda > 400$  nm) irradiation.

C1 in aqueous solution is 0.85 V and -1.47 V, respectively (all potentials discussed here are *vs*. SCE), as measured by cyclic voltammograms (SI, Fig. S12 and S13). The excited state energy  $(E_{00})$  of CNPs is 2.49 eV. The free energy change  $(\Delta G^0)$  was determined as -0.17 eV, indicating that PET from CNPs to the cobalt complexes in **PEI-Co** in the CNPs@**PEI-Co** assemblies is exothermic (Scheme 2).

Photoelectrochemical measurements of CNPs and CNPs@PEI-Co were performed. As shown in Fig. 4b, the CNPs modified electrode exhibits a transient photocurrent of 0.31  $\mu$ A cm<sup>-2</sup> upon irradiation by a Xe lamp ( $\lambda > 420$  nm). The photocurrent increased to 0.67  $\mu$ A cm<sup>-2</sup> after loading **PEI-Co** onto CNPs electrode. These photocurrents of CNPs and CNPs@PEI-Co were roughly stable in the test period. The comparison of linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) curves for CNPs and CNPs@PEI-Co modified electrodes shows that CNPs@PEI-Co have higher photocurrent density in LSV (Fig. 4c) and smaller radius of the semicircle in EIS (Fig. 4d) compared with those of CNPs. These results further demonstrate that PET from excited CNPs to **PEI-Co** takes place and leads more efficient catalysis in CNPs@PEI-Co.<sup>47, 48</sup>

### 2.5 Mechanism

Based on these results, a mechanism of H<sub>2</sub> production by the CNPs@**PEI-Co** assemblies can be proposed (Scheme 2). Under visible light irradiation, excited CNPs delivers a photoexcited electron to the cobalt centre in **PEI-Co** to generate active Co<sup>I</sup> species; subsequently, this Co<sup>I</sup> species binds a proton to undergo a catalytic H<sub>2</sub> production cycle (SI, Fig. S12).<sup>49-51</sup> The oxidized CNPs can be reduced to the initial state by ascorbate (SI, Fig. S11). The specific structure of CNPs@**PEI-Co** envelops the active cobalt centre and CNPs into an assembly of several



**Scheme 2.** Scheme of photocatalytic  $H_2$  production process in the APA system and energy diagram of the photoinduced electron transfer.

micrometers in size formed by PEI; apparently, the assembly is beneficial for H<sub>2</sub> production for three reasons. First, the assembly positions light harvester CNPs and catalytic cobalt centre adjacent to each other and locate at the surface of the assemblies, thus facilitating PET efficiency and light absorption. Second, abundant amino groups in PEI may be present in the vicinity of the cobalt centre in the CNPs@**PEI-Co** assemblies; hence, these amino groups function as protons relays to facilitate protonation at the catalytic metal centre during the course of hydrogen production; a similar strategy, having a pendant amino group as a proton relay at the secondarycoordination sphere of the metal centre, is observed in natural [FeFe]-hydrogenases.<sup>52, 53</sup> Third, the residual abundant amino groups in PEI framework act as a proton sponge to enhance local proton concentration in assemblies to enable their function within a wide pH range. All these characteristics of CNPs@**PEI-Co** assemblies are reminiscent of photosynthetic bacteria in nature, in which active catalytic centres of the metal clusters, light-harvesting pigments and protons

relay are precisely assembled in the proteins and stay at cell membrane for efficient photosynthesis.

#### 3. Conclusions

In conclusion, a kind of biomimetic artificial photosynthetic assemblies of a hollow-rod structure was successfully constructed by using self-assembly of synthetic building blocks containing only inexpensive elements.<sup>25-29</sup> The APA features morphological and structural characteristics like those of NPB and perform photosynthetic H<sub>2</sub> evolution under visible light irradiation. Due to the special structure and multiple functionalities of the CNPs@**PEI-Co** assemblies, the APA system demonstrates enhanced photocatalytic H<sub>2</sub> production within a broad pH range in aqueous solution. The performance of the artificial photosynthetic systems can be improved by mimicking the structure and function of natural biological systems.

## **Experimental section**

**Chemicals and Materials.** All chemicals, including 2, 6-bis(chloromethyl)pyridine, 2, 2dipicolylamine (DPA), N-Bromosuccinimide (NBS), Benzoyl peroxide (BPO), potassium carbonate, benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) and cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O) were purchased from commercial suppliers (Sinopharm chemical reagent co., LTD, Adamas, and Sigma-Aldrich) and used without further purification. N<sub>2</sub> (99.999%), CH<sub>4</sub> (99.99%) were purchased from commercial supplier (Huaerwen). All solvents of analytical grade were purchased from commercial suppliers and used without further purification. The ligand L1-L3,<sup>54, 55</sup> complex C1,<sup>56</sup> PEI-Co,<sup>31</sup> and CNPs<sup>40</sup> were synthesized according to literatures' methods.

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Synthesis of L1. Methyl 6-methylnicotinic acid (200 mg, 1.32 mmol), NBS (259 mg, 1.46 mmol), and BPO (32 mg, 0.13 mmol) were added to 20 mL of CCl<sub>4</sub>. The mixture was stirred and heated to reflux. After the completion of the reaction, the solution was filtered to remove the solid. The filtrate was washed by saturated NaHCO<sub>3</sub> aqueous solution and brine. The organic layer was dried over MgSO<sub>4</sub> and concentrated by rotary evaporation to give a solid. The solid was purified by column chromatography and eluting with CH<sub>2</sub>Cl<sub>2</sub>. The product L1 (yield: 41.8%) as a white solid was obtained by concentration under vacuum. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.17 (s, 1H), 8.33 (dd, J = 8.1, 2.2 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 4.60 (s, 2H), 3.97 (s, 3H).

Synthesis of L2. L1 (100 mg, 0.43 mmol), DPA (105 mg, 0.52 mmol), and K<sub>2</sub>CO<sub>3</sub> (120 mg, 0.87 mmol) were added in 10 mL of CH<sub>3</sub>CN at room temperature. The reaction mixture was stirred at 50 °C for 4h. After the completion of the reaction, the mixture was concentrated and purified by column chromatography and eluting with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH mixed solution. The product L2 (yield: 84.3%) as an oil was obtained by concentration under vacuum. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.16 - 9.07 (m, 1H), 8.54 (ddd, J = 4.9, 1.8, 0.9 Hz, 2H), 8.25 (dd, J = 8.2, 2.2 Hz, 1H), 7.73 - 7.61 (m, 1H), 7.58 - 7.50 (m, 2H), 7.15 (ddd, J = 7.5, 4.9, 1.2 Hz, 2H), 3.95 (s, 2H), 3.93 (s, 3H), 3.89 (s, 4H).

**Synthesis of L3**. **L2** (100 mg, 0.29 mmol) and NaOH aqueous solution (0.1 M, 20 mL) were dissolved in 20 mL of THF and stirred for 3h at 0 °C. After the completion of the reaction, the THF was removed by rotary evaporation. The HCl (3 M) was added into the residual solution to adjust the pH to 6-7 and the water was removed by rotary evaporation. The solid crude product was dissolved in CH<sub>3</sub>OH and dried over MgSO<sub>4</sub>. The solution was filtered and the filtrate was concentrated under vacuum to obtained the product **L3** (yield: 95%) as a pale yellow solid. <sup>1</sup>H

NMR (400 MHz, Methanol-d4)  $\delta$  8.97 (d, J = 2.0 Hz, 1H), 8.44 (dd, J = 5.0, 1.7 Hz, 2H), 8.21 (dd, J = 8.1, 2.2 Hz, 1H), 7.74 (td, J = 7.7, 1.8 Hz, 2H), 7.54 (dd, J = 7.9, 4.9 Hz, 3H), 7.23 (ddd, J = 7.6, 5.0, 1.2 Hz, 2H), 3.83 (d, J = 9.0 Hz, 6H). <sup>13</sup>C NMR (101 MHz, MeOD)  $\delta$  171.64, 161.72, 159.63, 151.15, 149.90, 139.14, 138.69, 132.23, 124.96, 124.03, 123.90, 61.18, 60.96. MS (ESI, m/z): Calcd. For C<sub>19</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> [M+Na]<sup>+</sup> : 357.1327; found, 357.1340.

Synthesis of C1. L3 (100 mg, 0.30 mmol) was dissolved in 3 mL of CH<sub>3</sub>OH to obtain a brown solution.  $CoCl_2 \cdot 6H_2O$  (64 mg, 0.27 mmol) was added into the solution at room temperature. The color of the solution changed from brown to green. The mixture was stirred at room temperature for 1 h. Diethyl ether (20 mL) was added into the solution to give green precipitates. The product C1 was obtained as a green solid (yield: 90%) after filtration, washing with water and ether, and drying under vacuum. MS (ESI, m/z): Calcd. For  $C_{19}H_{18}Cl_2CoN_4O_2$  [M-Cl]<sup>+</sup> : 428.0450; found, 428.0422.

**Synthesis of PEI-Co. C1** (40 mg) and PyBOP (53 mg) were dissolved in 15 mL of DMF and stirred at room temperature for 30 min. PEI (200 mg,  $M_w = 25$  k) in 3 mL of DMF was added drop by drop into the solution. The mixture solution was stirred at room temperature for 48 h. The solution was filtrated to remove the with flocculent. The filtrate was dialyzed (3000 D) in water and then freeze-dried to obtain the **PEI-Co** ([Co] =  $8.46 \times 10^{-6}$  mmol mg<sup>-1</sup>) as a brown solid. Two reference samples, **PEI-Co\*** ([Co] =  $2.88 \times 10^{-6}$  mmol mg<sup>-1</sup>) and **PEI-Co\*** ([Co] =  $5.24 \times 10^{-5}$  mmol mg<sup>-1</sup>), of different cobalt loading amount were also prepared by the same procedure.

**Synthesis of CNPs**. The CNPs was synthesized by hydrothermal treatment of poly-3thiopheneacetic acid in NaOH aqueous solution (100 mM, 40 mL) in a hydrothermal reactor (Shanghai LABE Instrument Co., Ltd.) at 210 °C for 6 h. After cooling to room temperature, the CNPs were collected and purified by sequential filtration, centrifugation, and dialysis.

**Photocatalytic experiments**. In a typical photocatalytic H<sub>2</sub> evolution experiment, the stock aqueous solution of CNPs, **PEI-Co**, and sodium ascorbate (NaHA) were added in a glass tube to obtain a mixture solution with certain components' concentration. The sealed tube was bubbled by N<sub>2</sub> for 20 mins under dark. The tubes were set in a photoreactor with blue LED lamp ( $\lambda_{max} = 450 \text{ nm}$ ) and irradiated at room temperature for certain time. The gaseous product was extracted and analyzed by a gas chromatography (Shanghai Tianmei, GC 7900) equipped with a thermal conductive detector (TCD) and flame ionization detector (FID) having high-purity Ar carrier gas. The CH<sub>4</sub> was used as an internal standard.

Electrochemical and photoelectrochemical measurements. Cyclic voltammetries were performed in a three-electrode system (0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution) of using glassy carbon electrode as a working electrode, saturated calomel electrode (SCE) as a reference electrode, and a platinum wire as a counter electrode. Photoelectrochemical measurements were conducted in a three-electrode cell system by using 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution as electrolyte. An FTO glass of loading CNPs or CNPs@PEI-Co was used as a photoelectrode, a Pt wire and a SCE were used as counter electrode and reference electrode, respectively. The photoelectrode was prepared by spin-coating CNPs or CNPs@PEI-Co slurry on an FTO glass (d = 4 mm) and then drying at 40 °C. The light source was a 300 W xenon lamp with a light filter ( $\lambda > 420$  nm).



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