Electronic Supplementary Information

pH triggered reversible photoinduced electron transfer to and from carbon nanoparticles

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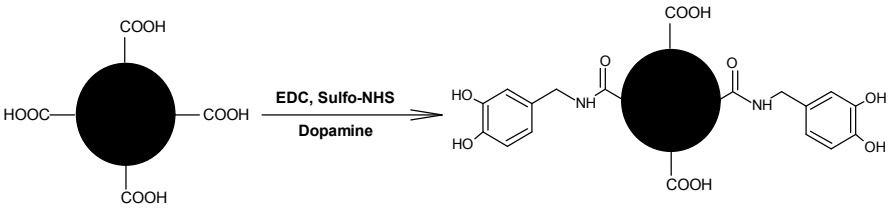
Materials. Citric acid, ethylenediamine, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC.HCl), N-hydroxysulfosuccinimide sodium salt (Sulfo-NHS), dopamine and reduced nicotinamide adenine dinucleotide (NADH) were purchased from Sigma-Aldrich and used as received. Triple distilled water was used for the preparation of the solutions.

Preparation of Carbon Nanoparticales (CNPs). Ci-tric acid (1.0 g) and ethylenediamine (0.149 mL) having mole ratio of NH2/COOH = 0.20 in the precursors were added to 10 mL of water, which was sonicated for 6 min. to get a clear solution. The solution was then put into a 750 W microwave oven operating at 80oC and incubated for 2 min. A yellow colored solution was obtained on cooling. The solution was centrifuged at 25000 rpm for 20 min. and the supernatant was collected. The resulting CNPs were dried in a rotavapor.



Scheme S1 Representation for partial derivatisation of carboxyl coated CNPs with dopamine.

Preparation of Dopamin Docked CNPs. The carbox-yl coated CNPs (0.2 g) were dissolved in 5 ml water and sonicated for 15 min. EDC.HCl (19.2 mg, 0.1 mmol) and Sulfo-NHS (21.7 mg, 0.1 mmol) were added into the CNP solution under N2 atmosphere and stirred for 1 h at room temperature. This is followed by addition of dopamine (0.1 mmol) to the mixture and stirred for 48 h. The reaction solution was dialyzed against water overnight, and the CNP-based dopamine was dried in rotavapor. The reaction pathway is briefly shown in Scheme 1.

Analytical Methods. The absorption spectra were recorded in a Varian Cary 300 Bio UV-Vis spectrophotometer. Fluorescence measurements were done on a QM-40 spectrofluorimeter procured from PTI. The fluorescence lifetimes were measured by the method of time-correlated single-photon counting (TCSPC) using a picoseconds spectrofluorimeter from Horiba Jobin Yvon IBH equipped with a FluoroHub single photon counting controller and FC-MCP-50SC MCP-PMT detection unit. A 377 nm laser head was used as the excitation source. The FTIR spectrum was recorded using a Perkin–Elmer

Spectrum RX1 spectrophotometer. The DLS measurements were taken using Malvern Zetasizer Nano equipped with a 4.0 mW HeNe laser operating at λ = 633 nm. All samples were measured in an aqueous system at room temperature with a scattering angle of 173o. Size distribution is calculated by Nano software using a non-negative least square analysis. AFM was performed using an NT-MDT NTEGRA instrument procured from NTMDT, CA, USA. The electrochemical studies were carried out with a Princeton Applied Research 263A potentiostat using platinum (Pt) electrode as the working electrode, a platinum wire as counter electrode, and an AgCl coated Ag wire, which was directly dipped in the electrolyte solution, as the reference electrode. Nitrogen gas was passed through the solution for 5 minutes to remove any incipient oxygen. The electrolyte used was 0.1 M KCl in water and measurements were performed at scan rate of 150 mV s^{-1}.

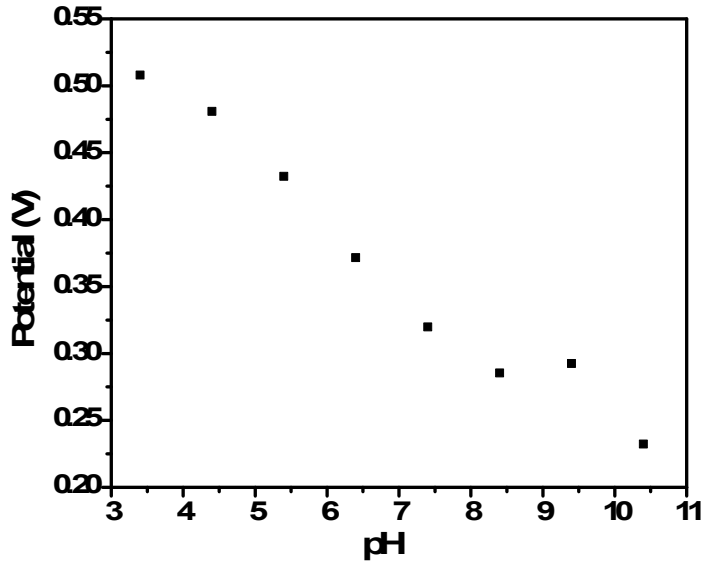


Fig. S1. Plot of the potential for oxidation versus pH.

The pH response can be analyzed using the Nernstian equation:

$$E = E^0 - 0.059\left(\frac{h}{n}\right) \times pH \qquad (1)$$

where, E are the average anodic and cathodic peak potentials, E^0 is the potential at pH=0, and h/n represents the proton to electron ratio. The potential does not change linearly since the rate of electron transfer in lower pH is different from that at higher pH as shown in Fig. S1.

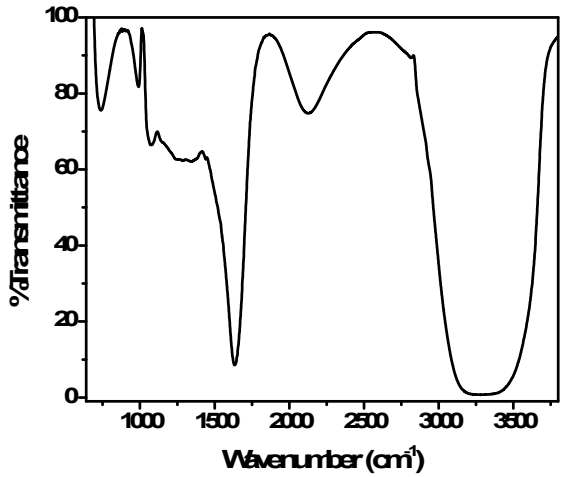


Fig. S2 FTIR spectrum of dopamine functionalised CNPs.

FTIR spectrum of dopamine functionalised CNPs shows no difference from that of the non-functionalised ones. Thus, it can be conferred that there is no unwanted aggregation due to functionalisation of the CNPs.