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Electrostatically stabilized hybrids of carbon and maghemite nanoparticles: electrochemical study and application

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Electronic Supplementary Information

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1. Instrumentation and Methods

1.1 Instrumentation

Optical spectroscopy measurements were performed by a Cary 50 spectrophotometer (Varian Inc., Palo Alto, CA, USA) in quartz cuvettes (1 cm p.l.). Fluorescence determinations were carried out by a Cary Eclipse fluorescence spectrometer (Varian Inc., Palo Alto, CA, USA).

Transmission electron microscopy (TEM) images were acquired by a JEOL 2010 microscope operating at 200 kV with a point-to-point resolution of 1.9 Å. Before measurement, ethanol suspensions of complexes between SAMNs and Q-CDs were treated by ultrasound for 5 minutes. A drop of the dilute suspension was placed onto a holey-carbon film supported by a copper-mesh TEM grid and air-dried at room temperature.

Atomic force microscopy (AFM) measurements were performed at room temperature, in air, using a multimode scanning probe microscope with a Nanoscope V controller (Bruker). AFM images were recorded on freshly cleaved mica surfaces (Structure Probe, Inc., U.S.A.), prepared by the deposition of a 10 µL sample of the suspended material. The dried samples were rinsed with double distilled water and dried in air. Images were acquired by a NSC 15 silicon AFM cantilevers (Mikromasch, Germany) in tapping mode at the cantilever's resonant frequency.

The transmission ^{57}Fe Mössbauer spectra were collected employing a Mössbauer spectrometer operating at a constant acceleration mode and equipped with 50 mCi ^{57}Co(Rh) source. For measurement at a low temperature (5 K) and under an external magnetic field (5 T), the sample was placed inside the chamber of the cryomagnetic system (Oxford Instruments, UK). The in-field low-temperature ^{57}Fe Mössbauer spectrum was then recorded in a parallel geometry, when an external magnetic field was applied in a parallel direction with respect to the propagation of γ-rays. For fitting the Mössbauer spectra, the MossWinn software program was used.[1] Isomer shift values are referred to α-Fe at room temperature.

A superconducting quantum interference device (SQUID, MPMS XL-7, Quantum Design, USA) was used for magnetization measurements. Hysteresis loops measurements were performed at the temperature of 300 K and 5 K and in externally magnetic fields ranging from − 5 to + 5 T. The temperature dependence of the magnetization was recorded in a sweep mode of 1.8 K min^{-1} in the zero-field-cooled (ZFC) and field-cooled (FC) measuring regimes. In order to acquire the ZFC magnetization, the sample was demagnetized at a temperature higher than blocking temperature (magnetic moments of all particles are randomly oriented), and after that, cooling down without applied field to a temperature lower than the blocking temperature, to finally apply a small external magnetic field to measure magnetization on warming. To obtain a FC magnetization curve, the same process was performed, but with applied external magnetic field during sample cooling.

Voltammetric experiments were carried out by a computer-controlled electrochemical system (PGSTAT 12, EcoChemie, The Netherlands). The standard three-electrode arrangement consisted of a SCE reference electrode (Amel, Italy), a Pt counter electrode (Amel, Italy) and carbon paste electrode (CPE) as working electrode, in a 5 mL electrochemical cell. Measurements were carried out at constant temperature (22.0 ± 0.2 °C). All experiments were repeated at least five times.

1.2 Electrochemical characterization

Cyclic voltammetry and chronoamperometry experiments were carried out at pH 7.0 (0.1 M potassium phosphate, 50 mM KCl as supporting electrolyte). Electron transfer properties of unmodified and modified electrodes were determined in 0.1 M phosphate buffer solution in presence of 5 mM $[Fe(CN)_6]^{3-/4-}$ redox probe by cyclic voltammetry and EIS.

EIS parameters were calculated according to impedance-plane plot (Nyquist diagrams), where the impedance Ω(ω) is represented as a complex number:

$$\Omega(\omega) = \frac{E}{I} = \Omega_0 e^{j\varphi} = \Omega_0(cos\varphi + j\sin\varphi)$$

The expression for $\Omega(\omega)$ is composed of a real and an imaginary part. In the Nyquist diagrams, the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis.[2]

1.3 Synthesis of iron oxide nanoparticles

The synthesis of iron oxide nanoparticles was already described,[3,4] and the nanoparticulated resulting material was characterized by ^{57}Fe zero-field and in-field Mössbauer spectroscopy, FTIR spectroscopy, high resolution transmission electron microscopy, XRD, magnetization measurements[5] and resulted in stoichiometric maghemite (γ-Fe_2O_3) with a mean diameter of 11 ± 2 nm, which can lead to the formation, upon ultrasound application in water (Bransonic, mod. 221, 48 kHz, 50 W) of a stable colloidal suspension, without any organic or inorganic coating or derivatization. The surface of these bare maghemite nanoparticles shows peculiar binding properties and can be reversibly derivatized with selected organic molecules. We called these bare nanoparticles as Surface Active Maghemite Nanoparticles (SAMNs).

1.4 Synthesis of carbon dots (QCDs)

All the nanomaterials employed in the present report were fabricated in house.

GA-CDs:[6,7] Lauryl gallate powder (1 gram) was homogenized and placed into a porcelain crucible. The crucible inserted in an oven equilibrated at 270 °C for 2 hours. The obtained carbonized dark brown material was extracted with 20 mL acetone and the insoluble residues were filtered off. The acetone extract was dried and the residue was dissolved in water at a concentration of 2 mg mL^{-1}. An equal volume of 0.5 M NaOH solution was added and the obtained mixture was stirred at RT overnight. The as prepared water-soluble carbon dots were dialyzed against deionized water (2 kDa cut off membrane) and used for experiments.

PEG-GDs:[8] PEG derived graphene dots (PEG-GDs) were obtained starting from commercial graphite from Fluka (cod. 78391, puriss, < 20 µm) according to a slightly modified Hummers method.[9] Graphite (400 mg) was stirred at room temperature into 20 mL of concentrated sulfuric acid. The reaction flask was then placed into an ice-bath and 2 g of $KMnO_4$ were very slowly added. This mixture was stirred at RT for 2 hours and cooled water (100 mL) was dropwise added. Finally, concentrated hydrogen peroxide (5 mL) was added to the reaction mixture. The as prepared graphene oxide (100 mg) was sonicated for 2 hours in the presence of concentrated sulfuric and nitric acid (3:1 volume ratio). Then, the mixture was refluxed at 80 °C for 8 hours. The graphene oxide was collected by centrifugation and washed 5 times with water, till neutral pH. Afterwards, KOH (10 mg) was added to 10 mL of the graphene oxide suspension, followed by the addition of 100 mg PEG-NH_2 (PEG-diamine, 2000 Da) and the reaction mixture was refluxed at 120 °C for 48 hours. The as prepared PEG decorated graphene dots (PEG-GDs) were dialyses against deionized water for further uses.

Q-CDs:[10] Quaternized carbon dots were synthetized by thermal oxidation of an ammonium carboxylate complex, a salt precursor made from the acid−base combination of tris(hydroxymethyl)aminomethane (Tris) and betaine. Betaine resulted attached on the outer surface of the nanoparticles through amide linkages formed in situ by thermal condensation of the ammonium carboxylate groups. Q-CDs were prepared as follows: 1.5 g betaine hydrochloride (Alfa Aesar) was dissolved in 5 mL of water. Subsequently, 1.2 g Tris (Aldrich) was added to the betaine hydrochloride solution until complete dissolution (1:1 molar ratio). The pH of the initially acidic solution became neutral after addition of the Tris base. The water-soluble organic salt was partly recovered from the solution using an excess of isopropanol (100 mL). The obtained syrup was then rinsed and washed three times with 100 mL of isopropanol. The organic salt in isopropanol was dried for 3 days at 80 °C. The resulting viscous white mass was directly heated at 250 °C in air for 2 h in a porcelain crucible. The resulting brown solid was extracted with water (25 mL) and filtered in order to remove any insoluble particulate. Q-CDs were precipitated from the colloid by adding 200 mL of acetone. The quaternary ammonium chloride nanomaterial, Q-CDs, is highly dispersible in water (> 20 mg mL^{-1}) and produce stable colloids.

1.5 Preparation of carbon paste and modified carbon paste electrodes

The carbon paste was prepared in the following proportions for unmodified electrode: 70% graphite powder, 30% silicone grease. Modified carbon paste electrodes were composed by 55% graphite powder, 30% silicone grease and 15% SAMN or SAMN@CNP or CNP@SAMN hybrids. The modified electrodes were prepared by mixing graphite powder with the nano-hybrids and then adding silicone grease and thoroughly mixing approximately 15 minutes to form homogenous carbon pastes. The resulting CPEs were inserted into the cavity of glass electrode holders (1.35 mm diameter, 0.01428 cm^2 geometric area). A copper wire had been inserted into the paste through the opposite side of the glass capillary to create the electrical contact with the potentiostat. Finally, the electrode surface was carefully smoothed on a weighting paper and rinsed with double distilled water before each experiment. All applied potentials were referred to SCE reference.

1.6 Electrochemical low volume flow cell

The electrochemical flow cell for polyphenol determination was constituted by two half cells, A and B (Fig. S8), in poly(methyl methacrylate). The cell is equipped with a carbon paste working electrode modified with the nanostructured material. Between the two half cells (A and B) a channel was defined by a teflon spacer (0.1 mm thickness), delimiting a 1 µL cell volume. Half-cell A contains the carbon paste working electrode and inlet and outlet channels (0.5 mm i.d.) obtained by drilling. The cell was connected to the injection system by PEEK tubing (0.5 mm i.d., 1.6mm o.d.). A platinum wire and an Ag/AgCl electrode, inserted into the inlet and outlet channel were used as counter and as reference electrode, respectively.

1.6 Polyphenol extraction from plant samples

Fresh samples from *Eryngium foetidum* (100 – 150 mg) were powdered by manual grinding in liquid nitrogen and then extracted in 99.6% ethanol. The extracts were homogenized and sonicated for 30 min (50/60 Hz). The homogenates were centrifuged for 20 min at 12.000 g, and properly diluted for further electrochemical measurements in 0.1 M sodium acetate, containing 0.1 M KCl, pH 5.0.

1.7 Quantitative determination of free phenolic acids by HPLC

Chlorogenic acid, ferulic acid, p-coumaric acid, caffeic acid, and gallic acid were separated and quantified using an HPLC equipped with a diode array detector. The liquid chromatography apparatus utilized for the analyses was a Jasco X.LC system consisting of a model PU-2080 pump, a model MD-2015 multiwavelength detector, a model AS-2055 autosampler, and a model CO-2060 column oven. ChromNAV chromatography data system was used as software. The separation of phenolic acids was obtained on a Tracer Extrasil ODS2 (5 mm, 250 6 45 mm – Teknokroma) operating at 35°C. The flow rate was set to 1 mL min^{-1}. The mobile phase consisted of 0.1% formic acid (A) and methanol (B). Elution gradient was carried out in 50 min and the flow rate was 0.8 mL min^{-1}. All standards were dissolved in 50% ethanol and the calibration curves were generated with concentrations ranging from 0.06 - 60 mg L^{-1}. High performance liquid chromatography (HPLC) analysis at 325 nm was used for identification of chlorogenic acid, caffeic acid, and ferulic acid. Identification of p-coumaric acid was performed at 310 nm. Phenolic acids were quantified following a calibration method. All standards were dissolved in methanol and the calibration curves were generated with concentrations ranging from 0.3 mg L^{-1} to 30 mg L^{-1}.

2. Results

2.1 Fluorescence characterization of quaternized carbon dots (Q-CDs)

Quaternized carbon dots, QCDs, were characterized by static and time resolved fluorescence. Fluorescence spectrum of an acqueus suspension of Q-CDs (15 µg mL^{-1}) showed an emission maximum at 428 nm, following an excitation in the range comprised between 375 and 400 nm (see Fig. S1). Moreover, Q-CD fluorescence intensity depended on nanoparticle concentration, as shown in Fig. S2. The phenomenon was attributed to fluorescence self-quenching of Q-CDs. In particular, Q-CD fluorescence increased linearly with concentration in the range comprised between 0 and 100 µg mL^{-1}, reaching the maximum value at about 200 µg mL^{-1}, then fluorescence decreased with Q-CD concentration. The quenching process, observed at Q-CD concentrations above 200 µg mL^{-1}, was described according to the Stern-Volmer relationship:[11]

$$\frac{I_f^0}{I_f} = 1 + k_q\tau_0 \cdot [Q\text{–}CD] \qquad (1)$$

Where I_f is the fluorescence intensity, I_f^0 the fluorescence of 5 µg mL^{-1} Q-CD and the product $k_q\tau_0$ is the quenching constant, which, under our experimental conditions, resulted of $3.44 \pm 0.3 \times 10^{-2}$ µg^{-1} mL. Moreover, fluorescence lifetime of Q-CD was determined by time-resolved analysis using a photoncounting spectrometer. Experimetal data were fitted with an exponential decay, characterized by a time constant of $\tau_0 = 3.10 \pm 0.05$ ns. From the above reported results, the quenching rate constant, k_q, was calculated (1.1×10^7 µg mL^{-1} s^{-1}).

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Table S1. Electrochemical parameters, as determined by cyclic voltammetry measurements, of carbon paste electrodes modified with different complexes of carbon dots and SAMNs in the presence 0.5 mM hydroquinone and 0.5 mM benzoquinone.

Anodic peak current (I_{pa}), cathodic peak current (I_{pc}) and peak potential difference (ΔE_p) were obtained from CV curves acquired in 0.1 M potassium phosphate, pH 7.0, containing 1.5 mM hydroquinone and 1.5 mM benzoquinone. Measurements were carried out at a scan rate of 5 mV s^{-1}.

Electrode modifier	**Δi_{pp} (µA)**	**i_a/i_c**	**ΔE_{pp} (V)**
None	16.6	1.24	0.109
SAMN	13.7	1.71	0.109
SAMN@GA-CD	18.4	1.48	0.137
GA-CD@SAMN	14.9	2.00	0.105
SAMN@PEG-GD	15.7	1.73	0.119
PEG-GD@SAMN	15.9	1.63	0.197
SAMNs@Q-CD	6.9	1.26	0.066
Q-CD@SAMN	6.1	1.38	0.066

Table S2. Analytical parameters obtained by chronoamperometry of carbon paste electrodes modified with different hybrids of carbon dots (CDs) and SAMNs on hydroquinone oxidation. Experiments were carried out in 0.1 M potassium phosphate, pH 7.0, 50 mM KCl as supporting electrolyte.

Electrode modifier	**Sensitivity ($nA\ \mu M^{-1}cm^{-2}$)**	**LOD (µM)**	**Linearity range (µM)**
None	46.36	2.34	5-25
SAMN	59.52	7.86	20-100
SAMN@GA-CD	nd	nd	nd
GA-CD@SAMN	nd	nd	nd
SAMN@PEG-GD	36.41	15.83	5-25
PEG-GD@SAMN	63.73	2.01	5-25
SAMN@Q-CD	35.85	23.32	20-100
Q-CD@SAMN	81.51	7.00	5-25

Table S3. Values of the Mössbauer hyperfine parameters, derived from the least-square fitting of the Mössbauer spectra of the Q-CD@SAMN sample, where T is the temperature of the measurement, B_{ext} is the induction of the external magnetic field, δ is the isomer shift, ΔE_Q is the quadrupole splitting, B_{hf} is the hyperfine magnetic field, B_{eff} is effective hyperfine magnetic field (i.e., a vector sum of B_{hf} and B_{ext}), and RA is the relative spectral area of individual spectral components identified during fitting. * The average hyperfine magnetic field, derived from the B_{hf} distribution (see inset in Fig. S6).

T (K)	B_{ext} (T)	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	B_{hf} ± 0.3 (T)	B_{eff} ± 0.3 (T)	RA ± 1 (%)	Assignment
300	0	Sextet	0.32	– 0.01	45.2*	------	100	γ-Fe_2O_3 T-, O-sites
5	5	Sextet	0.38	0.00	-------	53.9	37	γ-Fe_2O_3 T-sites
		Sextet	0.50	0.00	-------	46.8	63	γ-Fe_2O_3 O-sites

Table S4. Comparison of previously published electrochemical methods applied for chlorogenic acid determination.

working electrode	modifiers	analytical technique	sensitivity	LOD	linear range	refs.
CPE	Q-CD@SAMN	LSV	15.73 µC µM^{-1} cm^{-2}	26.4 µM	0.1 mM – 1 mM	This work
CPE	tetranuclear copper	SWV	0.44 µA µM^{-1}	0.8 µM	5 µM – 145 µM	12
CPE	defective mesoporous carbon, BMIM-PF$_6$	SWV	92.86 µA µM^{-1} cm^{-2}	0.01 µM	0.02 µM – 2.5 µM	13
GCE	aminosulfonic acid	CV	20.02 µA µM^{-1} cm^{-2}	0.04 µM	0.4 µM – 12 µM	14
GCE	chitosan, MWCNT	DPV	2285 µA µM^{-1} cm^{-2} 6.37 µA µM^{-1} cm^{-2}	11.7 nM	20 nM – 100 nM 100 nM – 225 nM	15
GCE	metal–organic frameworks, titanium dioxide	DPV	0.55 µA µM^{-1} 0.18 µA µM^{-1}	7 nM	10 nM – 1 µM 1 µM – 15 µM	16
GCE	vinyltrimethoxysilane, MWCNT, siloxane	DPV	0.054 µA µM^{-1}	32 nM	0.08 µM – 100 µM	17
GCE	MWCNT	DPV	2389 µA µM^{-1} cm^{-2}	0.21 µM	1 µM – 1 mM	18
PGE	none	DPV	not specified	71.4 nM	0.1 µM – 500 µM	19
PtE	none	CA	0.026 µA µM^{-1} cm^{-2}	19.2 µM	2.82 µM – 282 µM	20
BDDE	none	SW-AdSV	0.43 µA µM^{-1} cm^{-2}	1.79 uM	14 µM – 127 µM	21

Notes:
AdSV: adsorptive stripping voltammetry; BDDE: boron doped diamond electrodes; CA: chronoamperometry; CPE: carbon paste electrode; CV: cyclic voltammetry; DPV: differential pulse voltammetry; LOD: limit of detection; SWV: square wave voltammetry; MWCNT: multi walled carbon nanotubes; PGE: pencil graphite electrode; PtE: platinum electrode; SWCNT: single walled carbon nanotubes.

Figure S1. Fluorescence emission spectrum of Q-CDs. Q-CDs (15 µg mL^{-1}) were dissolved in water. Excitation wavelength was at 375 nm.

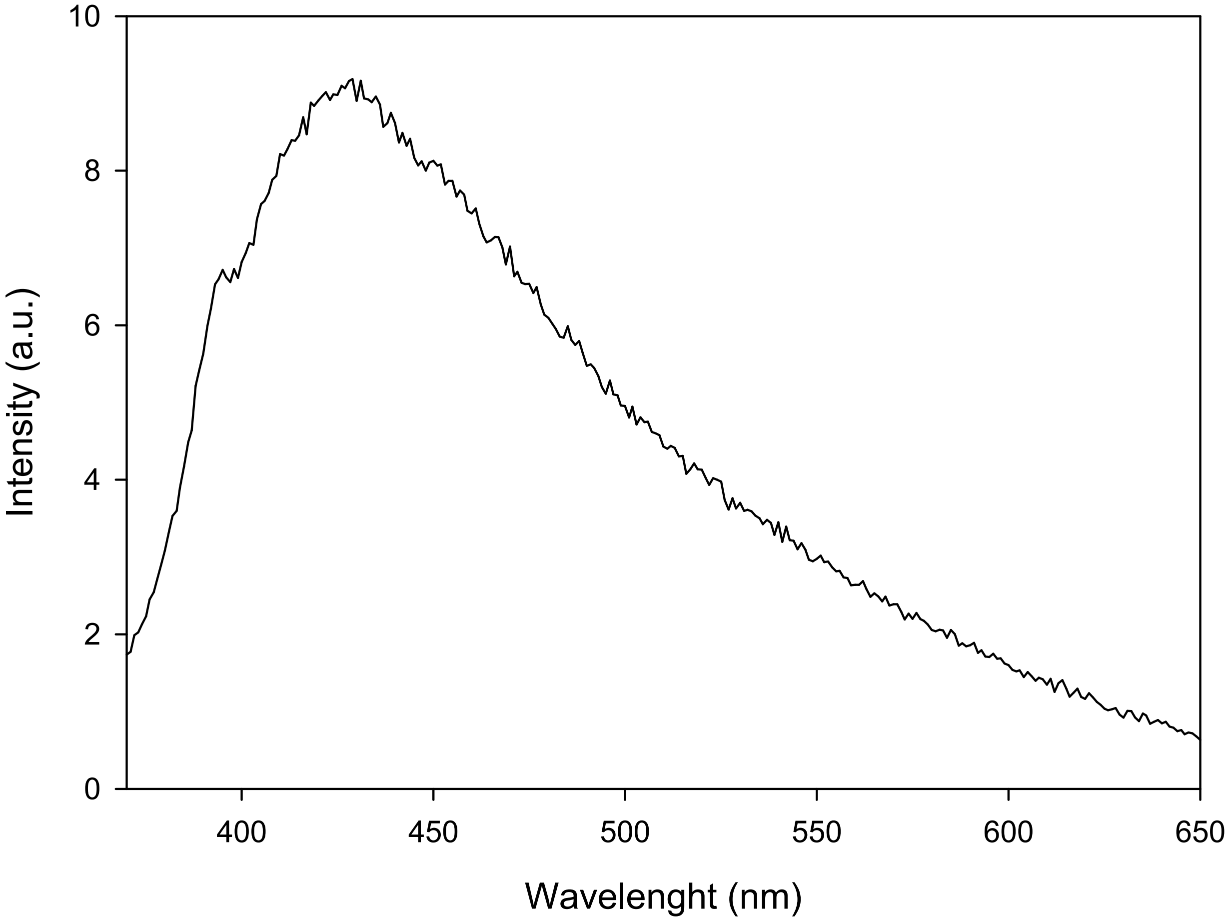

Figure S2. Dependence of fluorescence intensity on Q-CD concentration (3-30-50-70-100-200-300-500-700-1000 μg ml^{-1}). Q-CDs were dissolved in water. Excitation wavelength was at 375 nm.

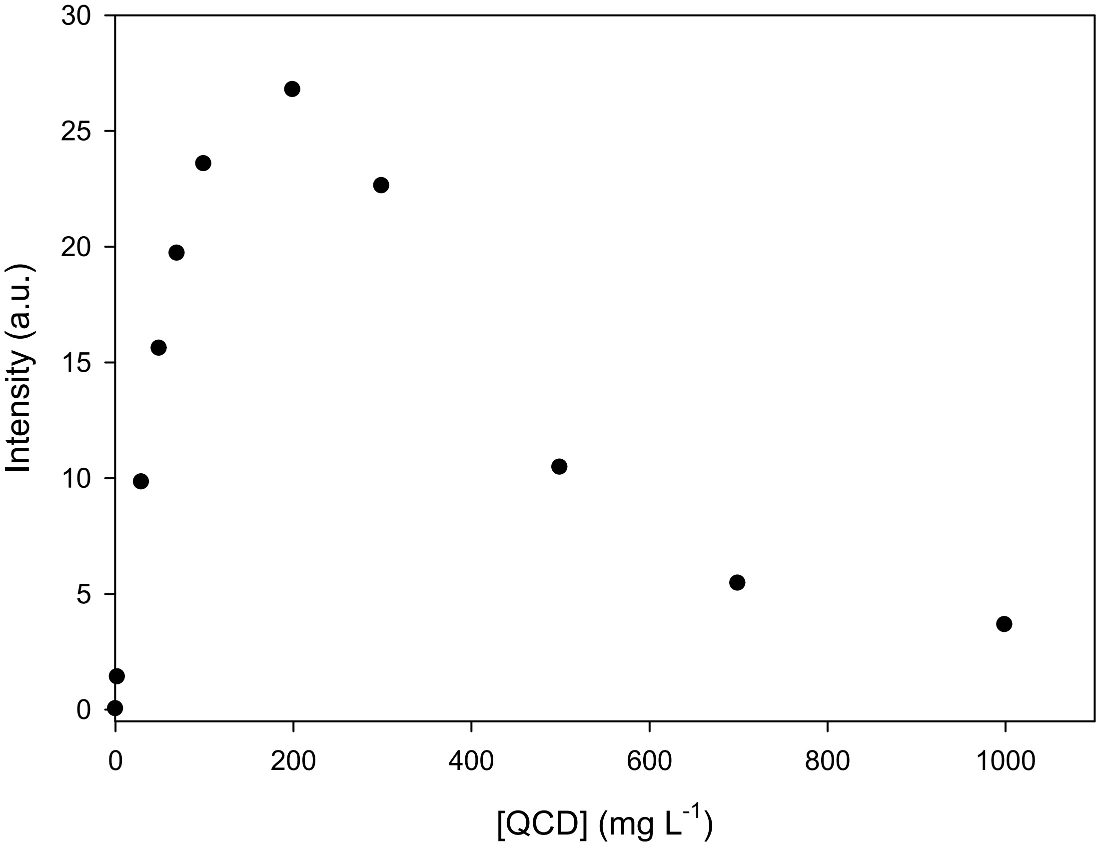

Figure S3. Cyclic voltammograms of electrodes modified with different hybrids, in the presence of $Fe(CN)_6^{3-/4-}$ redox couple, compared with CPE and SAMN/CPE.

All experiments were performed in 0.1 M PBS (pH 7.0) in the presence of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ at the scan rate of 50 mV sec^{-1}. Carbon paste electrode (solid black line) was compare to SAMN/CPE (solid red line), SAMN@GA-CD (solid gray line), GA-CD@SAMN (dashed gray line), SAMN@PEG-GD (solid blue line), PEG-GD@SAMN (dashed blue line), SAMN@Q-CD (solid green line), Q-CD@SAMN (dashed green line).

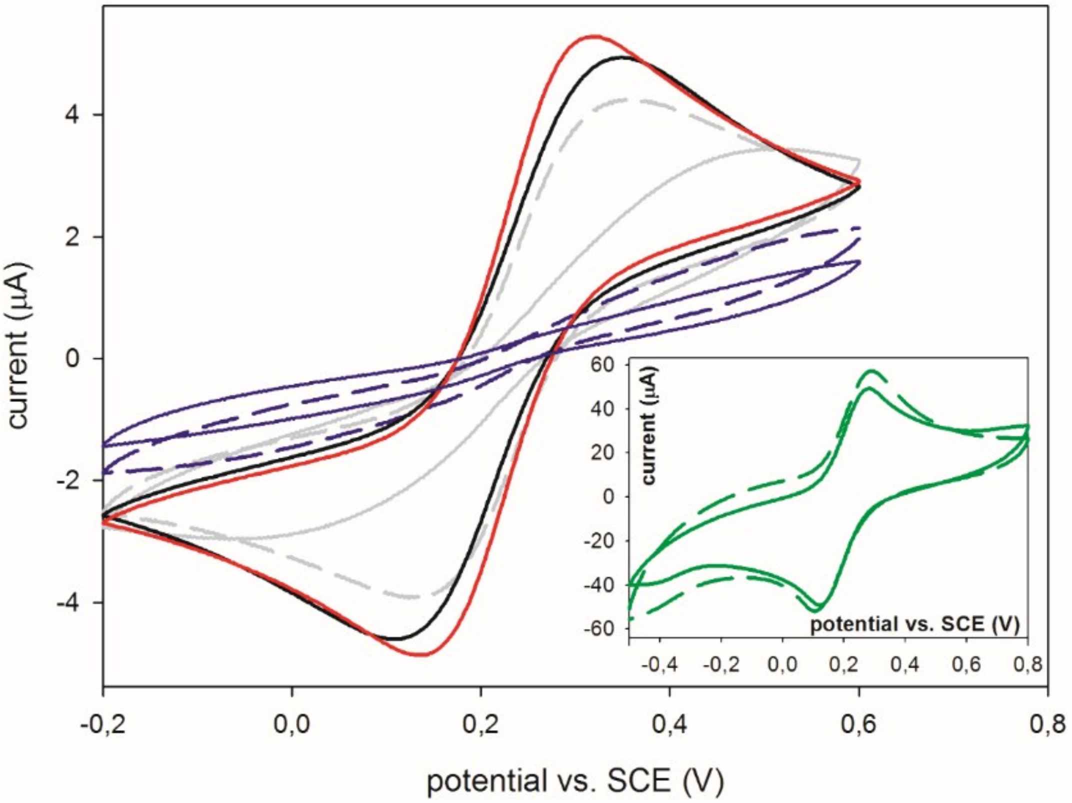

Figure S3. Cyclic voltammograms of electrodes modified with different hybrids compared with CPE and SAMN/CPE in the presence of bare buffer only (panel A), 3 mM H_2O_2 (panel B), 3 mM NADH (panel C) and 1.5 mM HQ and 1.5 mM BQ (panel D).

All experiments were performed in 0.1 M phosphate buffer solution, pH 7.0, with 50 mM KCl as supporting electrolyte, at the scan rate of 20 mV sec^{-1}. Carbon paste electrode (solid black line) was compare to SAMN/CPE (solid red line), SAMN@GA-CD (solid gray line), GA-CD@SAMN (dashed gray line), SAMN@PEG-GD (solid blue line), PEG-GD@SAMN (dashed blue line), SAMN@Q-CD (solid green line), Q-CD@SAMN (dashed green line).

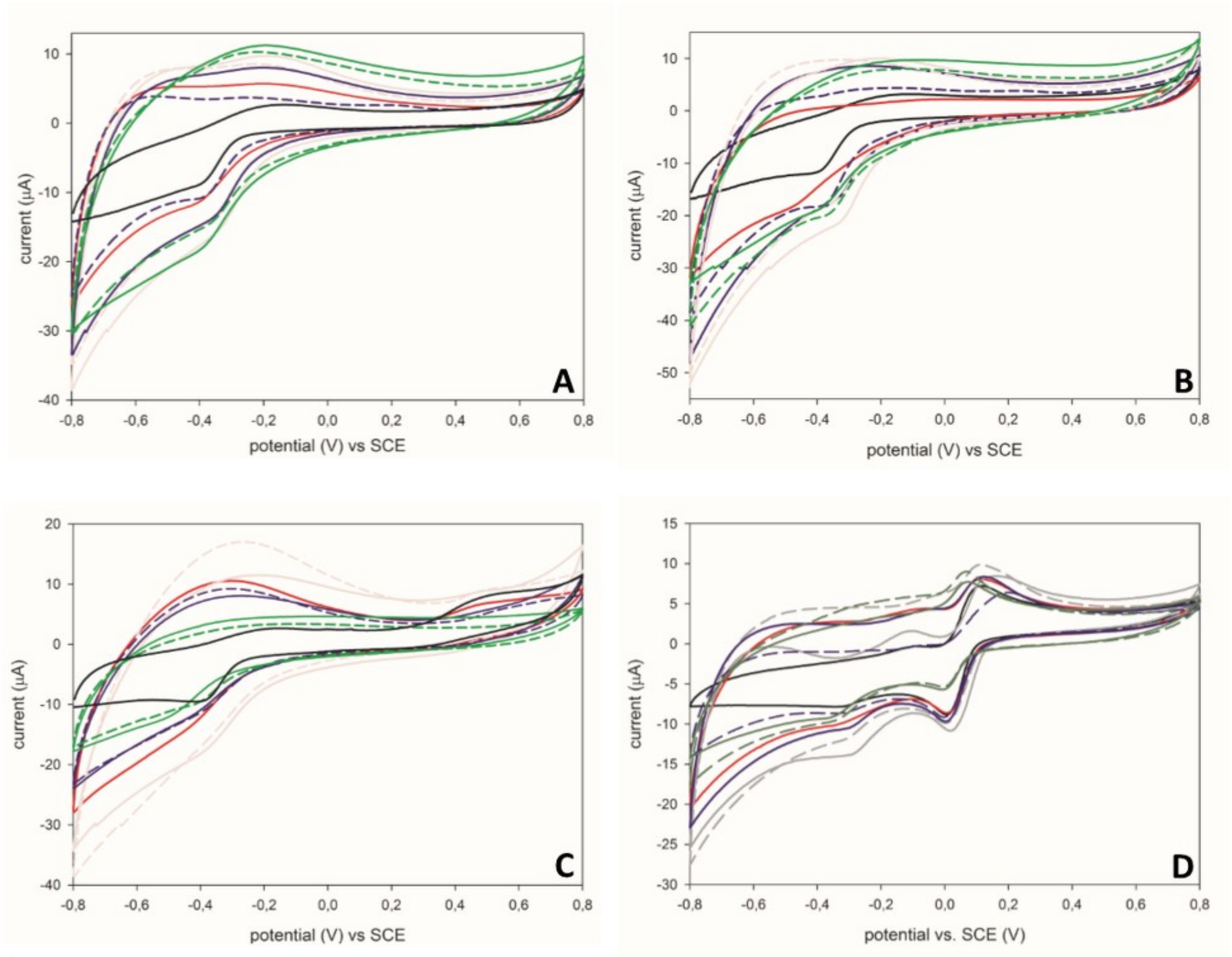

Figure S5. Cyclic voltammograms of electrodes modified with SAMN@Q-CD and Q-CD@SAMN hybrids in the presence of 1.5 mM HQ and 1.5 mM BQ in 0.1 M phosphate buffer solution, pH 7.0, with 50 mM KCl as supporting electrolyte. Measurements were carried out at different scan rates (5, 10, 20, 50, 100, 200 mV sec^{-1}, a – f). Working electrodes: (A) SAMN@Q-CD/CPE, (B) Q-CD@SAMN/CPE. Insert of A and B depict the linear relationship of v$^{1/2}$ on the anodic and cathodic peak currents of HQ/BQ.

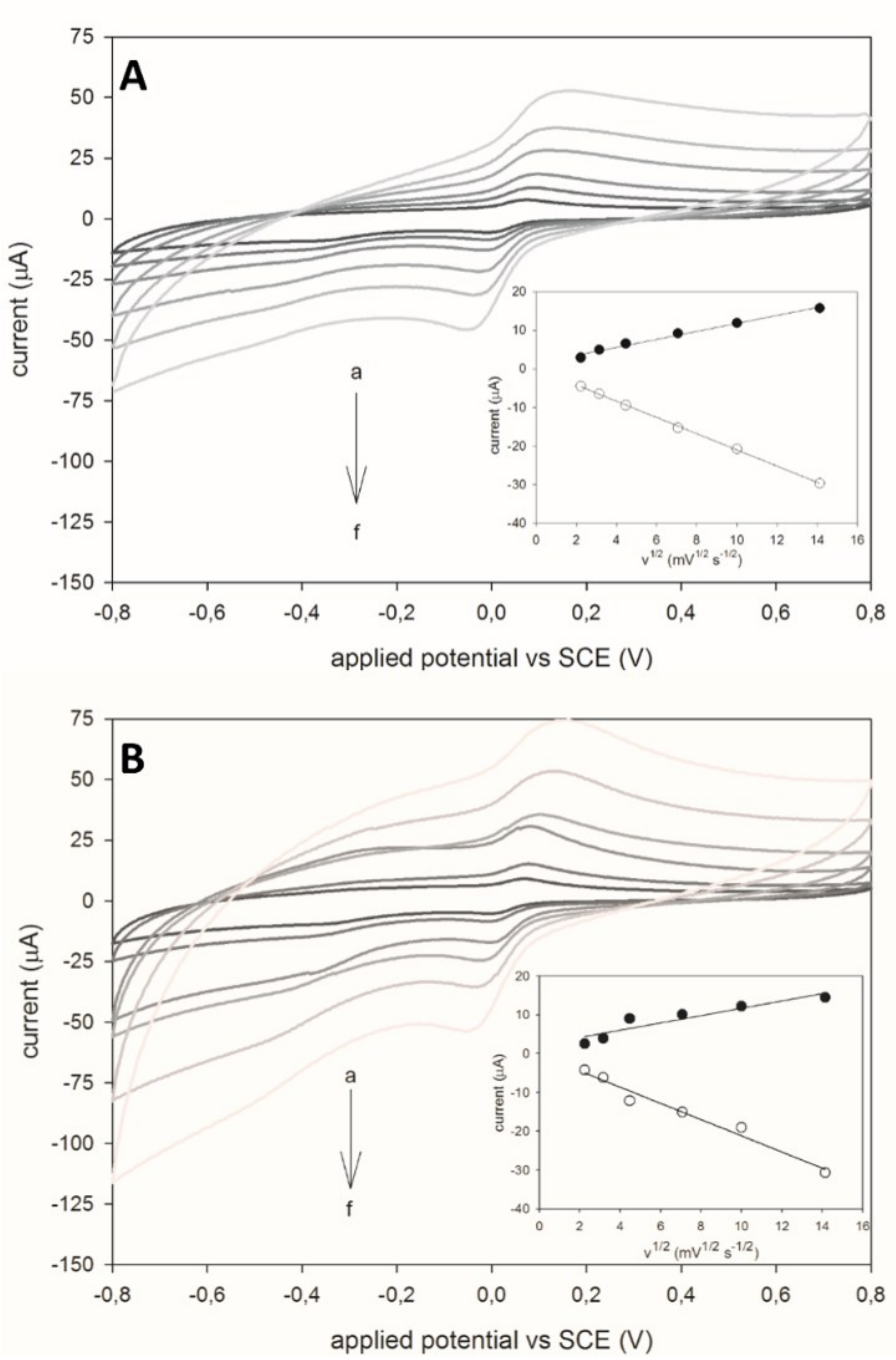

Figure S6. ^{57}Fe Mössbauer spectra of the Q-CD@SAMN sample, recorded at room temperature and without an external magnetic field.

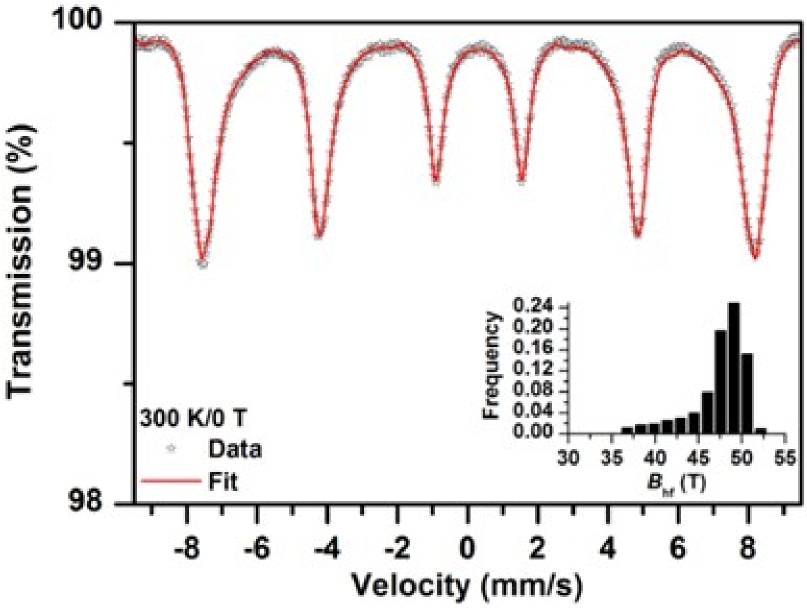

Figure S7. (a) 5 K and 300 K hysteresis loops and (b) ZFC/FC magnetization curves measured for the Q-CD@SAMN hybrid.

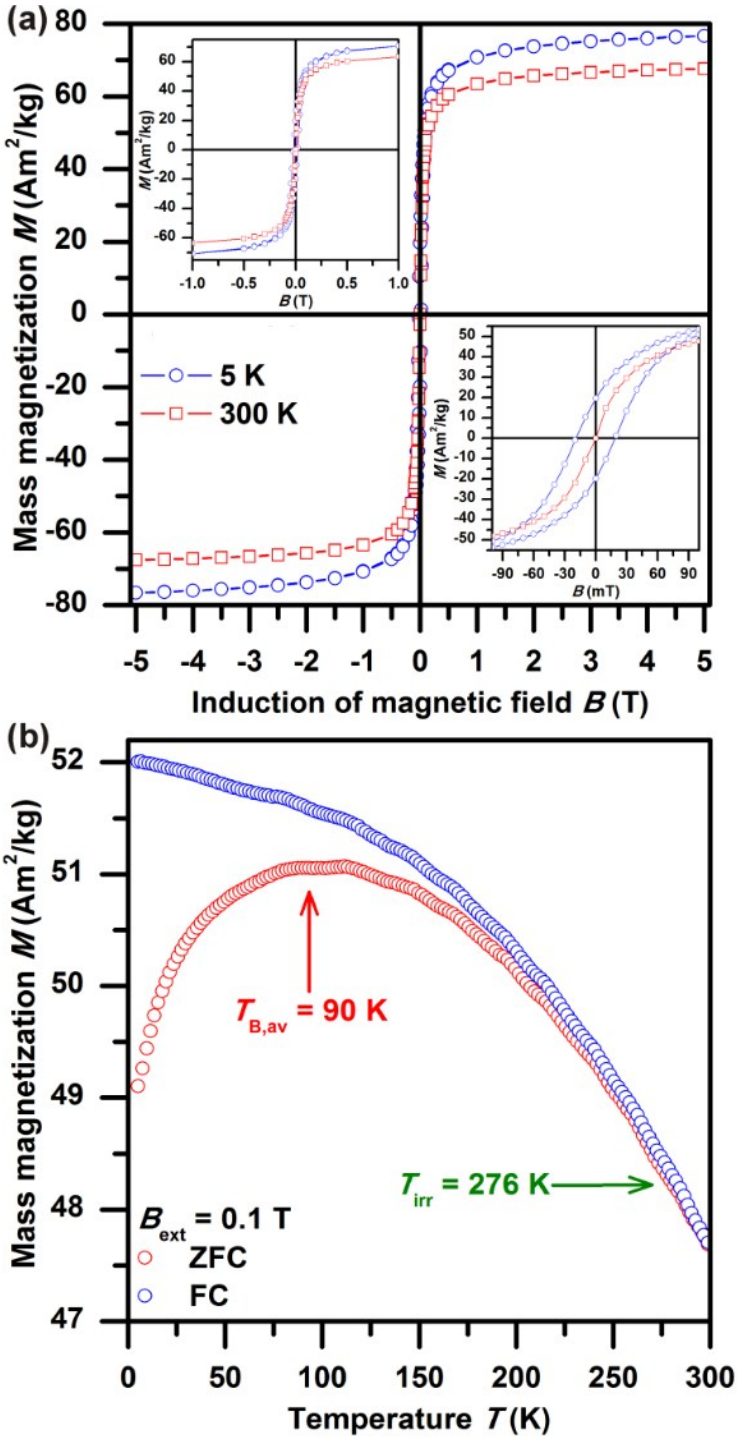

Figure S8. Schematic drawing of the electrochemical flow cell (not in scale). The cell is equipped with a planar carbon working. Between the two half cells (A and B) a channel was defined by a teflon spacer.