Supporting Information

Chlorophyll(a)/Carbon quantum dot Bio-Nanocomposite Activated Nano-Structured Silicon as an Efficient Photocathode for Photo-electrochemical Water Splitting

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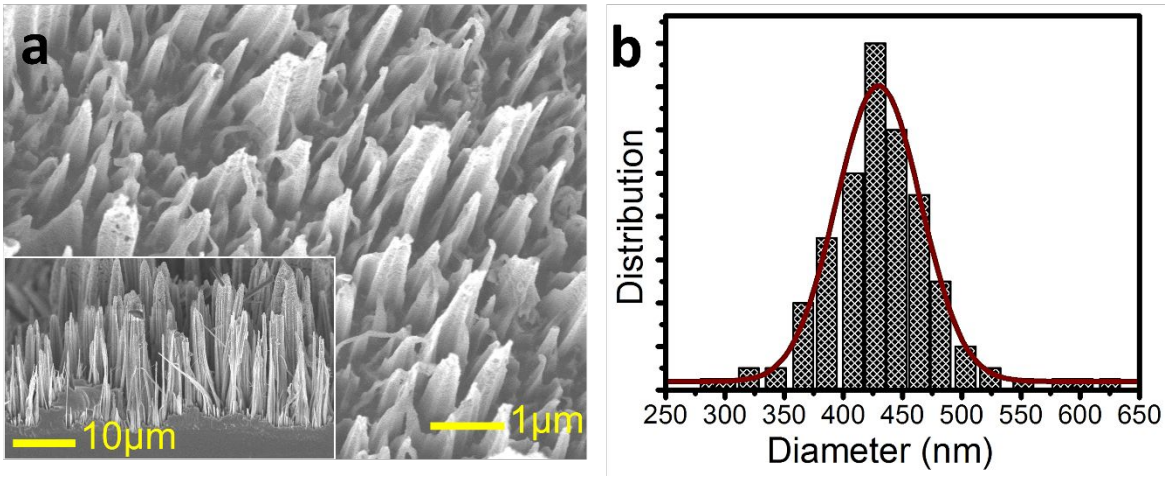

Figure S1. Dimension of SiNW array. (a) FE-SEM images of vertically aligned SiNW array with top and a cross-sectional view, (b) Average diameter distribution profile of SiNWs which is found to be 425 nm.

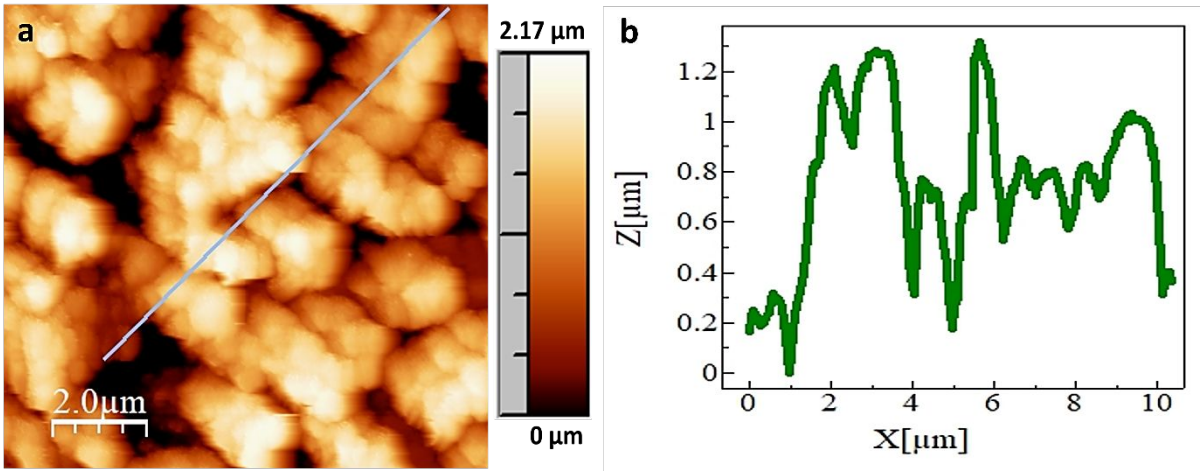

Figure S2. (a) AFM image of vertically aligned silicon nanowire array and (b) associated line profile of vertically aligned SiNW array indicating surface roughness.

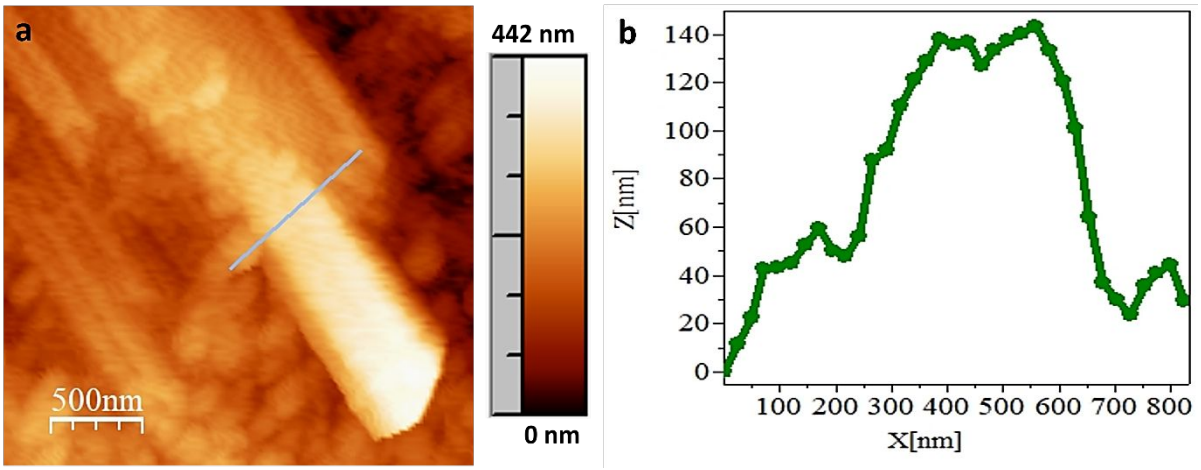

Figure S3. (a) AFM image of Chl/CQDs decorated SiNW, (b) Line profile of Chl/CQDs decorated SiNW.

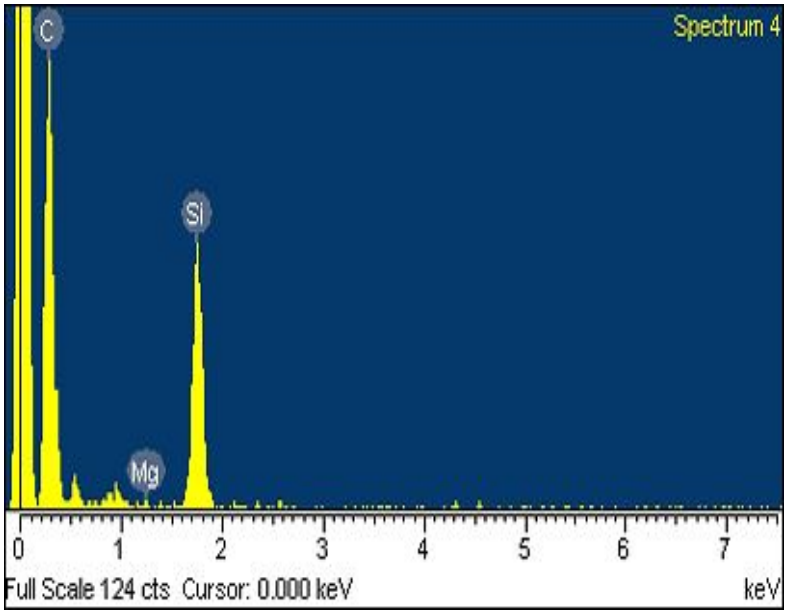

Figure S4. Energy-dispersive X-ray spectroscopy (EDS) spectra of Chl/CQDs decorated SiNW which reveals the presence of carbon, magnesium, and silicon.

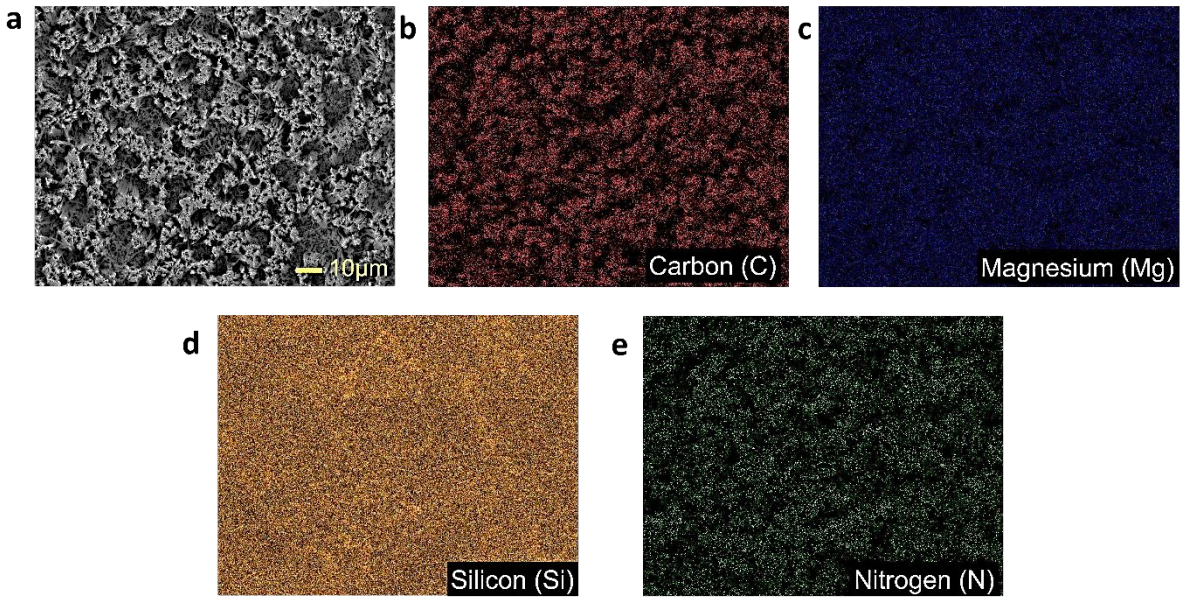

Figure S5. (a) FE-SEM image of Chl/CQDs decorated SiNW array (top view). SEM-EDS elemental mapping of (b) Carbon, (c) Magnesium, (d) Silicon, (e) Nitrogen. Uniform distribution of *b*-NC over SiNW array is shown.

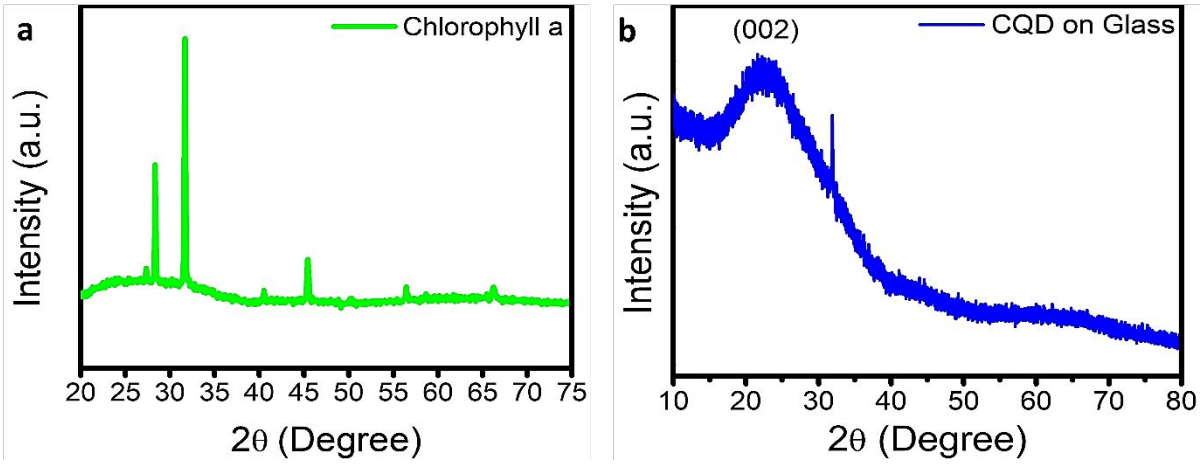

Figure S6. (a) XRD peaks of pristine Chlorophyll(a) deposited on glass. (b) XRD peaks of pristine CQDs deposited on glass. For x-ray diffractometer the source was Cu-Kα.

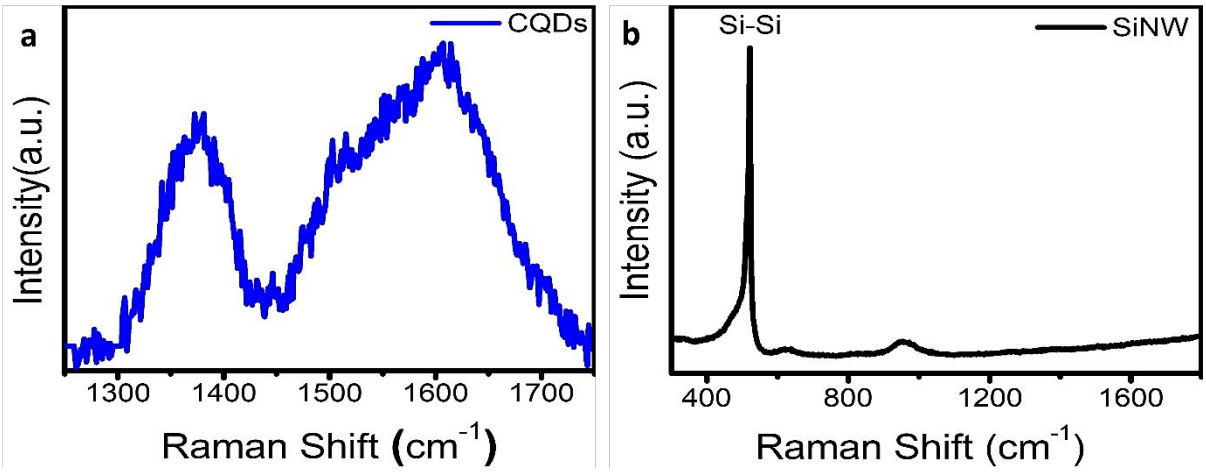

Figure S7. (a) Raman spectra of the pristine CQDs which exhibits two peaks correspond to D-band and G-band. (b) Raman spectra of SiNW array.

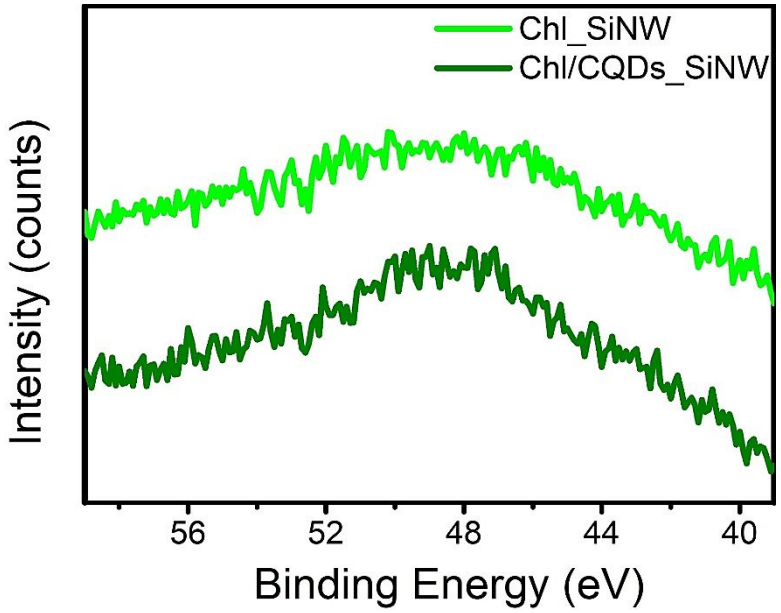

Figure S8. X-ray photoelectron spectra of Mg (2p) of Chl_SiNW, Chl/CQDs_SiNW.

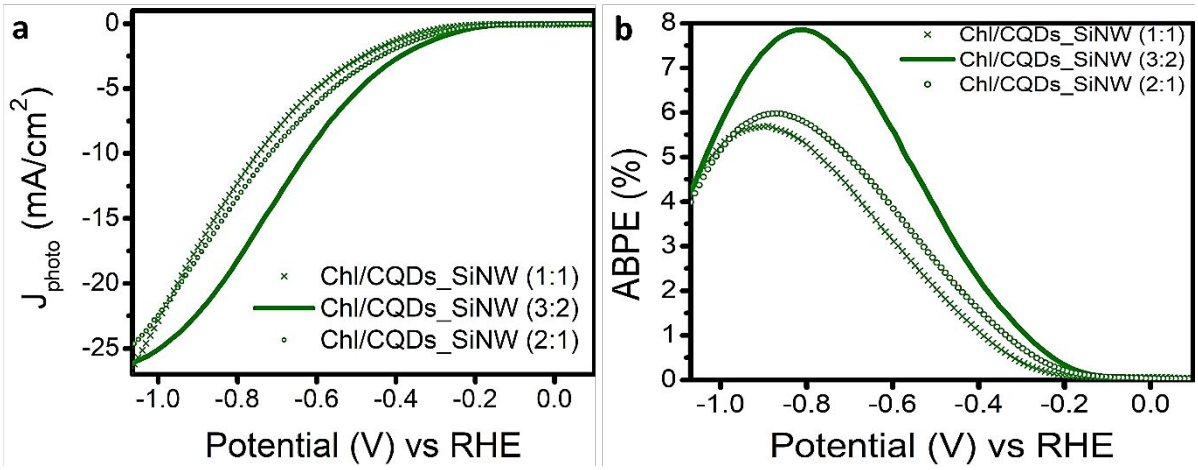

Figure S9. (a) Photocurrent density (J_{photo}) of Chl/CQDs_SiNW photoelectrodes with different ratio of Chl and CQDs (1:1), (3:2) and (2:1) (b) Corresponding ABPE.

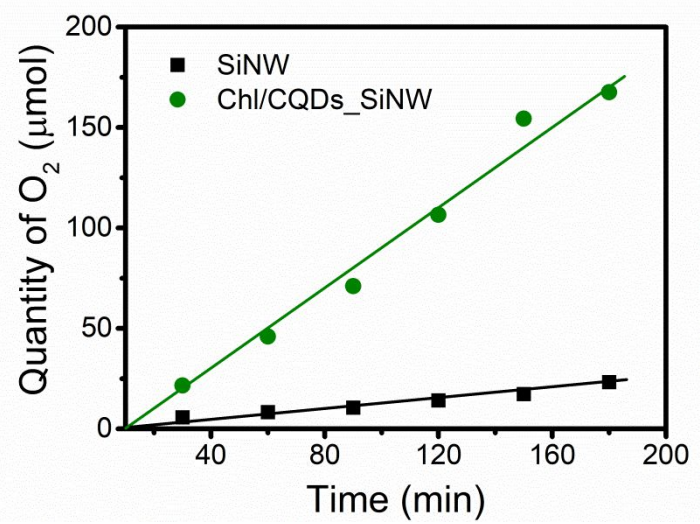

Figure S10: Quantification of O_2 Gas by GC under continuous illumination for 180 min where solid line corresponds to theoretical calculation. Experimentally obtained results are in good agreement with theoretically obtained results.

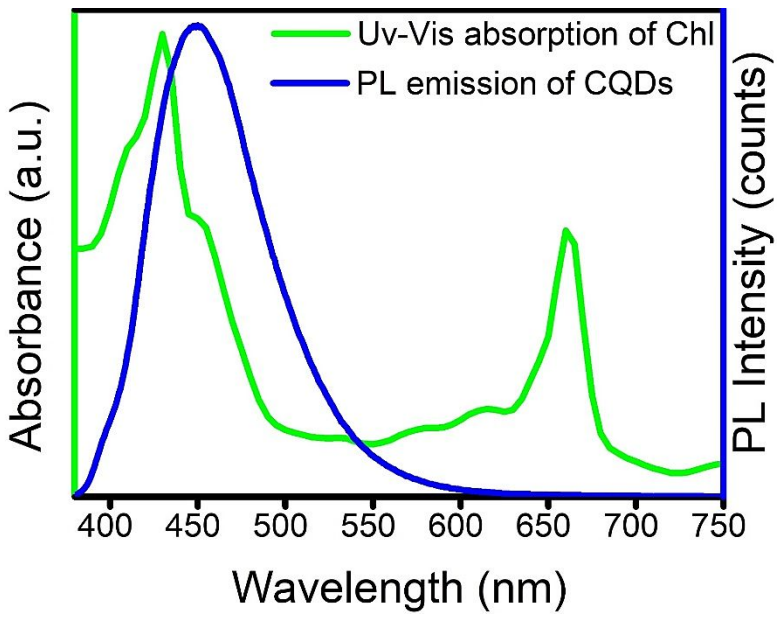

Figure S11. Overlapping of UV-VIS-NIR spectra and Photoluminescence spectra of Chl and CQDs respectively. For the Photoluminescence spectra the excitation wavelength was 365 nm and emission wavelength is 451 nm.

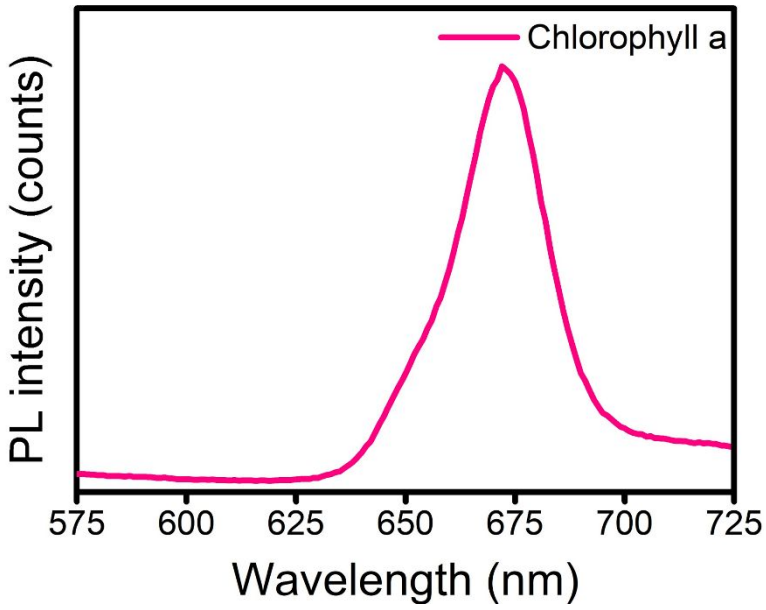

Figure S12. Photoluminescence spectrum of Chlorophyll(a) in aqueous dispersion, excitation wavelength was 500 nm, emission wavelength is 672 nm.

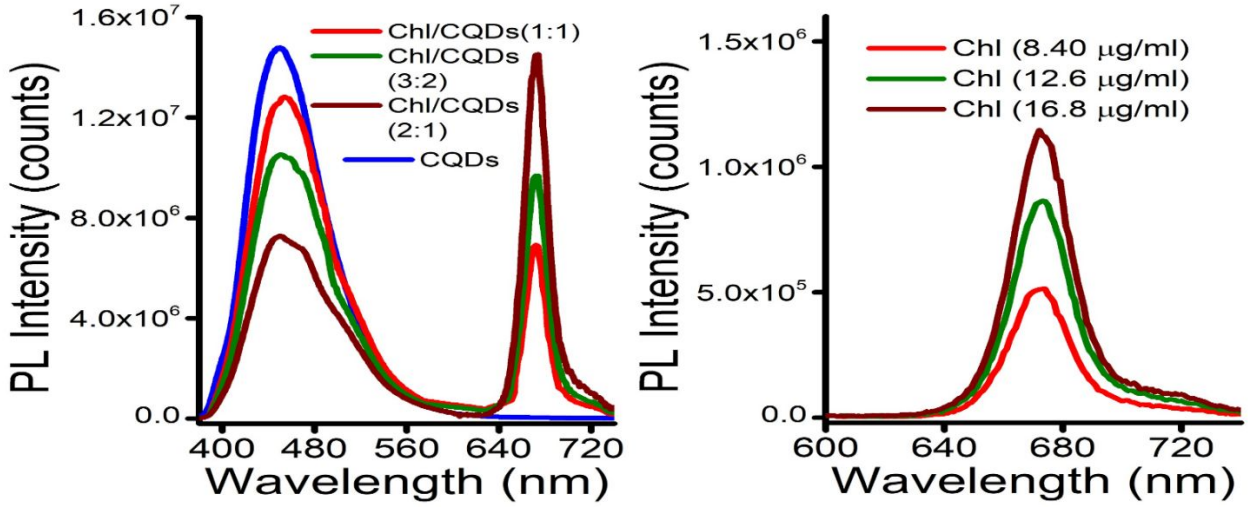

Figure S13. Comparison of photoluminescence spectra between chlorophyll(a) in *b*-NC (left figure) and chlorophyll(a) alone (without forming *b*-NC with CQDs) (right figure). PL measurement conditions were same for both the cases which are excitation wavelength 365 nm, dispersed in aqueous solution same as electrolyte used for PEC measurement, concentrations of Chl were same in both cases which are 8.40 μg/ml, 12.6 μg/ml and 16.8 μg/ml. Chl emission wavelength is 672 nm for both the cases.

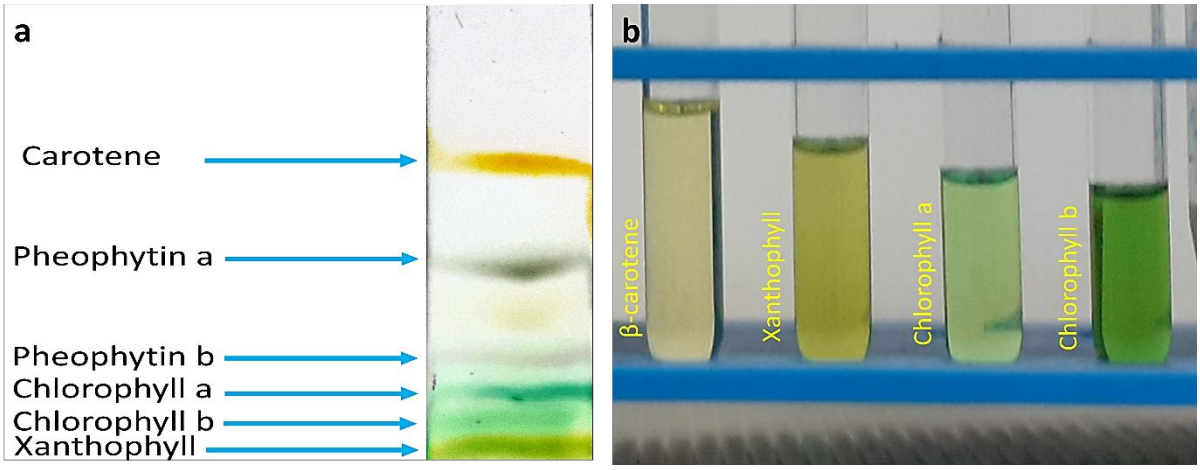

Figure S14. (a) Thin-layer chromatography of spinach extract showing different pigments, R_f value for Chlorophyll(a) was obtained as 0.44 (b) different pigment collected from column chromatography of spinach extract. Silica gel (60-120 mesh) column was used for chromatography.

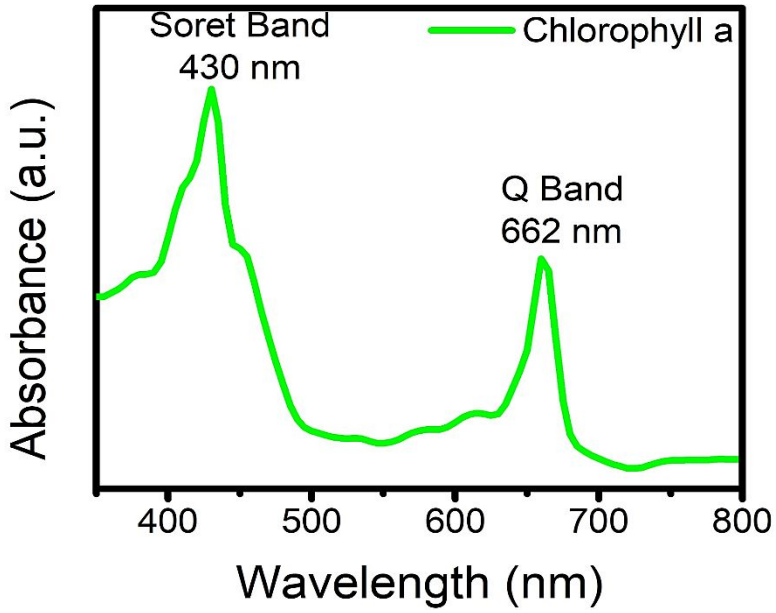

Figure S15. UV-VIS absorption spectra of Chlorophyll(a).

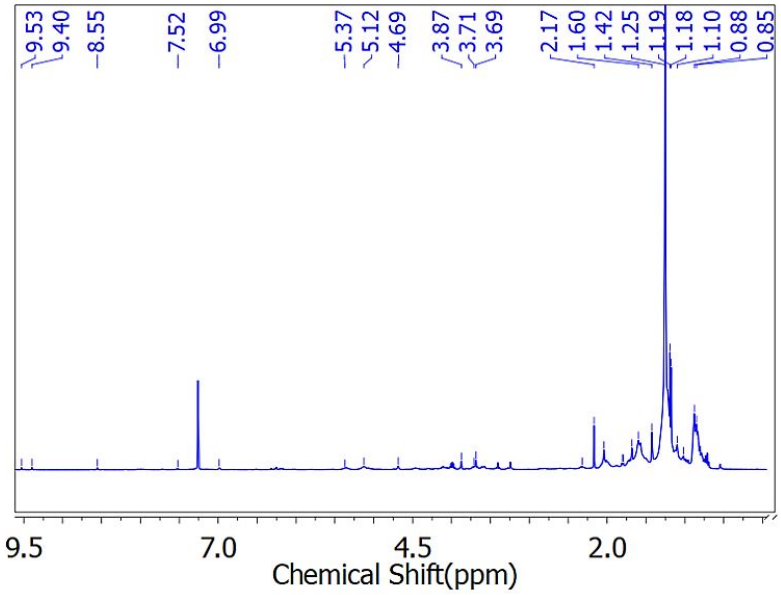

Figure S16. 1H NMR spectrum of Chlorophyll(a) in Deuterated chloroform ($CDCl_3$) at 500 MHz. Solution concentration was 535 µg/ml.

Table S1: Average lifetime, multiple components in lifetime of CQDs under different condition, and other basic information for TCSPC measurement.

Material	CQDs' Lifetime component ($T_1 \pm 3\sigma$) (ns)	Relative Amplitude B_1 (%)	Normalised pre-exponential (α_1)	CQDs' Lifetime component ($T_2 \pm 3\sigma$) (ns)	Relative Amplitude B_2 (%)	Normalised pre-exponential (α_2)	CQDs' Lifetime component ($T_3 \pm 3\sigma$) (ns)	Relative Amplitude B_3 (%)	Normalised pre-exponential (α_3)	CQDs' Average lifetime (T_{av}) (ns)	Chi Square value
CQDs	3.24 ± 0.34	22.67	0.935276006	9.67 ± 0.12	77.3	0.064723994	--	--	--	**3.66**	1.03
b-NC Chl/CQDs (1:1)	3.44 ± 0.15	6.19	0.008048659	52.61 ± 1.41	60.57	0.005155987	0.15 ± 0.01	33.24	0.986795354	**0.44**	1.07
b-NC Chl/CQDs (3:2)	1.51 ± 0.35	6.83	0.011348817	38.85 ± 3.09	42.43	0.002436247	0.13 ± 0.01	50.74	0.986214937	**0.24**	1.07
b-NC Chl/CQDs (2:1)	1.32 ± 0.21	7.03	0.005362731	23.50 ± 2.94	39.45	0.001687183	0.05 ± 0.01	53.52	0.992950086	**0.1**	1.08

Excitation wavelength was 365 nm and emission wavelength was 451 nm for CQDs lifetime study.

For the calculation of average lifetime we have used the following equation:

$$T_{av} = \sum_{i=1}^{n} \alpha_i T_i$$

where T_{av} is the average lifetime of CQDs, T_i is the lifetime of i_{th} component of CQDs, α_i is the respective normalized pre-exponential value, and B_i is the respective relative amplitude (in %).

The quoted errors in different lifetime components are three times standard deviation (3σ).