

Supporting Information

1 **Spectroscopic Analyses of Particle and Energy Aggregations at the Interface of**
2 **Silver Nanoparticles and Fluorescent Carbon Nanodots**

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23 MATERIAL AND EXPERIMENT

24 *Materials*

25 Deionized ultrapure water (DI water) with a conductivity of 18.2 M Ω -cm was used in all experiments.
26 Silver nitrate ($\geq 99.0\%$) was purchased from Honeywell FLUKA. Sodium Citrate ($\geq 99.0\%$) was
27 bought from Shimakyu Pure Chemicals. Sodium borohydride (99.0%), thionyl chloride (97.0%),
28 quinine hemisulfate salt monohydrate, and 2,2-Diphenyl-1-picrylhydrazyl (DPPH) were bought from
29 Sigma-Aldrich. Glycine ($\geq 99.0\%$) was purchased from VWR Life Science. 4-Aminophenyl disulfide
30 ($\geq 98.0\%$) was bought from Tokyo Chemical Industry Company. Alumina beads were bought from
31 Hayashi pure chemical industry.

32 *Instrumentation*

33 Absorption spectra of the AgNPs solution were recorded on a U-1800 spectrophotometer (HITACHI,
34 Japan). Transmission electron microscopy (TEM) images of AgNPs were recorded using a JEOL
35 JEM2010 HRTEM system with an accelerating voltage of 200 KV (JEOL, Ltd., Japan). Field Emission
36 Scanning Electron Microscope (FE-SEM) images of the beads were recorded using a JSM-6700F
37 system with an accelerating voltage of 200 KV (JEOL, Ltd., Japan). Fluorescence spectra were
38 acquired with a JASCO Spectrofluorometer FP-6500 and FT-IR with a Perkin Elmer Model Spectrum
39 One instrument. Elemental analyses were made with an Elementar Vario EL cube machine. A
40 microRaman system from HORIBA equipped with a 532nm laser (Shanghai DreamLasers Technology,
41 SDL-532-1000T) at 5.0 mW power was employed for the study of SERS (conditions: integral times 1s,
42 cycles 3). Room temperature for SERS measurements was controlled at 16°C.

43 *Preparation of silver nanoparticles*

44 Citrate-capped AgNPs (AgNPs^C) was prepared by our previous method. Silver nitrate (27 mg) was
45 dissolved in deionized water (150 mL) in a reflux system. Upon boiling, 1% (wt/vol) aqueous
46 trisodium citrate solution (3 mL) was added to the silver ion solution. The reflux system was kept

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47 at approximately 100°C in an oil bath for 1.5 h. Then, the Ag nanoparticle solution was cooled in an
48 ice bath. The suspension of citrate-capped AgNPs was stored in a dark glass bottle at room
49 temperature and used within a week. The morphology and UV-Vis spectrum of AgNPs^C were shown
50 in **Figure S1**.

51 Borohydride-reduced AgNPs (AgNPs^B) was prepared by dropping ice-cooled 0.02 M aqueous solution
52 of NaBH₄ to a stirred 0.01 M AgNO₃ solution (50 mL) at an approximate rate of 1 drop/second. When
53 150 mL of the NaBH₄ solution has been consumed, the suspension of AgNPs^B was ready and used
54 within two hours. The morphology and UV-Vis spectrum of AgNPs^B were shown in **Figure S2**.

55 ***Preparation of carbon nanodots (CDs)***

56 An aqueous solution of glycine (3 M, 30 mL) was placed in a 50-mL stainless bomb with Teflon liner.
57 The bomb was sealed and heated in an oven for three hours at 230°C. After cooling to ambient
58 temperature, the resultant solution was centrifuged at 1780 x g for ten minutes, and the supernatant
59 was passed through a 0.22 µm-pore filter disc. The filtrate was dialyzed using a 1,000 D membrane
60 and then lyophilized to give CDs^{Red} as a pale-brown solid (493 mg, 7.3% yield).

61 CDs^{Red} (10 mg/mL, 50 mL) and HNO₃ (65%, 25 mL) were placed in a 200-mL round bottom flask. The
62 mixture was heated with stirring at 110°C for twenty-four hours and then evaporated under reduced
63 pressure to give CDs^{Oxi} as a yellow solid (650 mg, yield undetermined).

64 CDs^{Oxi} (300 mg) and SOCl₂ (4 mL) were stirred and heated at 80°C for four hours. The mixture was
65 evaporated under reduced pressure and the residue was heated with EtOH (15 mL) at 60°C for
66 twenty-four hours. The resultant mixture was evaporated under reduced pressure to give CDs^{OEt} as
67 a brown solid (149 mg, yield undetermined).

68 ***Preparation of supported AgNPs^C and AgNPs^C-CDs***

69 AgNPs^C suspension (0.4 mL) was diluted to 2.0 mL with H₂O and then blended by a rotating motion

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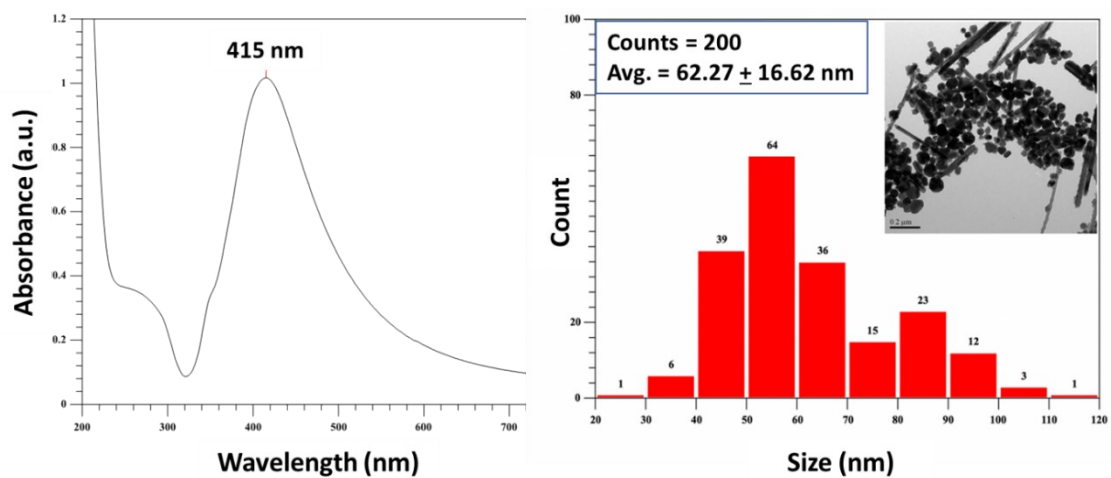
70 with ten alumina beads (average diameter = 7 mm) at room temperature for 3 hours. To make
71 supported AgNPs^C-CDs composites, AgNPs^C suspension (0.4 mL) was mixed with CDs^{Red}, CDs^{Oxi}, or
72 CDs^{OEt} (4 mg/mL, 0.1 mL) and then diluted to 2.0 mL with H₂O. Ten alumina beads were blended
73 similarly with the desired suspension of AgNPs^C-CDs at room temperature for 3 hours. These
74 substrate-decorated beads were removed and air-dried for an hour before the next steps (SERS and
75 SEM). One substrate-decorated bead was soaked in an ethanolic solution of 4-APDS (10⁻⁶ M, 0.5
76 mL) with agitation by a rotating motion at room temperature for 3 hours. The bead was removed
77 and air-dried for an hour before SERS study.

78 ***Preparation of supported AgNP^B and AgNPs^B-CDs***

79 Freshly prepared suspension of AgNPs^B (0.4 mL) was diluted to 2.0 mL with H₂O. It was centrifuged
80 at 1780 x g at room temperature for 15 minutes to remove any large particles due to premature
81 aggregation. The supernatant (~1.9 mL) was removed and diluted to 2 mL with H₂O. The resultant
82 AgNPs^B suspension was then used to prepare supported AgNPs^B and AgNPs^B-CDs for various studies
83 following the same method as AgNPs^C.

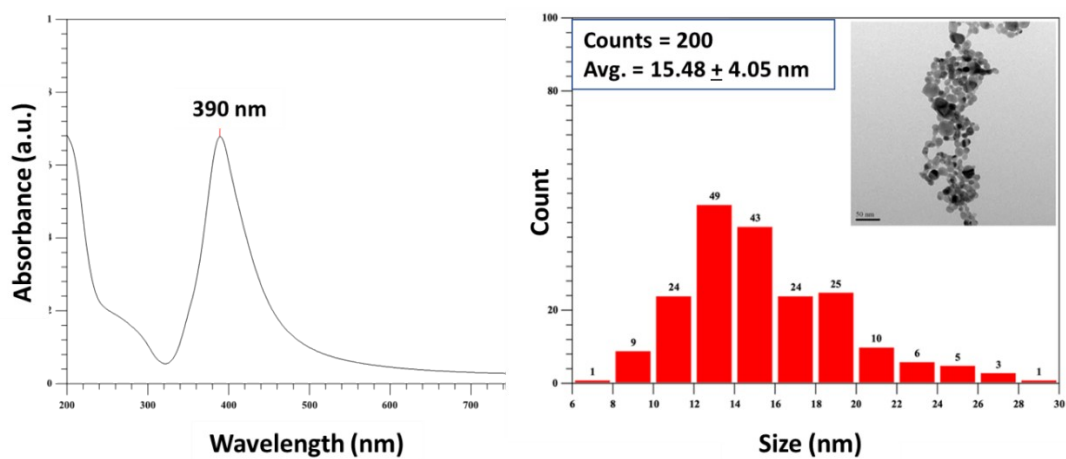
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85 **Figure S1** – A typical UV-Vis spectrum and TEM image with size-distribution of AgNPs^C



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87 **Figure S2** – A typical UV-Vis spectrum and TEM image with size-distribution of AgNPs^B

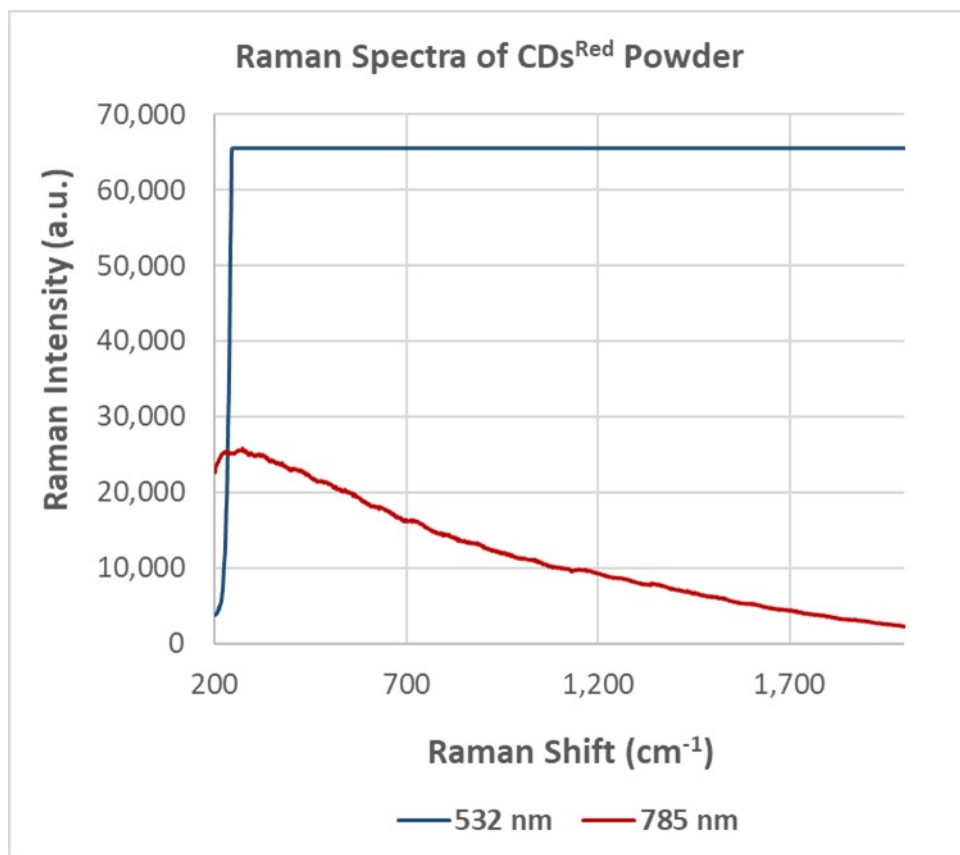


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90 **Figure S3** – Raman spectra of CDs^{Red} solid

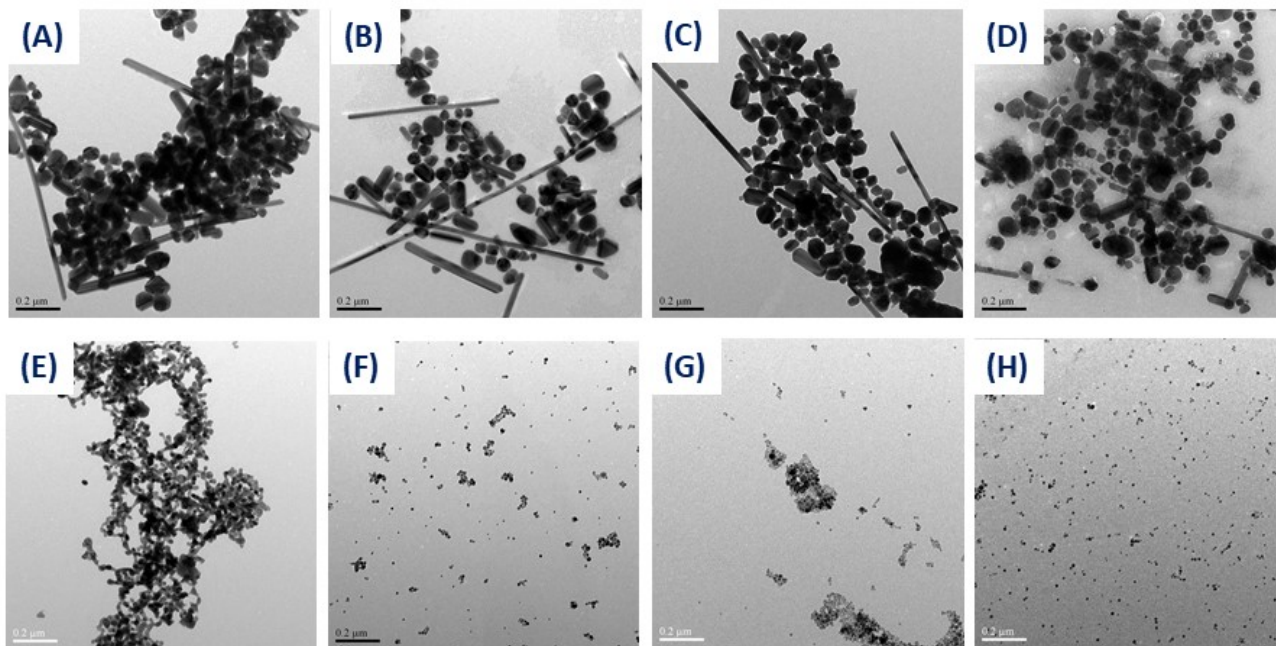
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93 **Figure S4** - TEM images of (A) AgNPs^C; (B) AgNPs^C-CDs^{Red}; (C) AgNPs^C-CDs^{Oxi}; (D) AgNPs^C-CDs^{OEt}; (E)
94 AgNPs^B; (F) AgNPs^B-CDs^{Red}; (G) AgNPs^B-CDs^{Oxi}; (H) AgNPs^B-CDs^{OEt}



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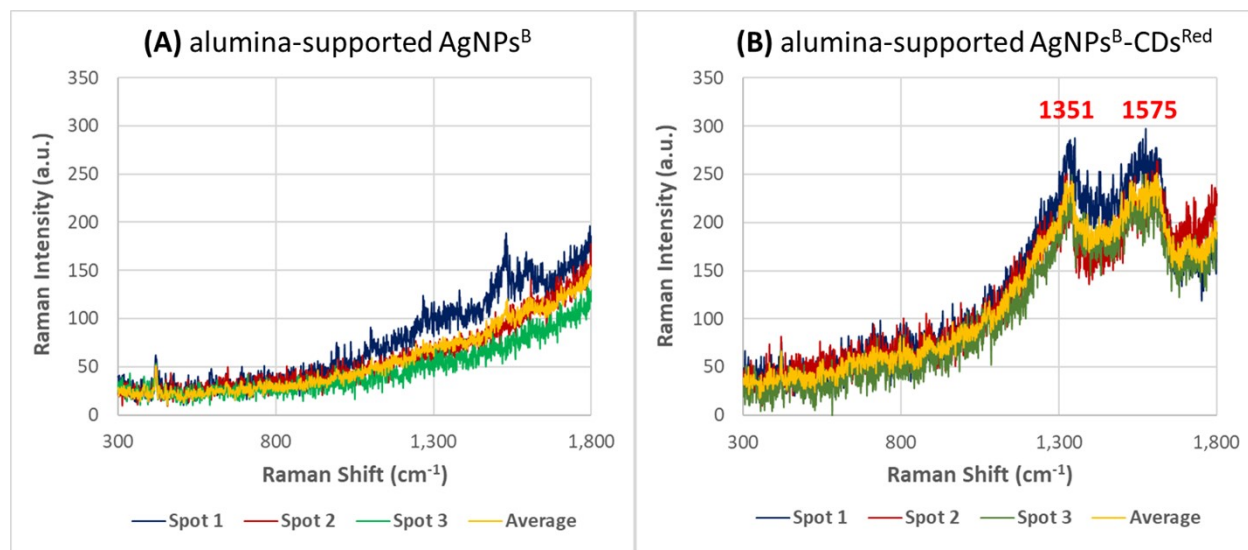
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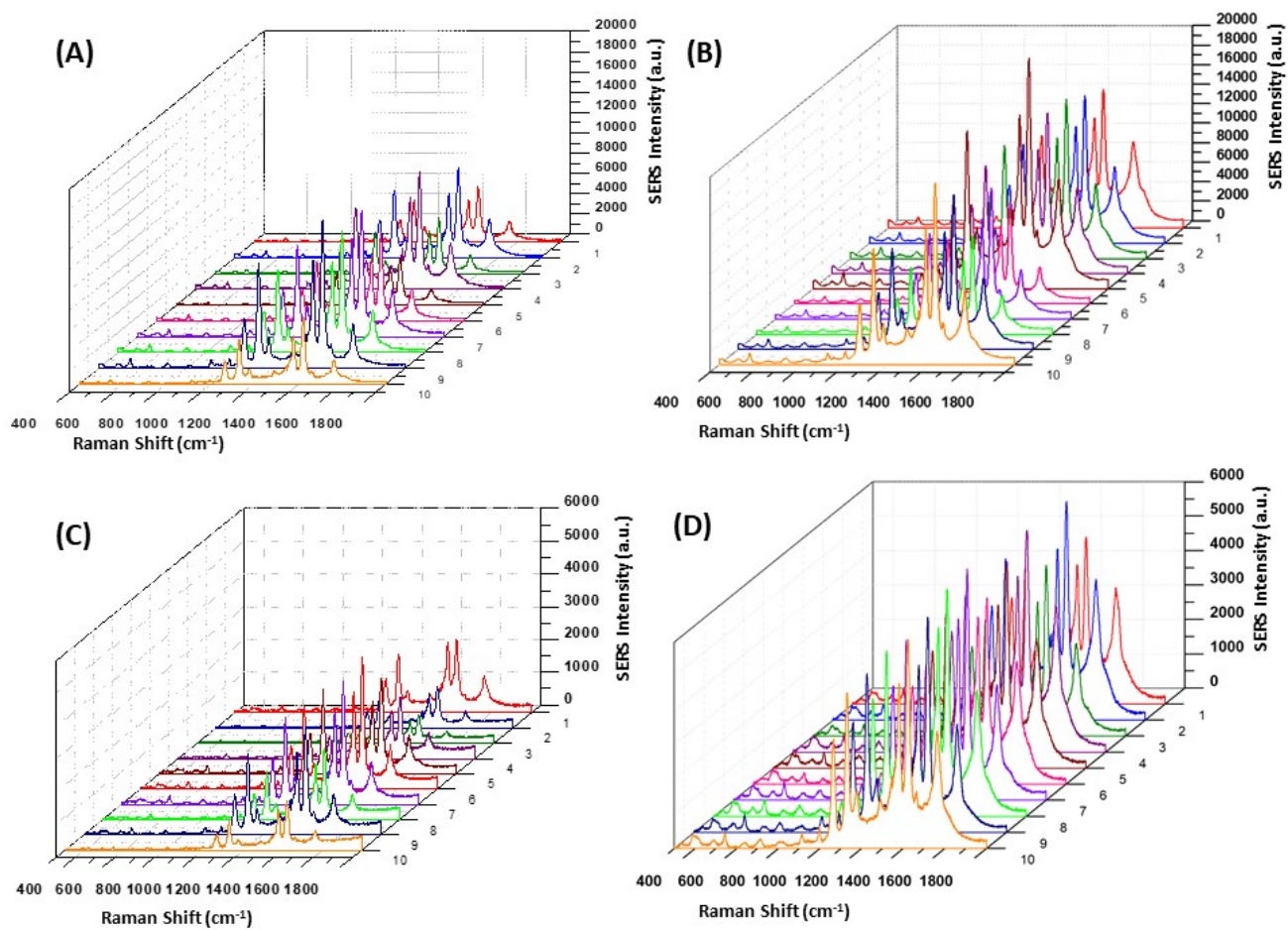
98 **Figure S5** – Raman spectra of alumina-supported AgNPs^B (A) and AgNPs^B-CDs^{Red} (B)

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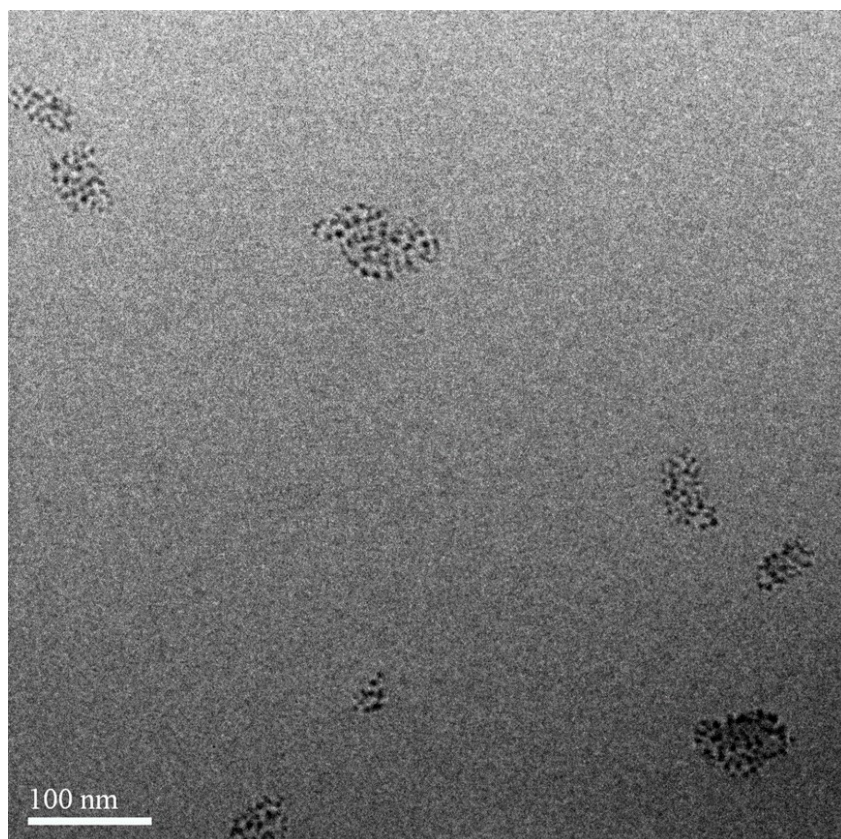
101 **Figure S6** - SERS spectra of 10^{-6} M 4-APDS measured at ten random spots on aluminum bead-
102 supported (A) AgNPs^C; (B) AgNPs^C-CDs^{Red}; (C) AgNPs^B; (D) AgNPs^B-CDs^{Red}



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105 **Figure S7** – The TEM image of cysteine-derived carbon dots



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108 **Figure S8** – Unmarked version of **Figure 8C** and **8D**

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