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Electronic Supporting Information

Fuel-independent and membrane-less self-charging biosupercapacitor

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EXPERIMENTAL DETAILS

Branched polyethyleneimine (PEI) solution (50% w/v in H_2O, Mn ~60,000, MW ~750,000), poly(allylamine hydrochloride) (PAH) (MW 17,500 g mol^{-1}), trisodium citrate dehydrate, $HAuCl_4 \cdot 3H_2O$ (99.995%), poly(sodium 4-styrenesulfonate) (PSS, MW 70,000 g mol^{-1}), (3-aminopropyl)triethoxysilane (APTES) solution (99%), toluene (99,8%), NaOH, KCl, NaCl, H_2SO_4, KH_2PO_4, K_2HPO_4, myoglobin (Mb) from equine heart (95-100%), ITO coated polyethylene terephthalate (PET) were all purchased from Sigma-Aldrich Chemicals (Germany). *Myrothecium verrucaria* bilirubin oxidase (3.61 mg mL^{-1} in 20 mM Tris buffer, containing 100 mM Na_2SO_4, pH 8.0) was produced and purified as described previously.[1] All chemicals were at least of analytical grade and used without further purification. All solutions were prepared using deionised water purified with a Milli-Q system (Millipore, USA).

AuNPs with an average size of 9.2 (NP_9) and of 35.9 nm (NP_{36}) were prepared by the common citrate-reduction procedure. As-prepared NP_9 were electrostatically coated with PEI ($NP^{(+)}$) or PAH followed by a subsequent coverage with PSS ($NP^{(-)}$), according to the previously reported protocols.[2] The concentration of $NP^{(-)}$ and $NP^{(+)}$ was 6 mM. Both $NP^{(-)}$ and $NP^{(+)}$ were centrifuged (12,000 rpm for 30 min) in 1 mL Eppendorf tubes with subsequent removal of 90% of the supernatant. NP_{36} were 50 times concentrated by centrifugation. All precipitated AuNP dispersions were re-suspended using Ultrasonic Cleaner USC1200TH from VWR International Ltd. (East Grinstead, UK), and stored at 4 °C.

Glassy carbon electrodes (GCE, ⌀4 mm, Tianjin Incole Union Technology Co., China) were sequentially polished with Al_2O_3 slurry (particle diameter sizes of 1.0, 0.3, and 0.05 µm, Electron Microscopy Sciences, USA) and sequentially ultrasonicated in ethanol (≥ 99.9%, AnalaR, France) and then in water for 20 min. A 5 µL portion of AuNPs suspension (coated NP_9 or NP_{36} for anodic and cathodic sides, respectively) was dropcast onto the GCE surface and dried overnight under room temperature. NP_{36}-modified GCEs were additionally treated in 0.5 M sulfuric acid by applying 30 cycles between 0.0 V and 1.9 V *vs*. standard hydrogen electrode (SHE) at a scan rate of 0.1 V s^{-1} to create a highly developed three-dimensional gold matrix (Figure 1D), similarly to the method used previously to immobilize BOx in direct electron transfer conditions.[3-4] For

biomodification 5 µL of a BOx or 5 µL of a Mb solution (1.5 mg mL^{-1} in 12 mM phosphate buffer, pH 7.0) was applied on the GCE modified with NP_{36} or coated NP_9, respectively, and kept in a moist chamber at 4°C for 1 h. Denaturation of Mb and BOx was carried out at 90°C for 30 min to avoid the reversible restitution of the structure in case of Mb[5] and achieve full deactivation of BOx enzymatic activity.[6]

All electrochemical experiments were performed using an Autolab PGSTAT30 (Metrohm AG, The Netherlands), equipped with GPES/FRA software. A three-electrode configuration was used to characterize the separate electrodes, where a platinum foil and an Ag|AgCl ($KCl_{sat.}$) electrode (Sensortechnik Meinsberg, Germany) were employed as counter and reference electrodes, respectively. A 12 mM phosphate buffer containing 137 mM NaCl and 2.7 mM KCl (PB), pH 7.5 was used as the electrolyte. The voltage changes during the charge/discharge cycling were monitored simultaneously with galvanostatic potentiometry experiments using a digital multimeter (UNI-T, UT61 Series, China). All potentials in this paper are given versus the SHE.

Scanning electron microscopy (SEM) images were obtained using a high-resolution scanning electron microscope EVO LS 10 from Zeiss (Germany) in high vacuum mode at 15 kV accelerating voltage and 50 pA probe current.

Atomic force microscopy AFM imaging measurements were carried out using a Scanning Probe Microscope (Model 5500, Agilent Technologies, USA). All samples were imaged in an Acoustic Alternating Current (AAC) mode with a resolution of 512 points/lines. Tips with a spring constant of 5 N m^{-1} (Bruker, USA) were applied. The height distributions were obtained by using roughness analysis tool in WSxM 5.0 software.[7]

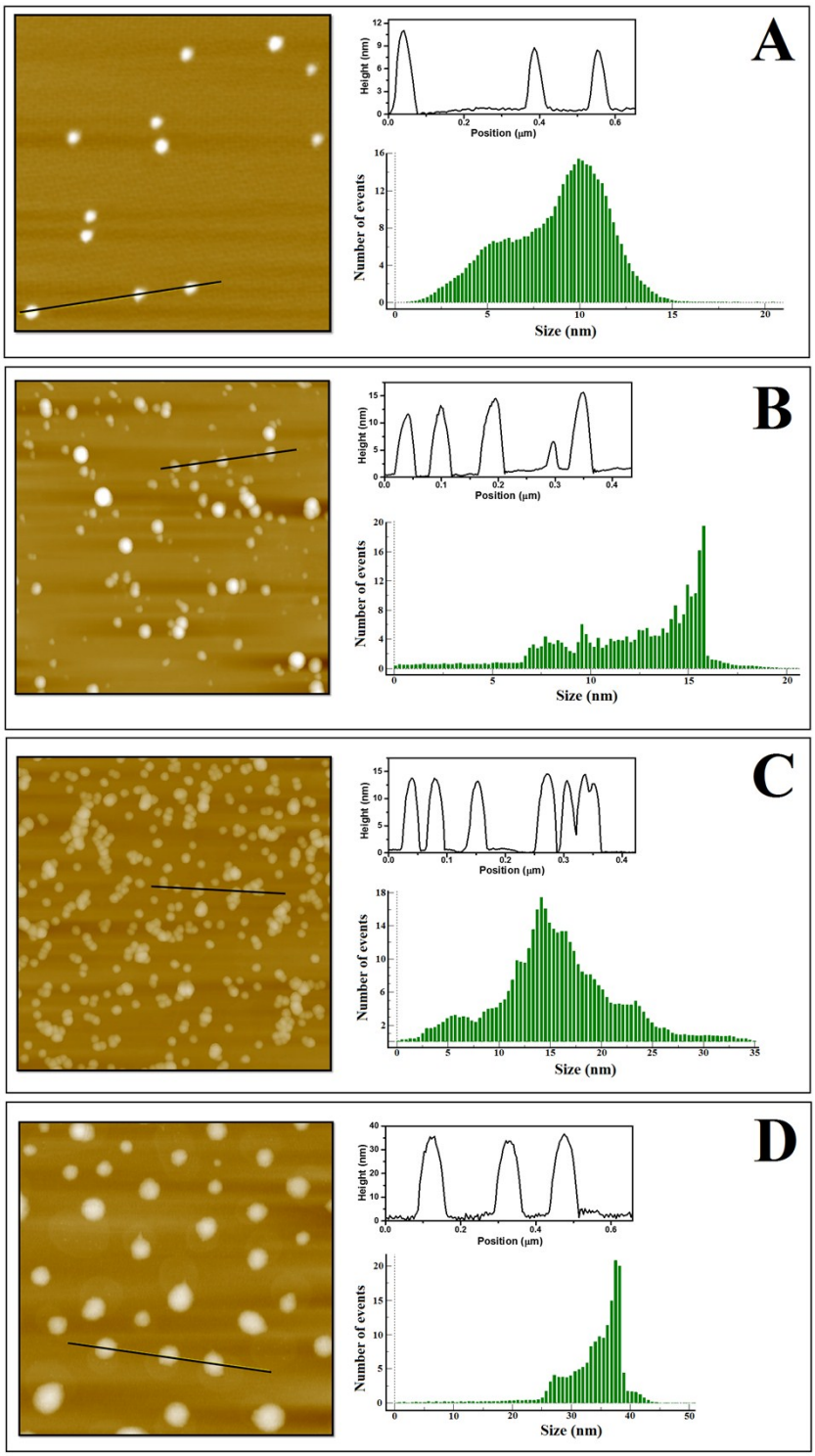

Fig. S1. Representative AFM images with highlighted height profiles and particle size distribution of freshly cleaved mica sheet modified with NP_9 (A), $NP^{(+)}$ (B), $NP^{(-)}$ (C) and NP_{36} (D). AFM images size: 1×1 μm^2.

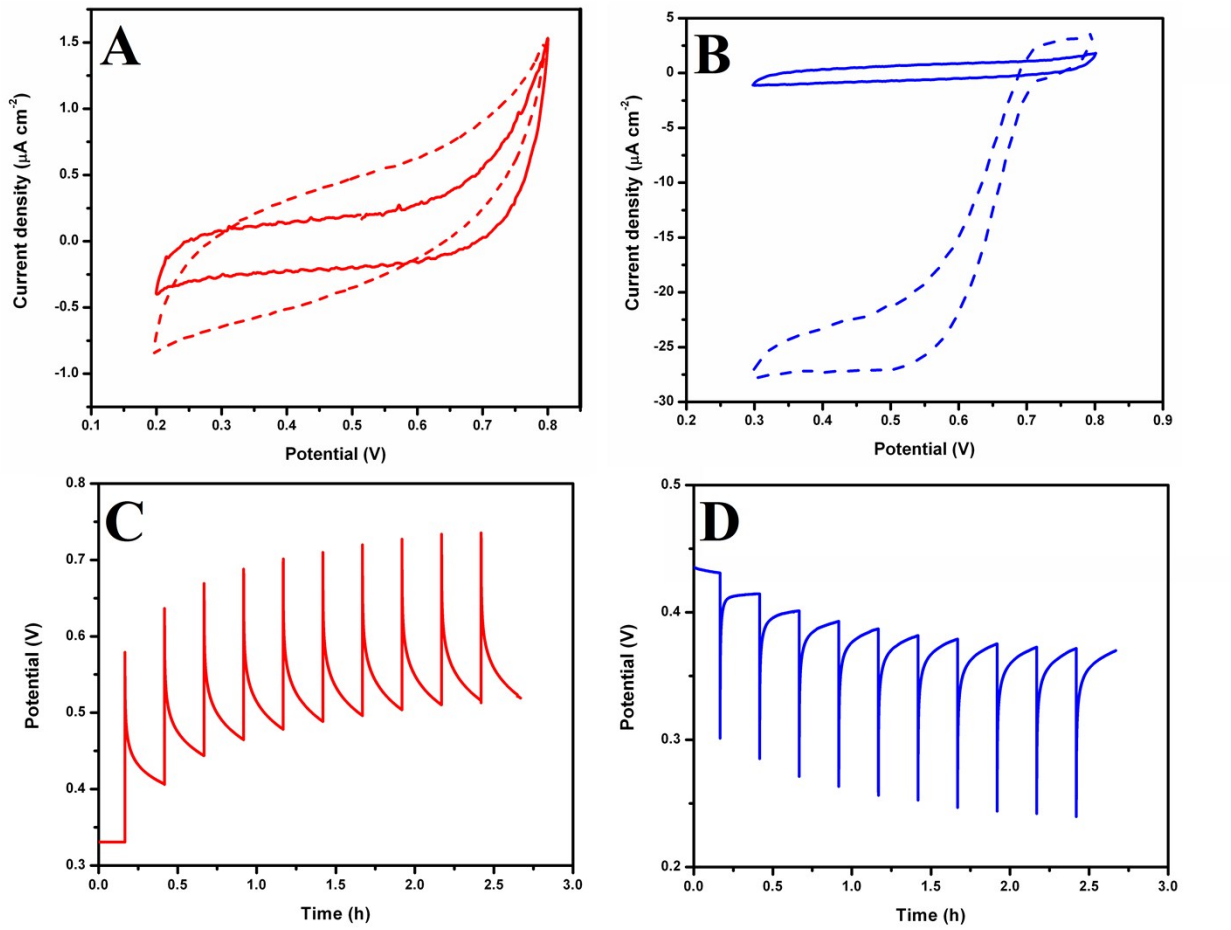

Fig. S2. (A) Cyclic voltammograms of $NP^{(-)}$ electrodes modified with native (dashed curve) and denatured (solid curve) myoglobin. (B) Cyclic voltammograms of NP_{36} electrodes modified with native (dashed curve) and denatured (solid curve) bilirubin oxidase. Scan rate 5 mV s^{-1}. (C, D) Representative charge/discharge curves of $NP^{(-)}$ electrodes modified with denatured myoglobin (C) and NP_{36} electrode modified with denatured bilirubin oxidase (D). Discharge was carried out by applying a pulse current of 10 μA cm^{-2} for 1 s.

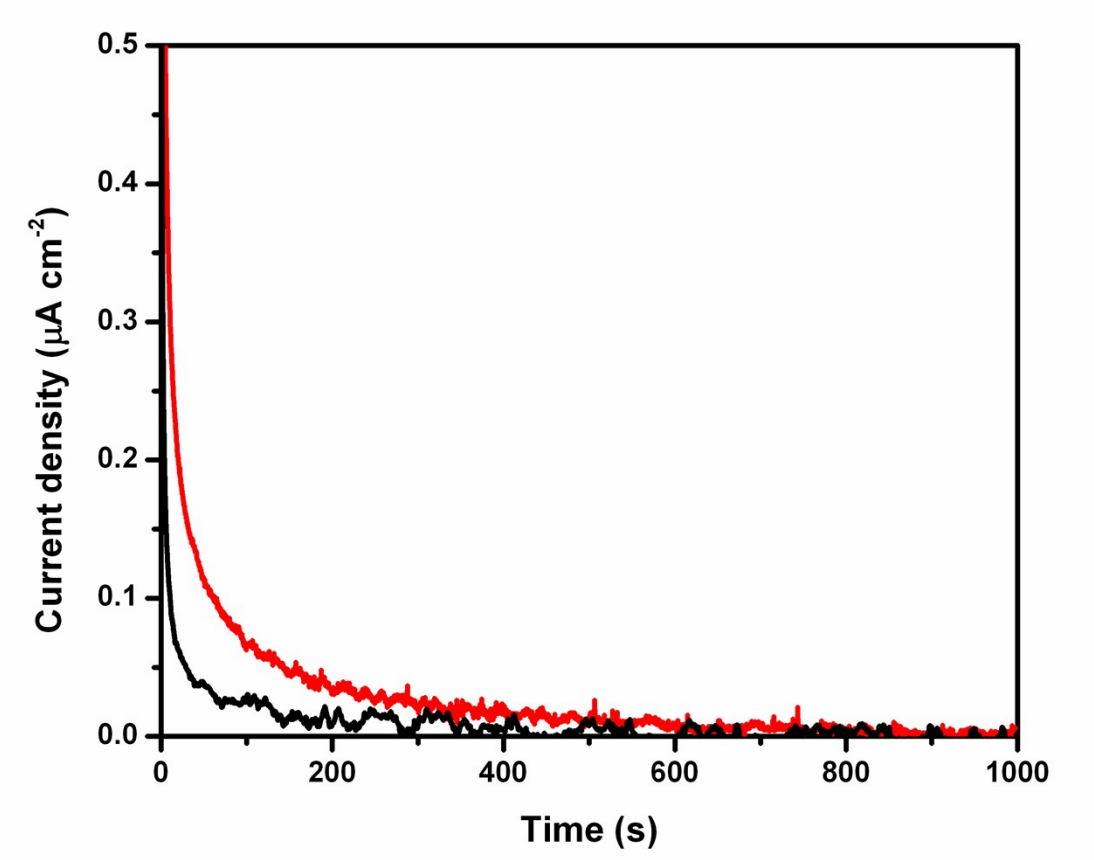

Fig. S3. Representative amperometric curves of $NP^{(-)}$ (black curve) and $Mb/NP^{(-)}$ electrodes (red curve) recorded at 0.4 V.

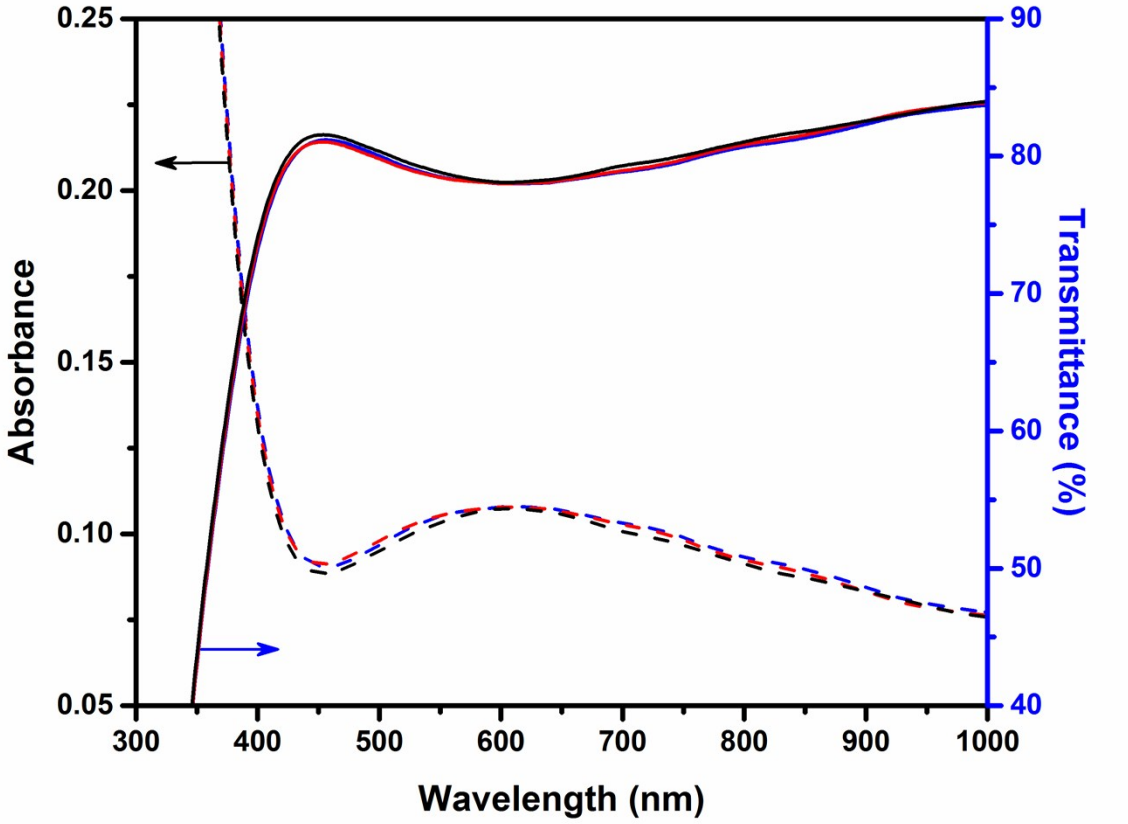

Fig. S4. UV–vis spectra of bare (black curves), $NP^{(-)}$-modified (red curves) and $Mb/NP^{(-)}$-modified (blue curves) transparent and flexible ITO coated PET films. ITO/PET films were kept overnight in 1% (v/v) APTES solution in toluene to create a positively charged ITO surface suitable for $NP^{(-)}$ adsorption.

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