Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for:

A tunable nanopore sensor for the detection of metal ions using translocation velocity and biphasic pulses.

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SI1. Schematic of Pulse data

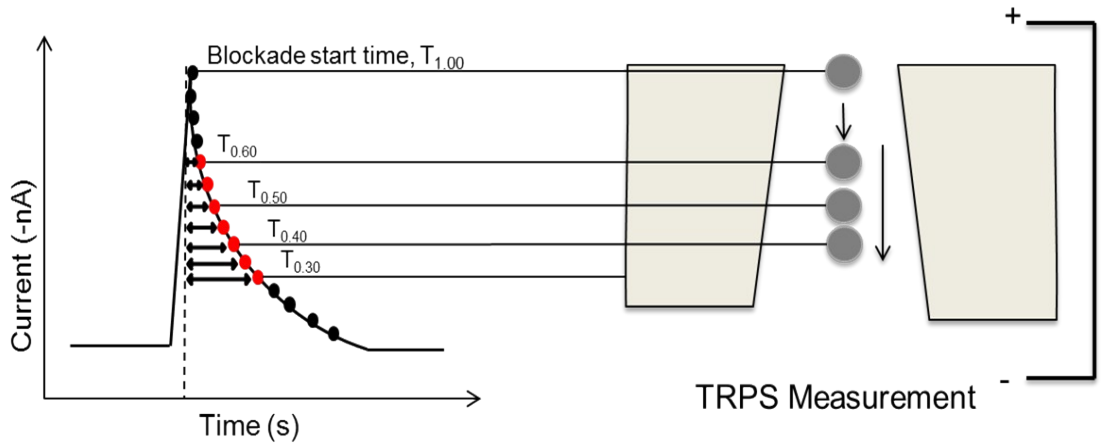

Figure SI1. *Schematic of the blockade times, $T_{0.3}$, $T_{0.4}$, $T_{0.5}$…, and the position of the particle in the pore (not to scale). Plotting 1/T gives the particles velocity through the pore.*

SI2. Silica NPs Analysis

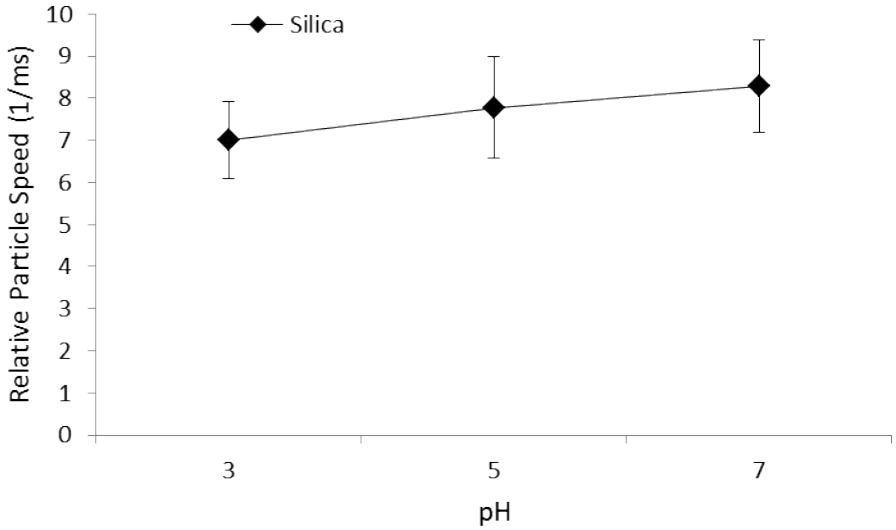

Figure S2. *Change in silica nanoparticle speed with changing pH, in 2mM KCl. Analysed on a NP200 pore, 47 mm stretch, 1.60V.*

SI3. IR Spectrum

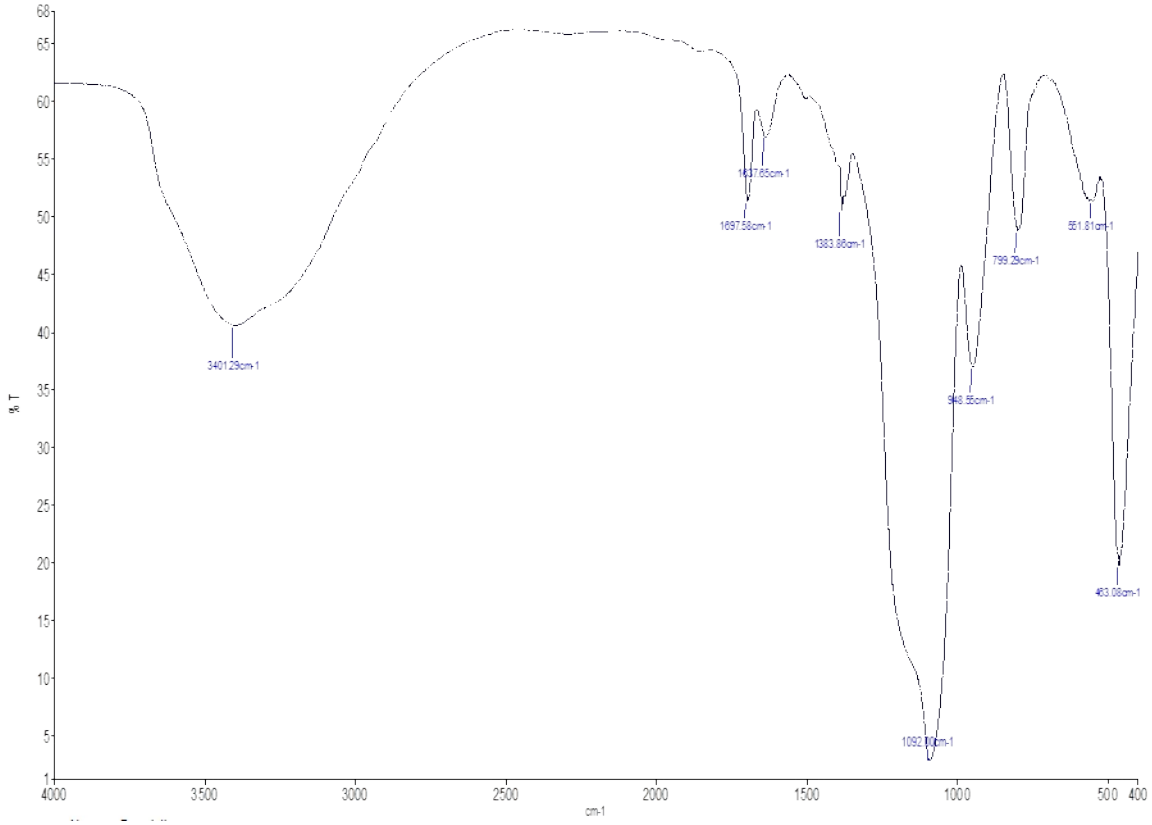

Figure S3. *IR spectrum of APTES modified silica nanoparticle, primary amine stretch at 1635 cm^{-1}.*

SI4. Nanopore Current Rectification

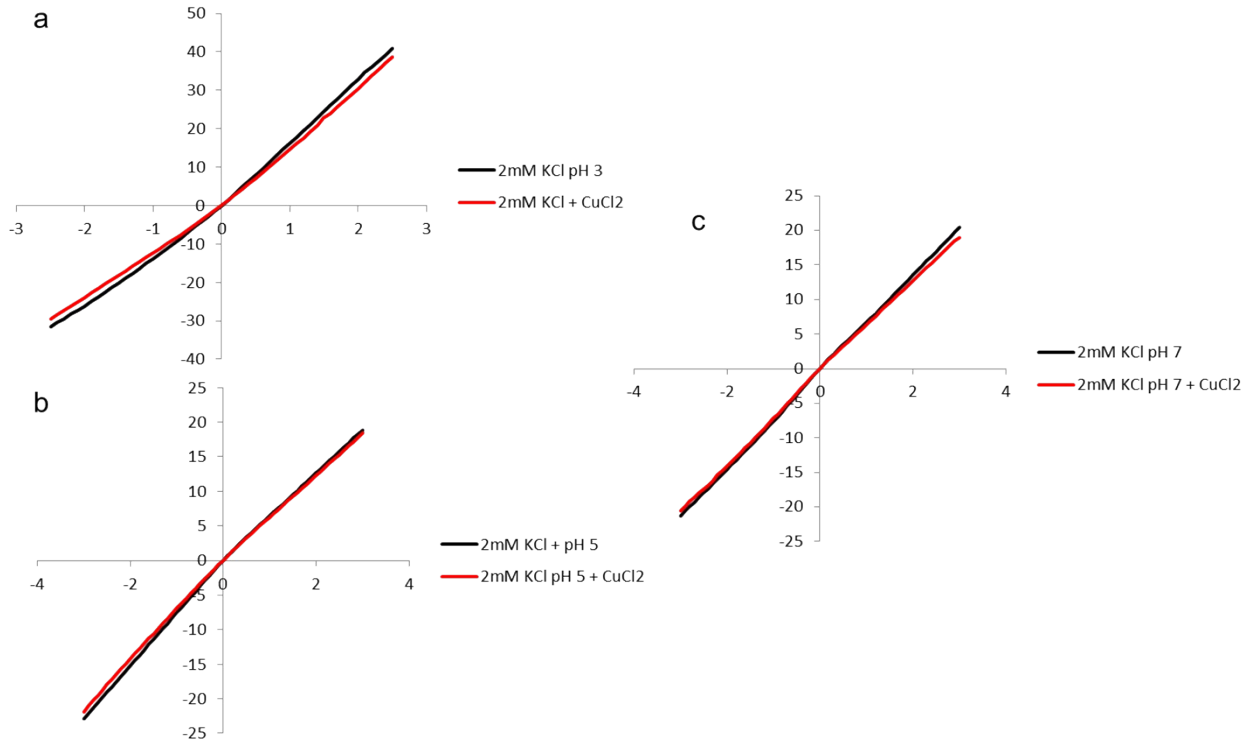

Figure S4. *Current-Voltage curves for 2mM KCl at a) pH 3, b) pH 5 and c) pH 7. The current was recorded again with 15.5 µM $CuCl_2$ present. Recorded on a NP00 pore, 47.11 mm stretch.*

SI5. Modified Silica Copper Incubation - pH

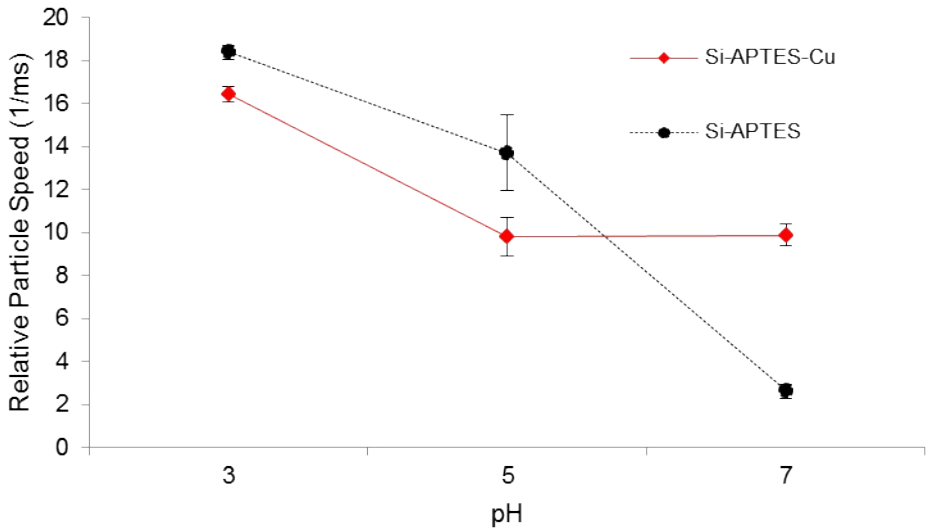

Figure S5. *The velocities of Si-APTES particles compared to those with copper bound as a function of pH. Samples analysed in 2mM KCl on a NP200 pore, 47 mm stretch, -3.18 V.*

SI6. ICP-OES Analysis in pH 7 solution

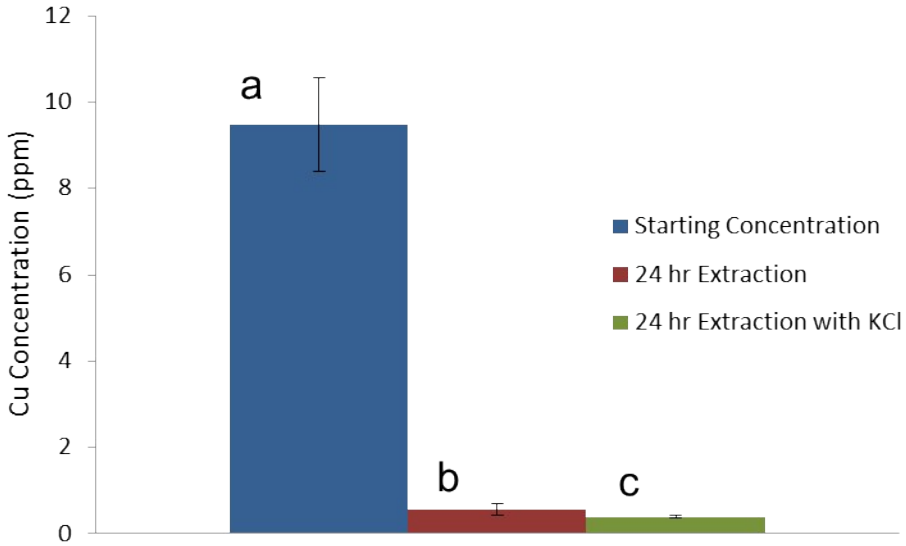

Figure S6. *Concentration of Cu a) before Si-APTES particles were incubated, b) after 24 hr incubation with the particles and c) after 24 hr incubation with the particles in the presence of 2mM KCl. Error bars represent one standard deviation from the mean of three repeats.*

SI7. SEM Images

Figure S7. *SEM image of Silica Nanoparticles.*

SI8. Size Distribution

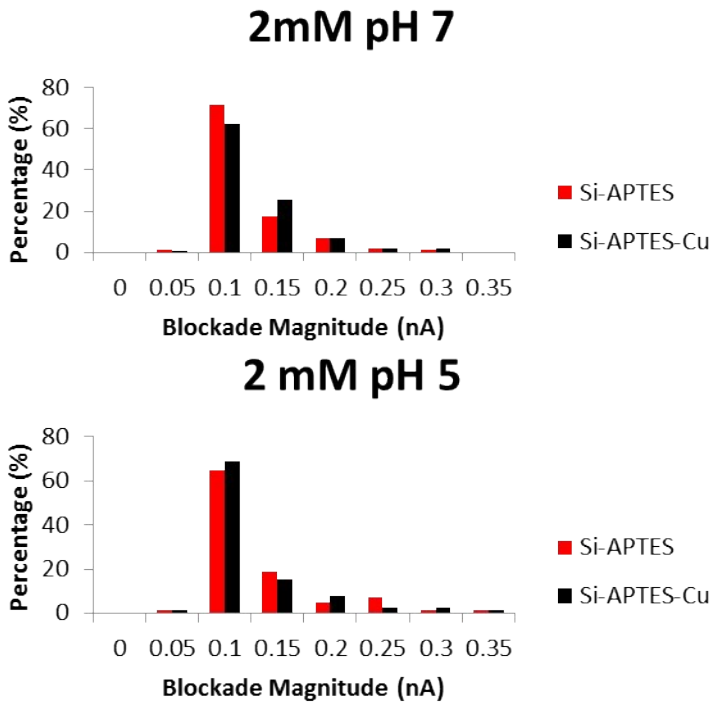

Figure S8. *Resistive Pulse magnitudes of particles with and without copper at pH 5 and pH 7. Samples analysed in 2mM KCl on a NP200 pore, 47 mm stretch, -3.18 V.*

SI9. Conductive and Resistive Pulse Magnitudes

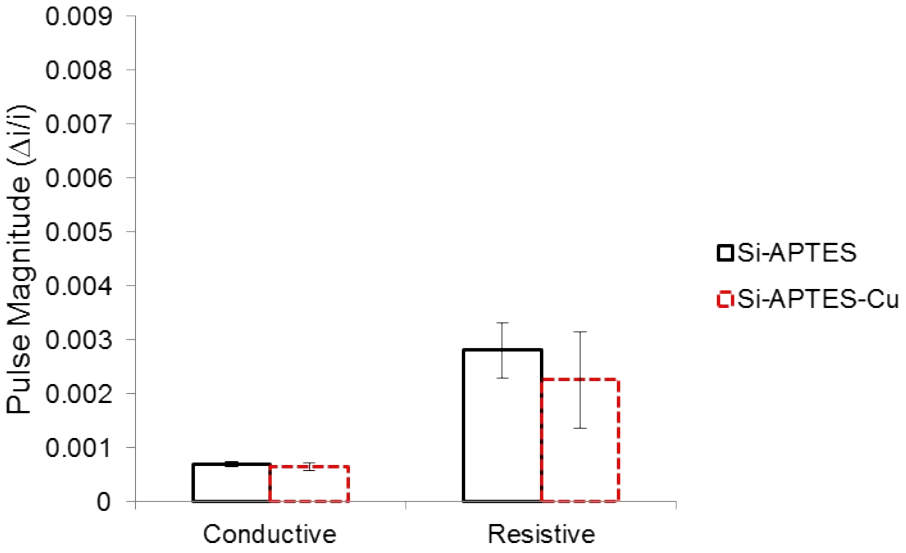

Figure S9. *Conductive and resistive pulse magnitudes for Si-APTES particles and Si-APTES particles incubated in a copper solution at pH 3.*

SI10. Time Analysis

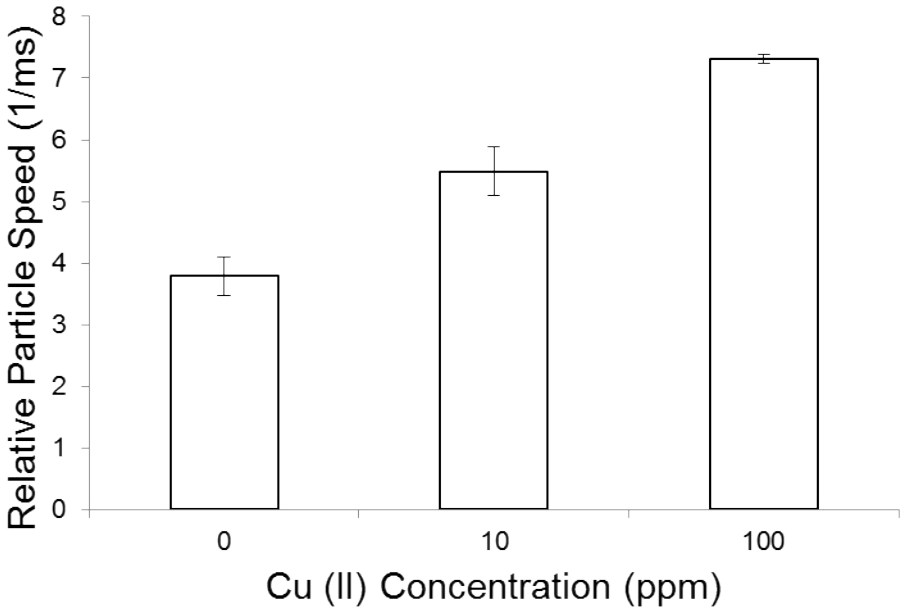

Figure S10. *Time assay: A change in particle speed occurs after 5 minutes of incubation with 10 ppm and 100 ppm Cu (II) solutions, measured in 5mM KCl pH 7.0. Error bars represent one standard deviation from the mean of three repeats. Samples run on a NP200 pore, 47.50 mm and -2.36 V.*

SI11. APTES Selectivity

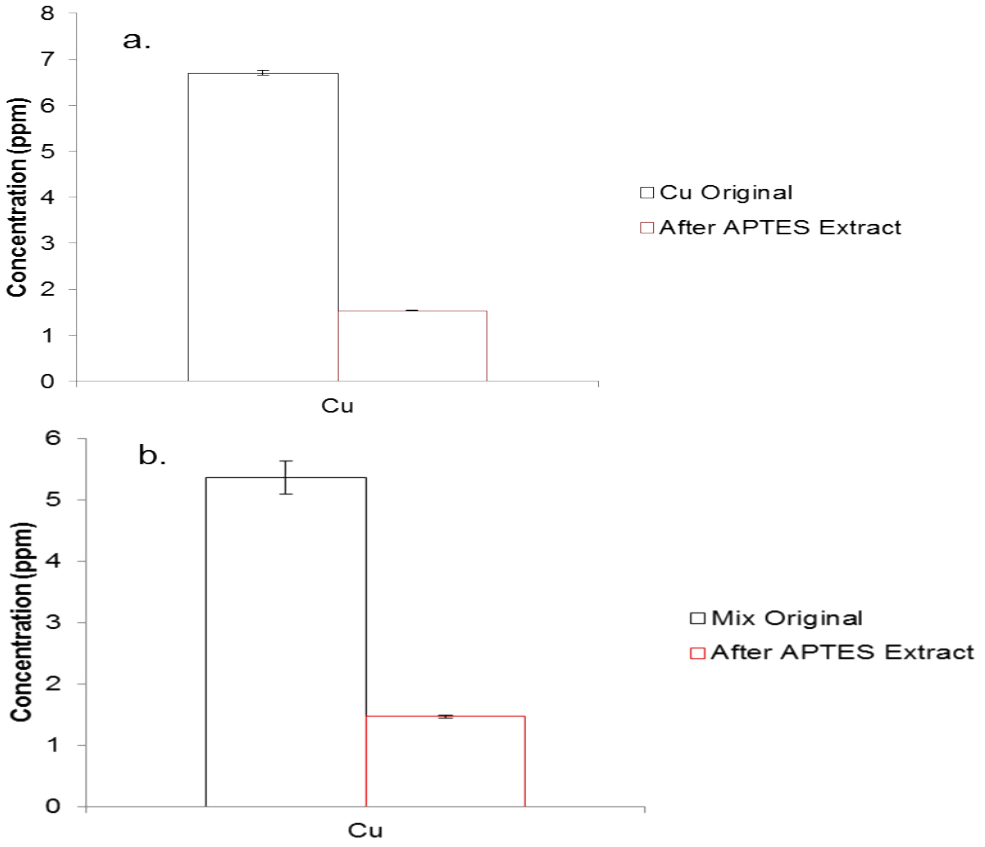

Figure S11. *a) Copper concentration before and after Si-APTES incubation. b) Copper concentration in a mixture of competing metal ions, before and after Si-APTES incubation.*