Supplementary Material

Development and application of Au Nanoparticle-nanopolymer composite spheres for environmental monitoring

Robert J. Rauschendorfer1, Kyle M. Whitham2, Star Summer2, Samantha A. Patrick2, Aliandra E. Pierce2, Haley Sefi-Cyr1,Soheyl Tadjiki3, Michael D. Kraft5, Steven R. Emory2, David A. Rider2,4, Manuel D. Montaño1,\*

1Department of Environmental Sciences, Western Washington University, Bellingham, WA, United States of America

2 Department of Chemistry, Western Washington University, Bellingham, WA, United States of America

3Postnova Analytics Inc., Salt Lake City, UT, United States of America

4Department of Engineering and Design, Western Washington University, Bellingham, WA, United States of America

5Scientific Technical Services, Western Washington University, Bellingham, WA, United States of America

**Table S1** Operating Conditions AF4.

**Table S2** Operating Conditions Sed-FFF for Au-Tracer@PS Analysis.

**Table S3** Operating Conditions Sed-FFF for Au-Tracer@PMMA Analysis.

**Table S4** Acquisition Parameters for Raman Microscope**.**

**Table S5** Typical running instrument conditions for ICP-MS.

**Figure S1** Comparison of digested Au-Tracer@PS stocked post filtration

**Figure S2** Sampling map of Bellingham Bay

**Table S6** Carbon and metal content in collected sediment

**Table S7** Measured sediment grain size (presented as wt%)

**Figure S3** Sediment grain size by weight %.

**Figure S4** DLS measurement of (A) Core material (B) Core@PMMA and (C) Au-Tracer@PMMA.

**Figure S5** Measured particle number concentration of Au-Tracer@PS particle suspension at different dilutions.

**Figure S6** SEM-EDS imaging of Au-Tracer@PS,

**Figure S7** AF4 and Sed-FFF fractograms of Au-tracer@PS material.

**Table S8** Calculated particle densities from Sed-FFF.

**Table S9** Raman Band Assignments for Core@PS.

**Table S10** Raman Band Assignments for Core@PMMA.

**Figure S8** TGA plots for components of Au-Tracer@PS and Au-Tracer@PMMA.

**Figure S9** Histogram distribution of Pt-Tracer@PS particles.

**Figure S10** Histogram distribution of Pd-Tracer@PS particles.

**Table S11** Measured pH values for DOC, salinity aggregation experiments.

**Table S12** Zeta potential values (measured in mV) of Au-Tracer@PS particles

**Figure S11** 197AuMass distribution of Au-Tracer@PS particles.

**Figure S12** Equivalent diameter of 197Au Mass of Au-Tracer@PS particles.

**Table S1.** Operating Conditions AF4.

|  |  |
| --- | --- |
| **AF4 (Postnova, AF2000)** | |
| **Instrument Parameter** | **Value** |
| Channel Flow Rate | 1 mL min-1 |
| Cross Flow Rate (Initial / Final) | 0.5 mL min-1 / 0.1 mL min-1 |
| Cross Flow Decay Type (Exponent) | Power (0.5) |
| Pre-decay period / Decay Period | 2 min / 35 min |
| Injection flow rate | 0.2 mL min-1 |
| Injection/focusing Time (Focus flow rate) | 15 min (1.3 mL min-1) |
| Injection Volume | 20 μL |
| Membrane | 10 kDa Regenerated Cellulose |
| Spacer | 350 μm |
| Carrier Solution | 0.05% (v/v) FL-70 + 3 mM NaN3 |

**Table S2.** Operating Conditions Sed-FFF for Au-Tracer@PS Analysis.

|  |  |
| --- | --- |
| **Sed-FFF (Postnova, CF2000)** | |
| **Instrument Parameter** | **Value** |
| Field | 1000 RPM |
| Channel Flow Rate | 2 mL min-1 |
| Relaxation Time | 5 min |
| Channel Thickness | 131 μm |
| Injection Volume | 50 μL |
| Carrier Solution | 0.05% (v/v) FL-70 + 3 mM NaN3 |

**Table S3.** Operating Conditions Sed-FFF for Au-Tracer@PMMA Analysis.

|  |  |
| --- | --- |
| **Sed-FFF (Postnova, CF2000)** | |
| **Instrument Parameter** | **Value** |
| Field | 300 RPM |
| Channel Flow Rate | 1 mL min-1 |
| Relaxation Time | 10 min |
| Channel Thickness | 131 μm |
| Injection Volume | 100 μL |
| Carrier Solution | 0.05% (v/v) FL-70 + 3 mM NaN3 |

**Table S4.** Acquisition Parameters for Raman Microscope**.**

|  |  |
| --- | --- |
| **Parameter** | **Setting** |
| Objective | Leica N Plan 50×L, NA = 0.50 |
| Laser & Excitation Wavelength | HeNe, 632.8 nm |
| Spot Size on Sample | 1.3 μm |
| Laser Power at Sample | 5.0 mW |
| Power Density | 3.8 mW/μm2 |
| Integration Time | 10 s |
| Spectra Averaged per Sample | 12 |

**Table S5** Typical running instrument conditions for ICP-MS.

|  |  |
| --- | --- |
| **ICP-MS (Agilent 7500ce)** | |
| **Instrument Parameter** | **Value** |
| Nebulizer Gas Flow | 0.81 ml/min |
| Sample Flow Rate | 0.34 ml/min |
| Spray Chamber | Scott Double Pass |
| ICP RF Power | 1500 W |
| Dwell time | 10 ms |
| Transport efficiency | 4-6% |
| Analytes | 197Au, 105Pd, 195Pt |
| Analysis Time | 30 s |

Chart, bar chart

Description automatically generated

**Figure S1** Comparison of digested Au-Tracer@PS stocked post filtration with 0.22 μm cellulose syringe filter in three different media. Measurements were taken from a freshly-prepared stock and one equilibrated for 48hrs.

**Map

Description automatically generated**

**Figure S2** Sampling map of Bellingham Bay (*Source: GeoJSON open source mapping software*).

**Table S6** Carbon and metal content in collected sediment

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Site** | **TC Conc. (g/kg)** | **BC Conc. (g/kg)** | **Mn Conc. (mg/kg)** | **Ni Conc. (mg/kg)** | **Cu Conc. (mg/kg)** | **Zn Conc. (mg/kg)** | **Al Conc. (g/kg)** | **Fe Conc. (g/kg)** | **Mg Conc. (g/kg)** | **Ca Conc. (g/kg)** |
| A | 1.4 ± 0.1 | 0.07±0.01 | 451 ± 6 | 129 ± 15 | 26 ± 1 | 44 ± 2 | 22 ± 2 | 61 ± 6 | 56 ± 5 | 15 ± 2 |
| B | 1.6 ± 0.2 | 0.07±0.03 | 267 ± 11 | 121 ± 18 | 24 ± 3 | 42 ± 2 | 22 ± 3 | 62 ± 4 | 55 ± 6 | 17 ± 1 |
| C | 6.5 ± 0.5 | 0.07±0.01 | 319 ± 11 | 99 ± 1 | 40 ± 3 | 58 ± 1 | 30 ± 2 | 69 ± 1 | 48 ± 0.4 | 17 ± 2 |
| D | 2.2 ± 0.1 | 0.09±0.02 | 350 ± 5 | 118 ± 4 | 27 ± 4 | 48 ± 1 | 24 ± 3 | 62 ± 5 | 53 ± 3 | 17 ± 0.2 |

**Table S7** Measured sediment grain size (presented as wt %)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Site** | **Percent Coarse Sand (2000-500µm)** | **Percent Medium Sand (500-250µm)** | **Percent**  **Fine Sand**  **(250-125µm)** | **Percent**  **Very Fine Sand**  **(125-63 µm)** | **Percent**  **Silt**  **(<63µm)** |
| A | 0.52 ± 0.07 | 13.77 ± 1.97 | 72.46 ± 1.35 | 11.43 ± 2.35 | 1.83 ± 0.76 |
| B | 2.55 ± 1.19 | 25.95 ± 4.36 | 51.19 ± 12.39 | 15.87 ± 9.12 | 4.40 ± 3.39 |
| C | 0.82 ± 0.34 | 0.96 ± 0.39 | 1.80 ± 0.25 | 16.84 ± 1.56 | 79.54 ± 1.04 |
| D | 0.41 ± 0.02 | 6.02 ± 0.37 | * 1. ± 1.01 | 48.52 ± 1.00 | 10.18 ± 0.36 |



**Figure S3** Sediment grain size by weight %.

****

**Figure S4** DLS measurement of (A) Core material (B) Core@PMMA and (C) Au-Tracer@PMMA particles.

****

**Figure S5** Measured particle number concentration of Au-Tracer@PS particle suspension at different dilutions (n=3) as determined by spICP-MS. The steady decrease at higher concentrations (lower dilution factors) is likely a consequence of ‘coincidence’ where high particle concentrations result in overlapping signals upon detection.

Chart, bubble chart

Description automatically generated

**Figure S6** SEM-EDS imaging of Au-Tracer@PS,

**Chart

Description automatically generated**

**Figure S7** FFF fractograms of Au-tracer@PS material. (A) SedFFF-UV-vis fractogram of Au-tracer@PS particle suspension in comparison to a 512 polystyrene particle standard. (B) AF4-UV-vis fractogram of Au-tracer@PS particle suspensions in comparison to a 512 polystyrene and 600nm polystyrene particle standard.

**Table S8** Calculated particle densities from Sed-FFF.

|  |  |
| --- | --- |
| **Sample** | **Calculated density(kg/m3)** |
| 512 nm Polystyrene standard | 1045 |
| 499 nm Polymethylmethacrylate standard | 1164 |
| Au-Tracer@PS | 1135 |
| Au-Tracer@PMMA | 1210 |

**Table S9** Raman Band Assignments for Core@PS.

|  |  |  |  |
| --- | --- | --- | --- |
| **Core** | | **Core@PS** | |
| **Raman Shift (cm-1)** | **Assignment** | **Raman Shift (cm-1)** | **Assignment** |
| 1601 (shoulder) (m) | PS ring stretch | 1601 (s) | PS ring stretch |
| 1590 (s) | P2VP ring stretch | 1590 (m) | P2VP ring stretch |
| 1567 (m) | PS ring stretch | ----- | ----- |
| ----- | ----- | 1568 (m) | PS ring stretch |
| 1447 (m) | P2VP ring stretch | 1447 (m) | P2VP ring stretch |
| 1330 (w) | PS/P2VP CH2 twist |  |  |
| ----- | ----- | 1328 (w) | PS/P2VP CH2 twist |
| 1210 (m) | PS C=C of ring & backbone | ----- | ----- |
| ----- | ----- | 1202 (m) | PS C=C of ring & backbone |
| ----- | ----- | 1153 (m) | P2VP CH in plane bend |
| 1149 (m) | P2VP CH in plane bend | ----- | ----- |
| 1087 (w) | P2VP CH in plane bend | ----- | ----- |
|  | ----- | 1051 (s) | PS CH in plane bend |
| 1050 (s) | PS CH in plane bend | ----- | ----- |
| 1030 (w) | PS CH in plane bend | 1030 (m) | PS CH in plane bend |
| 1000 (shoulder) (s) | PS/P2VP ring breathing | 1000 (s) | PS/P2VP ring breathing |
| 992 (s) | P2VP ring breathing | 992 (shoulder) (s) | P2VP ring breathing |
| 914 (w) | P2VP C-C vibrating | ----- | ----- |
| 812 (w) | P2VP C=C of ring & backbone | ----- | ----- |
| ----- | ----- | 794 (m) | PS C=C of ring & backbone |

**Table S10** Raman Band Assignments for Core@PMMA.

|  |  |  |  |
| --- | --- | --- | --- |
| **Core** | | **Core@PMMA** | |
| **Raman Shift (cm-1)** | **Assignment** | **Raman Shift (cm-1)** | **Assignment** |
| ----- | ----- | 1725 (w) | PMMA C=O |
| 1601 (shoulder) (m) | PS ring stretch | ----- | ----- |
| 1590 (s) | P2VP ring stretch | ----- | ----- |
| ----- | ----- | 1588 (s) | P2VP ring stretch |
| 1567 (m) | PS ring stretch | 1567 (s) | PS ring stretch |
| 1447 (m) | P2VP ring stretch | 1447 (m) | P2VP ring stretch |
| 1330 (w) | PS/P2VP CH2 twist | ----- | ----- |
| ----- | ----- | 1327 (w) | PMMA CH2 twist |
| 1210 (m) | PS C=C of ring & backbone | 1210 (m) | PS C=C of ring & backbone |
| ----- | ----- | 1150 (m) | P2VP CH in plane bend |
| 1149 (m) | P2VP CH in plane bend | ----- | ----- |
| 1087 (w) | P2VP CH in plane bend | ----- | ----- |
| 1050 (s) | PS CH in plane bend | 1050 (s) | PS CH in plane bend |
| 1030 (w) | PS CH in plane bend | ----- | ----- |
| ----- | ----- | 1029 (w) | PS CH in plane bend |
| 1000 (shoulder) (s) | PS/P2VP ring breathing | 1000 (shoulder) (s) | PS/P2VP ring breathing |
| 992 (s) | P2VP ring breathing | 992 (s) | P2VP ring breathing &  PMMA O-C rocking |
| ----- | ----- | 965 (shoulder) (w) | PMMA CH2 wagging3 |
| 914 (w) | P2VP C-C vibrating | ----- | ----- |
| 812 (w) | P2VP C=C of ring & backbone | ----- | ----- |
| ----- | ----- | 811 (m) | P2VP C=C of ring &  PMMA C-O-C |



**Figure S8** TGA plots for components of Au-Tracer@PS and Au-Tracer@PMMA. To ensure complete volatilization and/or combustion of organic materials the purge gas of the TGA furnace was switched from inert N2 to air at a temperature of 650°C. The resulting plateau after this event represents the metal mass percent in each sample.



**Figure S9** Histogram distribution of Pt-Tracer@PS particles showing relative monodispersity of Pt-NP loading

****

**Figure S10** Histogram distribution of Pd-Tracer@PS particles showing relative monodispersity of Pd-NP loading.

**Table S11** Measured pH values for DOC, salinity aggregation experiments.

|  |  |  |  |
| --- | --- | --- | --- |
| **Salinity conc. (g L-1)** | **Dissolved Organic Carbon Conc. (mg L-1)** | | |
| **0** | **1.5** | **3.0** |
| 0 | 6.51 ± 011 | 7.31 ± 0.19 | 7.25 ± 0.06 |
| 5 | \*\*\* | 5.39 ± 0.26 | 5.10 ± 0.04 |
| 15 | 6.55 ± 0.09 | 5.35 ± 0.18 | 4.50 ± 0.22 |
| 30 | 6.63 ± 0.34 | 5.21 ± 0.18 | 4.67 ± 0.05 |

**Table S12** Zeta potential values (measured in mV) of Au-Tracer@PS particles in different aquatic media

|  |  |  |  |
| --- | --- | --- | --- |
| **Salinity (g L-1)** | **Dissolved Organic Carbon (mg L-1)** | | |
| **0** | **1.5** | **3.0** |
| 0 | 28.6 (±0.5) | 16.4 (±0.7) | 7.9 (±0.1) |
| 1 | 19.5 (±0.4) | --- | --- |
| 5 | 6.8 (±2.3) | -4.76\* | -2.14\* |
| 30 | -0.7 (±1.2) | -1.06\* | -2.8\* |



**Figure S11** 197AuMass distribution of Au-Tracer@PS particles as measured by spICP-MS (n=5)

Chart, histogram

Description automatically generated

**Figure S12** Equivalent spherical diameter based on 197Au Mass of Au-Tracer@PS particles as measured by spICP-MS assuming a spherical geometry and a particle density of 19.3 g cm-3 (n=5).