

Supporting information

Oleylamine-Stabilized Gold Nanostructures for Bioelectronic Assembly. Direct Electrochemistry of Cytochrome *c*.

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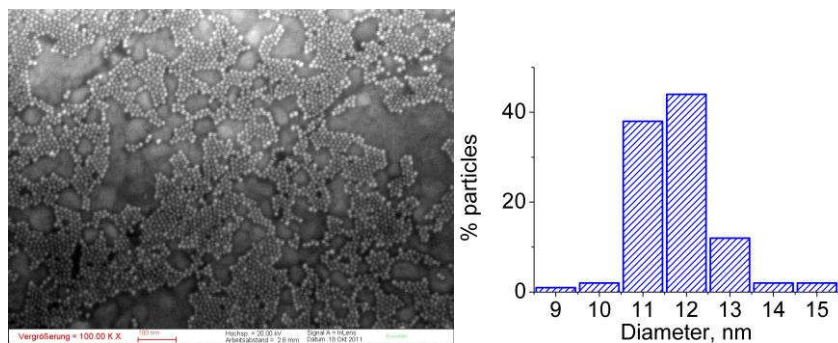


Figure S1. SEM image of Au OANPs produced by oleylamine synthesis and dispersed on a gold surface. Histogram of the particles diameter distribution.

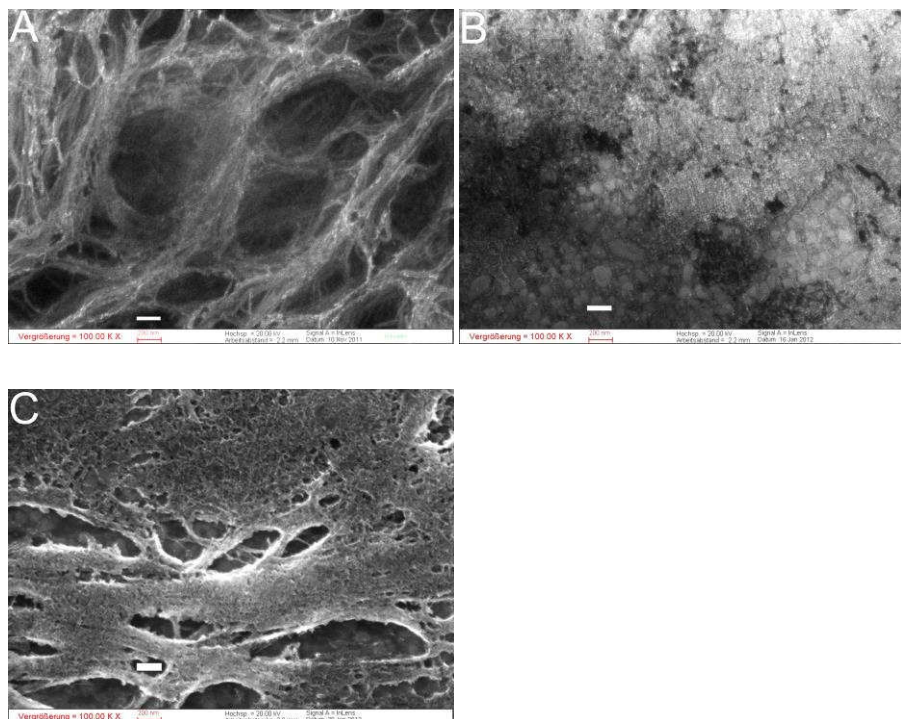


Figure S2. SEM images of (A) bundles of gold NWs produced by oleylamine synthesis and dispersed on a gold surface. The NWs were deposited from the hexane solutions, left to adhere overnight and washed three times with hexane. (B) As (A) but the solution of the NWs in hexane was subjected to US for 10 min before being deposited on the flat gold surface. (C) NWs after exposure to OP for 20 min (C). Scale bars are 200 nm.

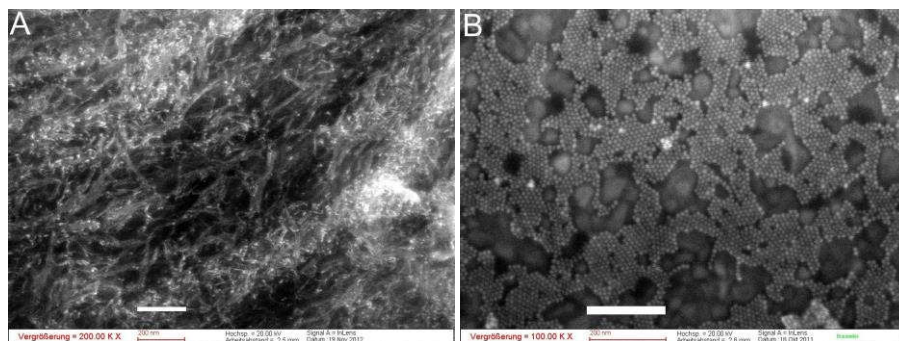


Figure S3. SEMs of OANW samples treated in hexane only (A), in ethanol (B). Scale bars are 200 nm.

Electrochemistry of cyt *c*. Figure S4 demonstrates the stability of the electrochemically active cyt *c* electrostatically adsorbed on the thiol-functionalized electrodes during repetitive electrochemical cycles in the low ionic strength buffer. No changes in the voltammetric response were observed.

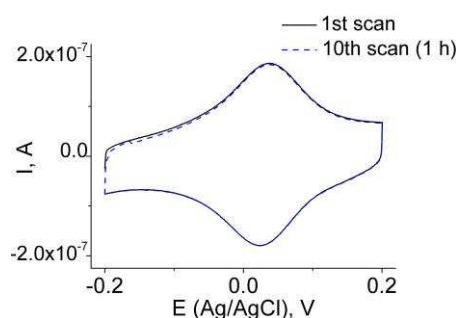


Figure S4. CVs of cyt *c* on Au-NPs-SAM-cyt *c* electrodes: first scan (solid line), tenth scan (dotted green line). The time interval between the first and the tenth scan was 1 h. Other conditions: scan rate - 50 mV s⁻¹, measurements were performed in 4.4 mM phosphate buffer, pH 7.0.

Comparison of CVs of the SAM-modified electrodes without cyt *c* and with immobilized cyt *c* (Figure S5) shows that the electrodes without immobilized cyt *c* demonstrate mainly capacitive background currents, which increase with increasing the effective surface area of the electrodes (due to the immobilized nanostructures). Thus, the redox peaks, which are observed for the electrodes with immobilized cyt *c* can be assigned to the reduction and oxidation of the heme group of cyt *c*.

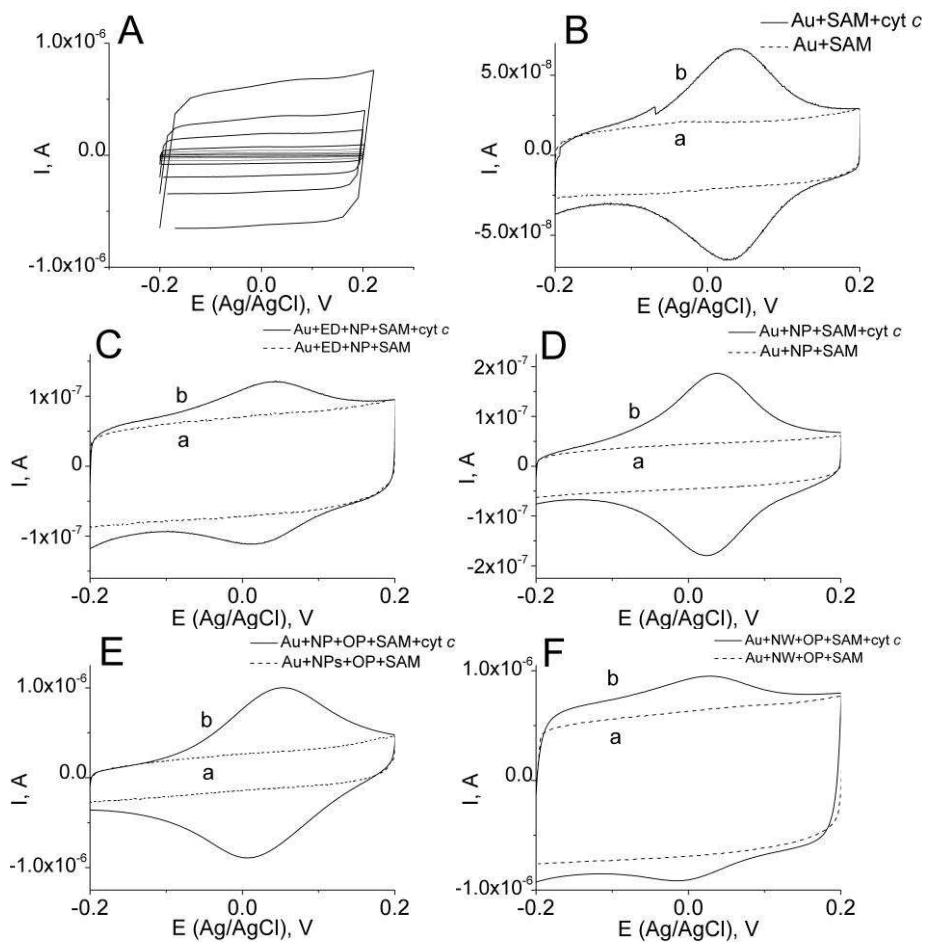


Figure 5. CVs of: (A) flat Au-SAM electrode without immobilized cyt c , scan rate: 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, and 2 V s^{-1} from inner to outer curve. (B) flat Au-SAM (line a) and Au-SAM-cyt c (line b) electrodes. (C) Au-ED-NP-SAM (a) and Au-ED-NP-SAM-cyt c (b) electrodes, (D) Au-NP-SAM (a) and Au-NP-SAM-cyt c (b) electrodes, (E) Au-NP-OP-SAM (a) and Au-NP-OP-SAM-cyt c (b) electrodes, (F) Au-NW-OP-SAM (a) and Au-NW-OP-SAM-cyt c (b) electrodes.

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(b) electrodes. Other conditions: scan rate - 50 mV s⁻¹ (B-F), measurements were performed in 4.4 mM phosphate buffer, pH 7.0.

XPS analysis. Control sample was OANWs adhering to the Si/SiO₂ surface and washed three times with hexane. OANW-thiol sample was further treated with 5 mM mercaptohexanol (MH) in hexane for 30 min and washed with hexane. The samples were subjected to the XPS analysis (Table S1). Appearance of the lower energy sulfur peak at about 163 eV, indicates the formation of the sulfur gold bond.

Table S1. XPS analysis of OANW samples.

OANW on Si/SiO ₂				OANW-MH on Si/SiO ₂			
peak	E _B , eV	Conc.	At%	peak	E _B , eV	Conc.	At%
O-Au, O+C O+Si	531.41	4.32	20.71	O-Au,	531.31	3.09	25.62
	532.74	16.39		O+C	532.65	22.53	
				O+Si			
C-C, C-H	285.06	49.19	67.14	C-C, C-H	285.03	55.82	55.82
C+O	285.68	17.95					
S2p	168.38	0	0	S-1	163.65	1.78	2.61
				S-O	168.26	0.83	
Au+0, Au-1, Au-O	84.26	0.13	0.18	Au+1	84.87	0.11	0.11
	85.76	0.05					
Si-O	103.52	10.54	10.54	Si+?	101.88	15.83	15.83
				Si-O	103.49		

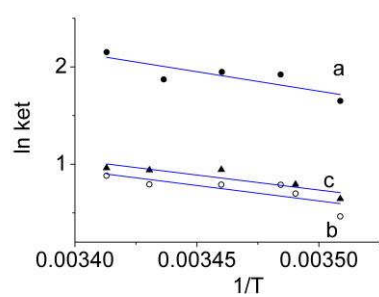


Figure S6. Arrhenius plots for electron transfer in cyt *c* immobilized electrodes: Au/MHA-ME/cyt *c* (a), Au/OANP-OP/MHA-ME/cyt *c* (b), Au/OANW-OP/MHA-ME/cyt *c* (c).