Supporting information

Time-Resolved Selective Electrochemical Sensing of Carbon

Particles

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Figure S1 a schematic diagram of the experimental setup.

Materials	Zeta potential (mV)
ZnO	-10.7 ± 1.0
Cr_2O_3	-1.2±0.2
NiO	-12.3±1.5
SiO ₂	-10.3 ± 1.2

Table S1a. ζ potentials of other particles tested at a concentration of 10 μ M in 0.2 M phosphate buffer

solution (pH 7.0)

Table S1b. Comparison of ζ potentials of representative particulate matters

Particulate matters	Solvents and electrolytes	ζ potential (mV)	reference
Zinc oxide	PBS (pH=7.4)	-22.3 ± 1.3 mV to -21.7 ± 1.1 mV	Nanotechnology, 2009, 20, 115101– 115107
Silica particle	H_2O	-25.6 mV	Adv. Nano Res., 2015, 3, 243–255
Nickel hydroxide powder	Isopropyl alcohol	-5 mV	J. Power Sources, 2009, 186, 557–564
Nickel oxide	Glucose solution (pH=7.0)	~-30 mV	Mat. Sci. Semicon. Proc., 2013, 16, 1747–1752
Chromium (III) oxide	Sodium chloride /H ₂ O	~-10 mV	Environ. Sci. Pollut. Res, 2013, 20, 3657– 3669
Carbon black	Organic solvents and H ₂ O	+9.2 to -124.9 mV Depends on solvents and size. In water, +29.4 mV	Carbon, 2007, 45, 2806–2809
Carbon Black	0.2 M phosphate buffer	-11.1±1.6 mV (pH 6), -13.5±2.2 mV (pH 7); -12±1.9 mV (pH 8)	This work
Oxide particles	0.2 M phosphate buffer, pH 7.0	ZnO (-10.7±1.0) mV; Cr ₂ O ₃ (-1.2±0.2) mV, NiO (-12.3±1.5) mV; SiO ₂ (-10.3±1.2) mV	This work

Electrode	Electrolyte	PZC Value	Reference
Au polycrystalline	0.1 M sodium fluoride	-0.094 V vs. SCE	Electrochim. Acta, 1992, 37(1), 139–141.
Au (100)	0.005 M potassium sulfate	0.00 V vs. SCE	J. Electroanal. Chem., 1995, 386, 1–10
Polycrystalline Au	0.10 M perchloric acid	+0.128± 0.010 V (vs. SHE)	J. Phys. Chem. B, 2004, 108, 48, 18391–18394
Polycrystalline Au	0.10 M perchloric acid/40% heptane	+0.15 V (vs. SHE)	J. Phys. Chem. B, 2002, 106, 23, 5810–5813
Au (111) electrode	0.5 M perchloric acid	+0.3 V (vs. RHE)	J. Phys. Chem. 1996, 100, 10664–10672
Au (111) electrode	0.10 M perchloric acid	+0.3±0.04 V (Ag/AgCl)	J. Electroanal. Chem., 1996, 414, 85–89
Au polycrystalline	0.2 M phosphate solution	+0.14±0.005 V (vs. Ag/AgCl, 1 M KCl).	This work

Table S2. Comparison of representative PZC value of gold electrodes



Figure S2. ζ potentials of carbon black particle suspension at varying concentrations at constant pH of 7.0 in 0.2 M phosphate buffer solution.



Figure S3. The current transients recorded for carbon black particles under different bias potentials.



Figure S4. Cyclic voltammogram of gold microelectrode in 0.2 M phosphate buffer (pH7.0). At potential sweep rate of 50 mV s⁻¹.



Figure S5. Chronoamperometric curves for particle collisions by setting a bias potential at -0.2 V at gold electrode in pH7.0 phosphate buffer solution containing 40 μ M of carbon particles.



Figure S6. (a) CVs comparison of microelectrode before collision events and after collision events in 0.1 M KNO₃ containing 1mM K₃Fe(CN)₆. Scan rate:20 mV s⁻¹. (b) a collision experiment performed in 10 μ M carbon suspension solution by holding constant potential at +0.4 V. The duration time was 600 s.



Figure S7. Chronoamperometric curves for particle collisions by setting a biased potential at +0.2 V (a) and +0.8 V (c) at gold electrode in pH7.0 phosphate buffer solution containing different concentrations of carbon particles from 2.5 to 40 μ M. The linear relationship between the observed collision spikes and the concentrations of carbon particle by setting constant potential at +0.2 V (b) and +0.8 V (d).



Figure S8. The comparison of LOD and LOQ at different biased potentials.



Figure S9a. Overall plots of raw data & majority of spikes as marked.



Figure S9b. Spike magnitude distribution.

Table S3. The spike magnitude from the raw data are summarized.

Applied	Number of	Spiking rate (Hz)	Average spike magnitude (mA
potential	spikes		cm ⁻²)
+0.2V	46	0.0788	0.1992
+0.4V	54	0.1080	0.2033
+0.8V	69	0.1380	0.2084

Note: In process of magnitude of spike, the following strategies have been adopted. According to raw data curves, majority points were in equilibrium status except the first 1/6 of +0.4 V and +0.8 V data points. For convenience, the last 5/6 points were included for +0.4 V and +0.8 V when detecting the spikes. Any points satisfying 2 criteria can be defined as a "spike", including (1) it is on the peak of a tip (2) the magnitude > +0.10 mA cm⁻² Accordingly 3 criteria were used to detect the peak points: (1) the current density is larger than the value of its left point; (2) the current density is larger than the value of its left point; (2) the current density is larger than the value of the local 30 points (except itself) is larger than +0.10 V. Once a point is defined as a spike, the average of the values of the left 15 points and the right 15 points can be calculated. The magnitude of this spike can be evaluated by the difference of the point voltage value and the average value just calculated.



Figure S10. Comparison of chronoamperometric curves for particle collisions by setting different potential (a) -0.2 V, (b) +0.2 V, (c) +0.4 V and (d) +0.8 V at gold microelectrode in 0.2 M phosphate buffer solution (pH7.0) with and without stirring.



Figure S11. Typical steady-state response of the microelectrode on successive injection of 0.5 mM SiO₂, 0.5 mM ZnO, 0.5 mM NiO, 0.5 mM Cr₂O₃ and 10 μ M carbon particles. Biased potential: + 0.2 V vs.

Ag/AgCl.



Figure S12. Nyquist plots for the solutions in the presence of SiO₂, NiO, ZnO, Cr₂O₃, and carbon particles in 0.2 M phosphate buffer (pH 7.0). All the spectra were obtained at the particle concentration of 10 μ M.

Sample	Serial Resistance (R_s/Ω)
SiO ₂	1008.6±9.5
ZnO	968.7±5.5
NiO	979.7±6.3
Cr_2O_3	1063.2±12.2
Carbon	916.5±3.44

Table S4 The R_s value of different particles suspension solution



Figure S13. Chronoamperometry current transients in the presence of (a) SiO₂, (b) ZnO, (c) NiO and (d) Cr_2O_3 particles. Electrode potential was held at +0.4 V and the concentrations of all particles were 10 μ M. The supporting electrolyte was 0.2 M phosphate buffer solution (pH7.0). Stirring rates were 300 rpm. The sampling rates were 50 ms.



Figure S14. Chronoamperometry current transients in the presence of (a) SiO₂, (b) ZnO, (c) NiO and (d) Cr_2O_3 particles. Electrode potential was held at +0.4 V and the concentrations of all particles were 10 μ M. The supporting electrolyte was 0.2 M phosphate buffer solution (pH7.0). Stirring rates were 600 rpm. The sampling rates were 50 ms.



Figure S15. Chronoamperometric curves tested (a) in absence of polystyrene and (b) in the presence of 10 μ M (~4 g L⁻¹) polystyrene in pH7.0 phosphate buffer solution by setting a biased potential at +0.4 V; The chronoamperometric curves tested at different biased potentials of (c) -0.2 V and (d)+0.8 V in pH7.0 phosphate buffer solution containing 10 μ M (~4 g L⁻¹) polystyrene. Stirring rates in these experiments were 300 rpm. The sampling rates were 50 ms.