

Electronic Supplementary Information

for

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

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Table of Contents

- 1. Instruments and methods**
- 2. SEM images**
- 3. UV-vis absorption and PL spectra of CNPs**
- 4. Confocal laser scanning microscope (CLSM) images**
- 5. Inactivation studies**
- 6. Lifetime**
- 7. Quenching experiments**
- 8. Cyclic voltammetry**
- 9. Free-energy change estimation**

1. Instruments and methods

The SME images were recorded by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7610FPlus) at an acceleration voltage of 5 kV. The confocal images were recorded by confocal laser scanning microscope (CLSM, FV1200) from Olympus operating at excited wavelength of 405 nm, and recording signal 500~600 nm. Fourier transform infrared (FT-IR) spectra were recorded on an INVENIO-R spectrometer using the KBr pellet as the background. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 UV-vis spectrophotometer. The photoluminescence (PL) measurements were carried out by a RF-5301PC. The lifetime of CNPs was measured by time-correlated single photon counting system (Fluorescent spectrometer F900, Edinburgh Instruments Ltd., UK) equipped with a 355 nm laser. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance III 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Inductively coupled plasma (ICP) measurements were recorded on an iCAP 7200 plus. Atomic absorption spectrometry (AAS) were carried out using an ICE 3000. Surface zeta potential were examined by Nano ZS90. Electrochemistry and photoelectrochemistry measurements were carried out by an electrochemical workstation (CHI 660E, Shanghai CH instrument).

2. SEM images

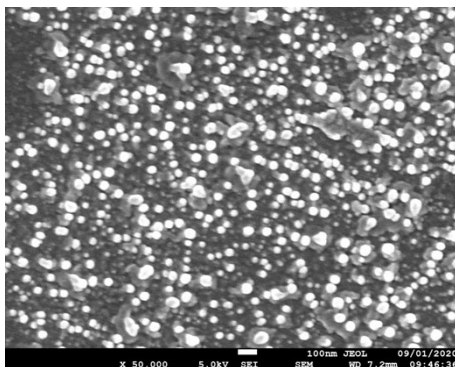


Figure S1. SEM image of CNPs

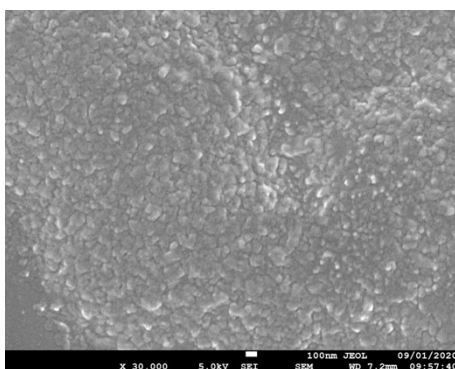


Figure S2. SEM image of PEI

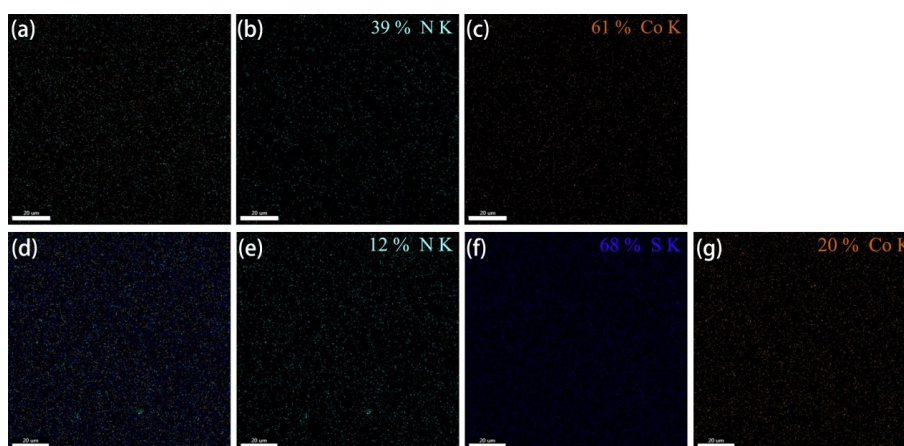


Figure S3. EDS images: (a-c) PEI-Co; (d-g) CNPs@PEI-Co

3. UV-vis absorption and PL spectra of CNPs

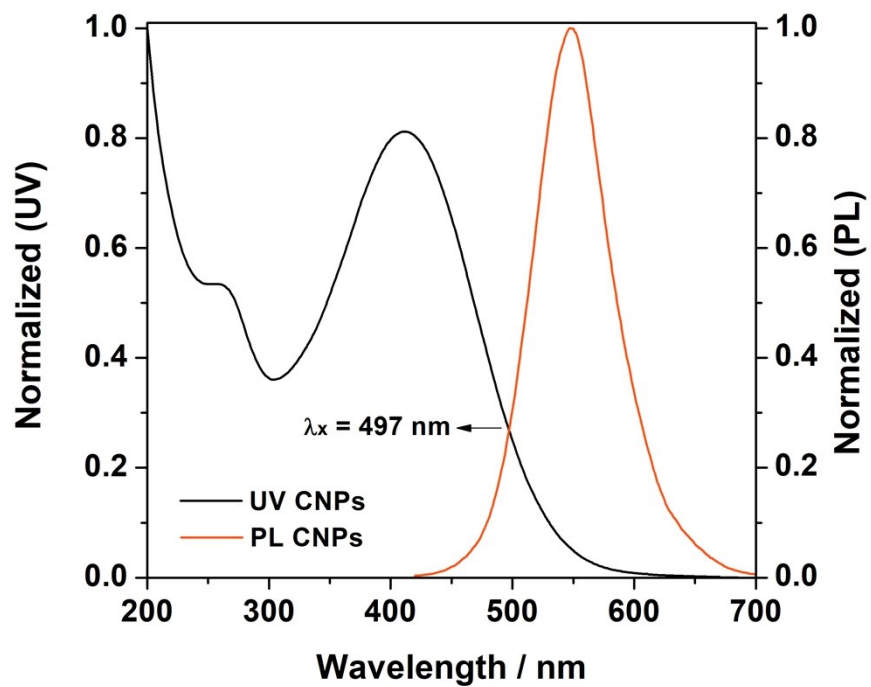


Figure S4. Normalized UV-vis absorption and PL spectra of CNPs.

4. CLSM images

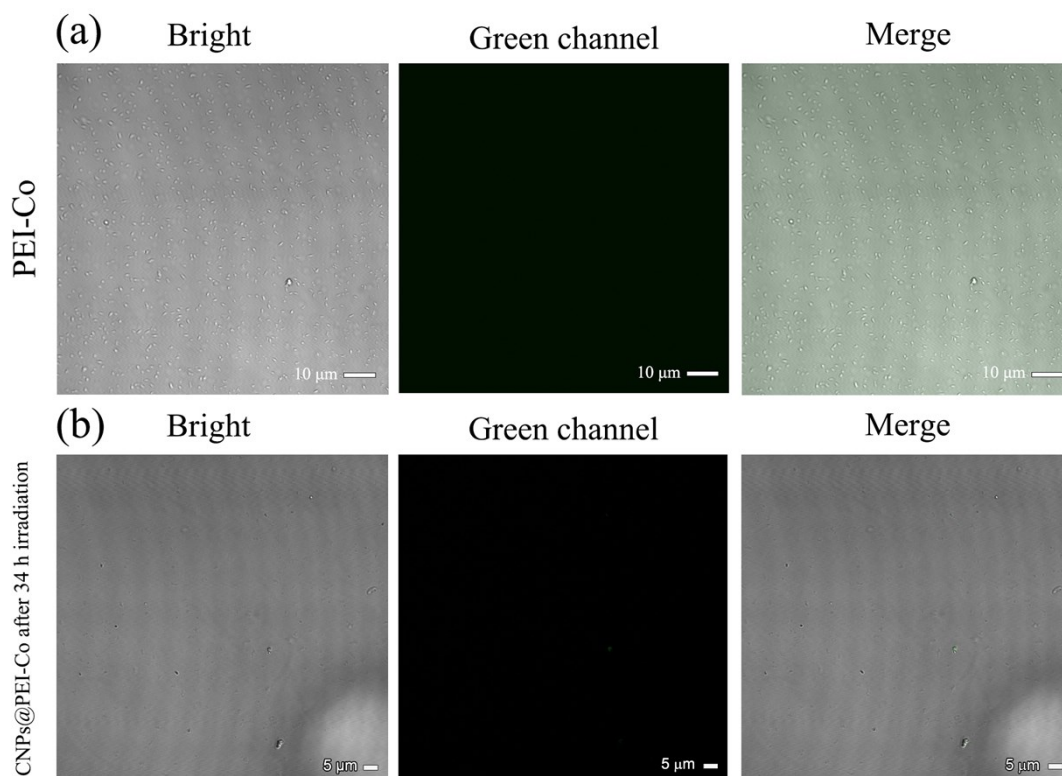


Figure S5. (a) CLSM images of PEI-Co in aqueous solution. (b) CLSM images of CNPs@PEI-Co assemblies after 34 hours of photocatalysis.

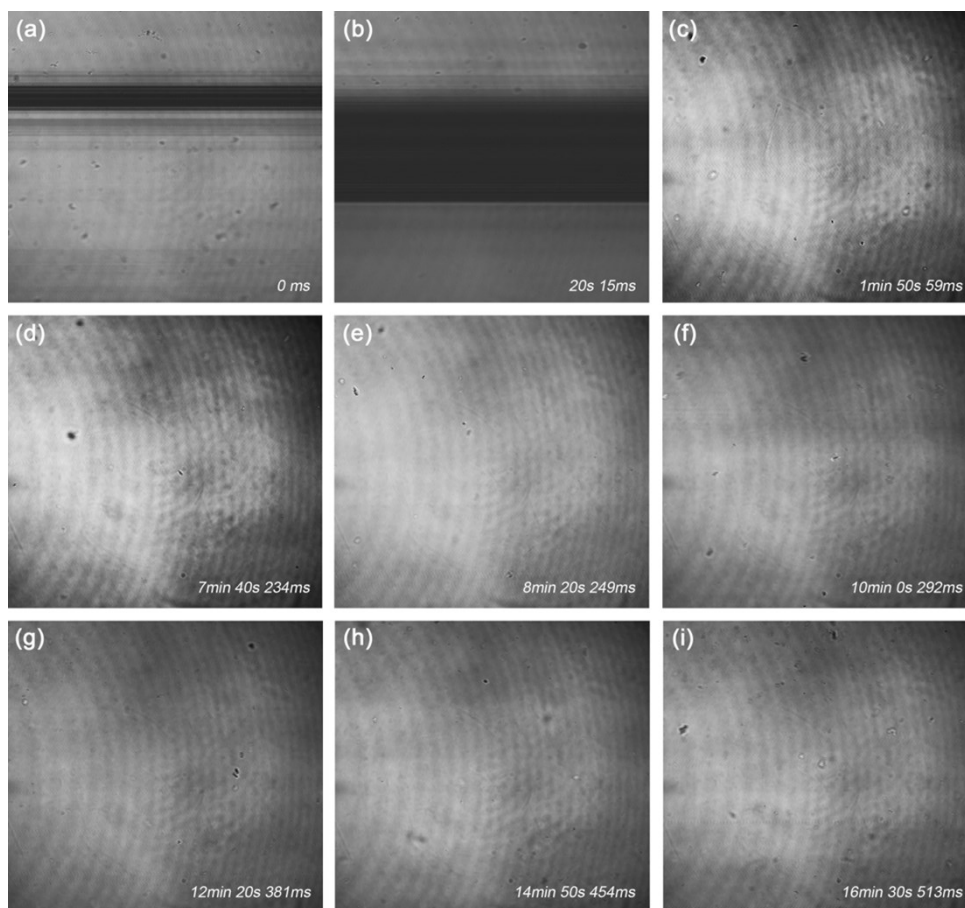


Figure S6. CLSM images (bright channel) of the self-assembly process of CNPs@PEI-Co

**A CLSM video file of the self-assembly process is attached.*

5. Inactivation studies

Table S1. TONs of samples by adding fresh PEI-Co or CNPs, respectively, into the inactive samples for another 10 h of irradiation.

| Entry | Re-added | H ₂ / μmol | TON (H ₂) |
|-------|----------|----------------------------------|-----------------------|
| 1 | / | 5.54 | 130.9 |
| 2 | PEI-Co | 0.21 | 5.1 |
| 3 | CNPs | 0.18 | 4.3 |

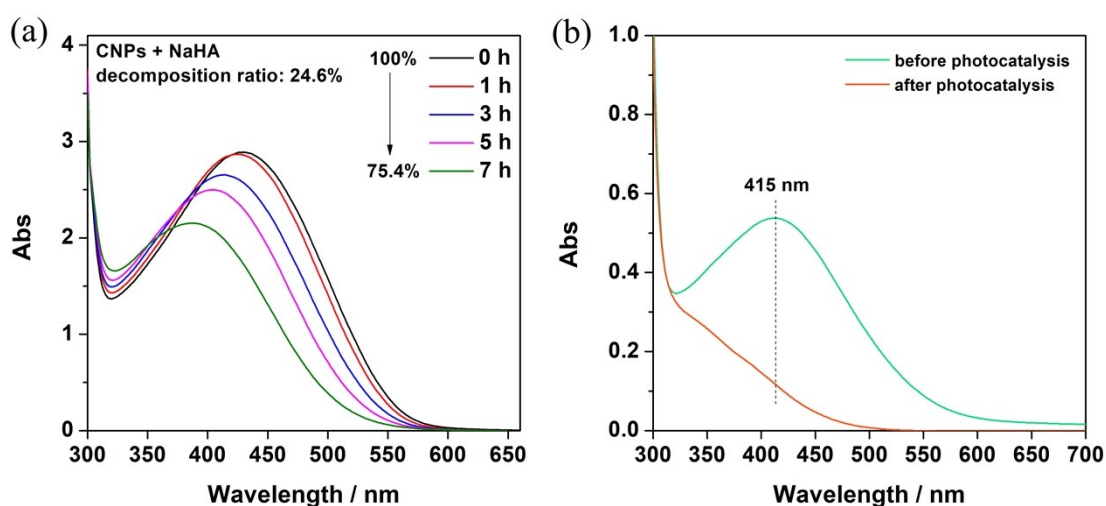


Figure S7. (a) UV-vis absorption spectra of CNPs (0.14 mg mL⁻¹) in aqueous solution in the presence of NaHA (0.02 M) in N₂ atmosphere for irradiation under a blue LED lamp ($\lambda_{\text{max}} = 450$ nm). (b) The comparison of the UV-vis absorption spectra of the photocatalytic sample before and after photocatalysis (irradiation time: 34 h)

6. Lifetime

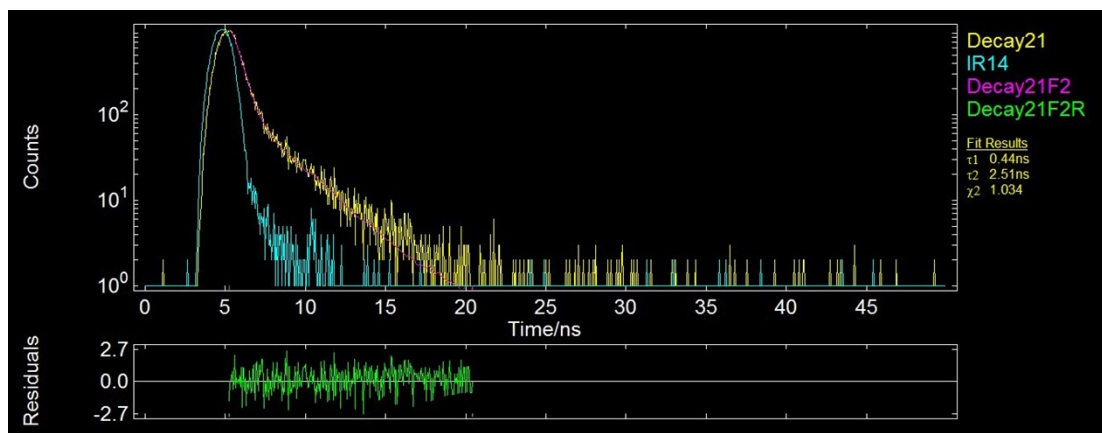


Figure S8. Kinetic decay of CNPs in aqueous solution

7. Quenching experiments

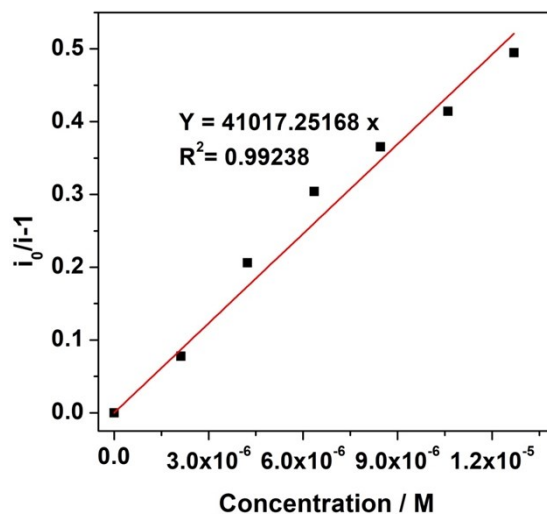


Figure S9 The Stern-Volmer equation fitting for the emission quenching of the CNPs by PEI-Co.

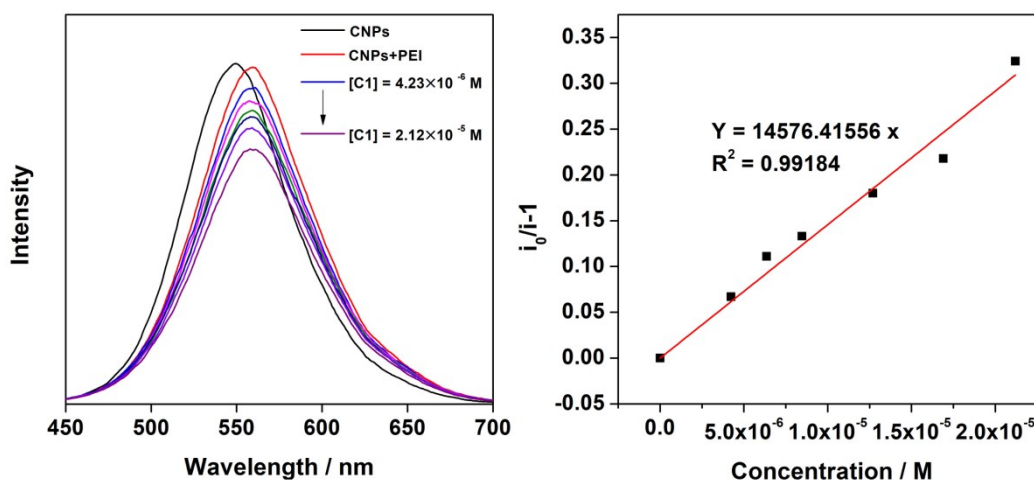


Figure S10. The emission quenching of the CNPs by C1 in the presence of PEI (right) and the Stern-Volmer equation fitting (left).

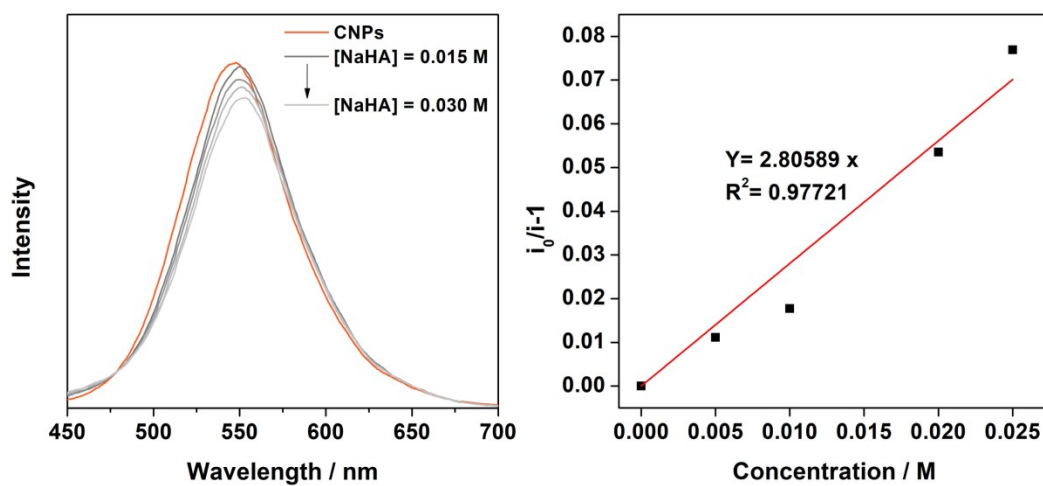


Figure S11. The emission quenching of the CNPs by NaHA (right) and the Stern-Volmer equation fitting (left).

8. Cyclic voltammetry

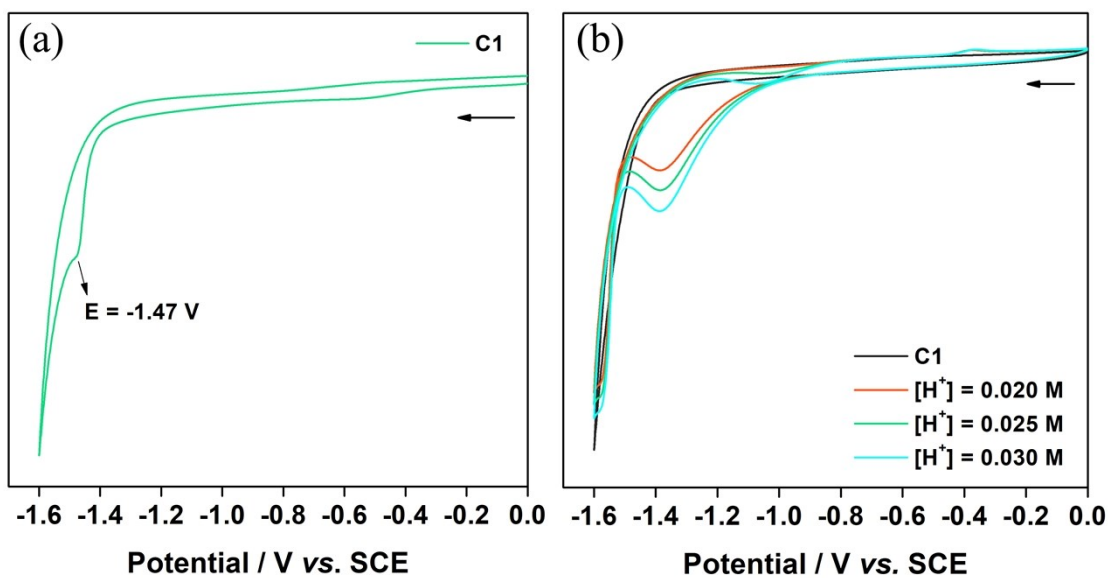


Figure S12. CV of C1 in the absence (a) and presence (b) of protons (proton source: HCl).

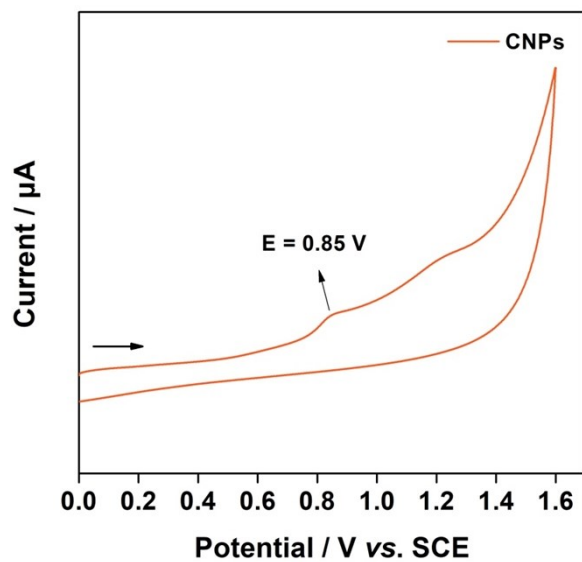


Figure S13. CV of CNPs.

9. Free-energy change estimation

$$E_{00}(\text{CNPs}) = hc/\lambda_x = 2.49 \text{ eV}$$

$$E_{ox}(\text{CNPs}) = 0.85 \text{ V}$$

$$E_{red}(\text{C1}) = -1.47 \text{ V}$$

$$\Delta G^0 = E_{ox}(\text{CNPs}) - E_{red}(\text{C1}) - E_{00}(\text{CNPs}) = -0.17 \text{ eV}$$