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# Supporting Information to

# Title Bulbous gold-carbon nanodot hybrid nanoclusters

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## Contents

**General**

All chemicals were used as received from commercial sources. Average hydrodynamic radii of nanoparticles were measured with a Zetasizer Nano ZS from Malvern Instruments Ltd. featuring a dynamic light scattering analyzer. Absorption spectra were recorded with a Lamba 2 UV-vis spectrometer from Perkin Elmer in 10 mm quartz cuvettes. Fluorescence spectra were recorded with a Fluoromax 3 spectrofluorometer from Horiba in 10 mm quartz cuvettes. Bright field and dark field TEM analysis was performed with a TEM 912 Omega from Zeiss. Specimen grids were prepared by drop casting of the sample solution onto the TEM grids and subsequent drying in a desiccator. For dark field imaging the direct transmitted beam was blocked with the objective aperture and only the beam deflected by carbon or gold atoms was recorded. TEM images of the cells loaded with the NPs were received using a Zeiss 906 TEM. Transient absorption spectroscopy was performed with either 387, 505, or 550 nm laser pump pulses (1 kHz, 150 fs pulse width) from an amplified Ti:sapphire laser system CPA 2110 from Clark-MXR Inc. The viability assays were measured with a Synergy HT microplate reader from BioTek.

## Absorption spectroscopy

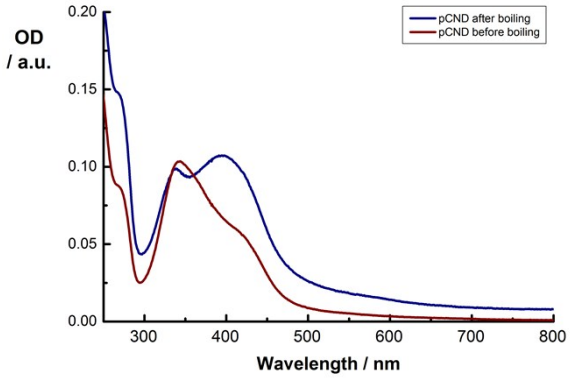


**Figure S1.** Absorption spectra of pCND in $H_2O$ before boiling (red) and after boiling (blue).

## Dynamic light scattering analysis

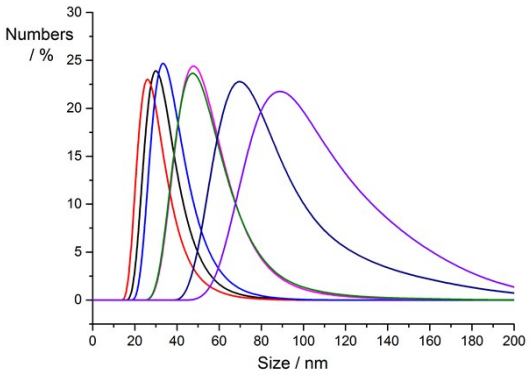


**Figure S2.** Dynamic light scattering plots of various $HAuCl_4$ (red) 0.75 mM (black) 1.00 mM (blue) 1.25 mM (green) 2.00 mM (magenta) 2.50 mM (navy blue) 3.00 mM (violet) 4.00 mM

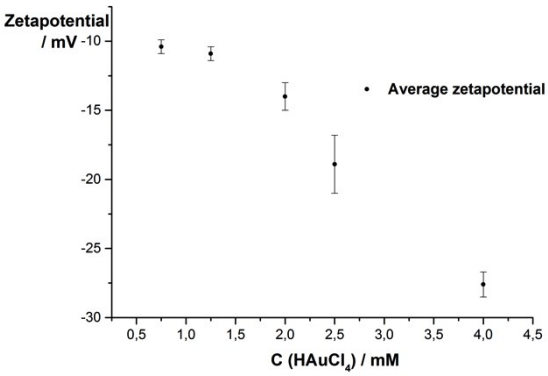


**Figure S3.** Zetapotential plot versus the conc. of $HauCl_4$

## Raman spectroscopy

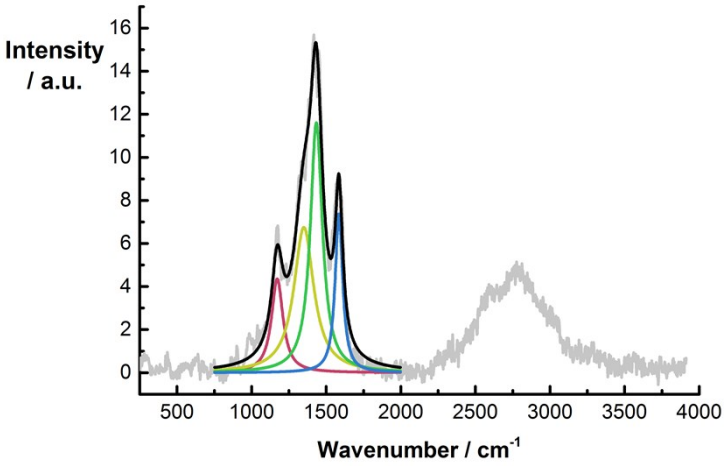


**Figure S4.** Raman spectrum of Au@pCND (gray) obtained upon 457 nm laser excitation with multiple Lorentzian peak fitting of the D- and G-band region.

## Time-correlated single-photon counting

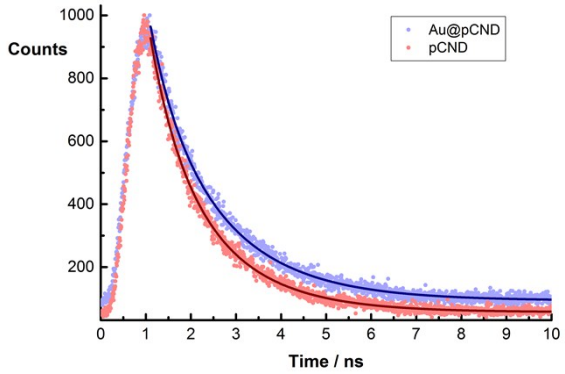


**Figure S5.** Time-emission profiles of pCND (red) and Au@pCND (blue) at 500 nm obtained by means of TCSPC upon excitation at 410 nm.

## Transient absorption characterization

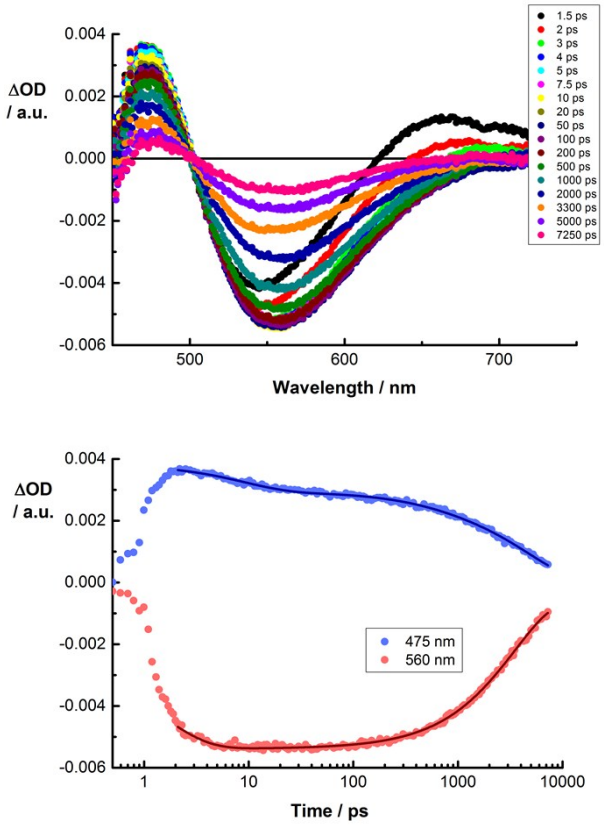


**Figure S6.** Left: Transient absorption spectra of 30 min boiled pCND obtained upon laser flash photolysis excited with 387 nm laser pulses in $H_2O$ with time delays between 1.5 and 7250 ps. Right: Corresponding time-absorption profiles at 475 nm (blue) and 580 nm (red).

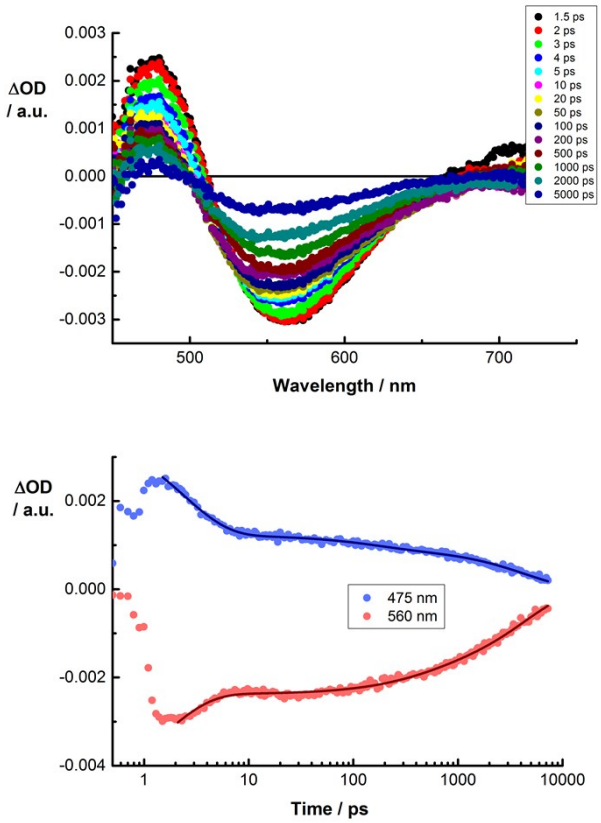


**Figure S7.** Left: Transient absorption spectra of Au@pCND obtained upon laser flash photolysis excited with 387 nm laser pulses in $H_2O$ with time delays between 1.5 and 5000 ps. Right: Corresponding time-absorption profiles at 475 nm (blue) and 560 nm (red).

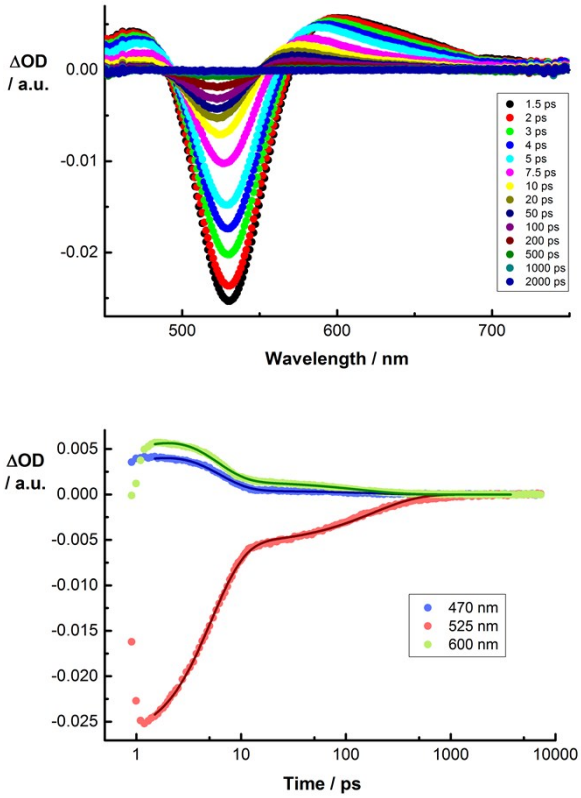


**Figure S8.** Left: Transient absorption spectra of citric acid stabilized AuNP obtained upon laser flash photolysis excited with 387 nm laser pulses in $H_2O$ with time delays between 1.5 and 2000 ps. Right: Corresponding time-absorption profiles at 470 nm (blue), 525 nm (red) and 600 nm (green).

## Transmission electron microscopy

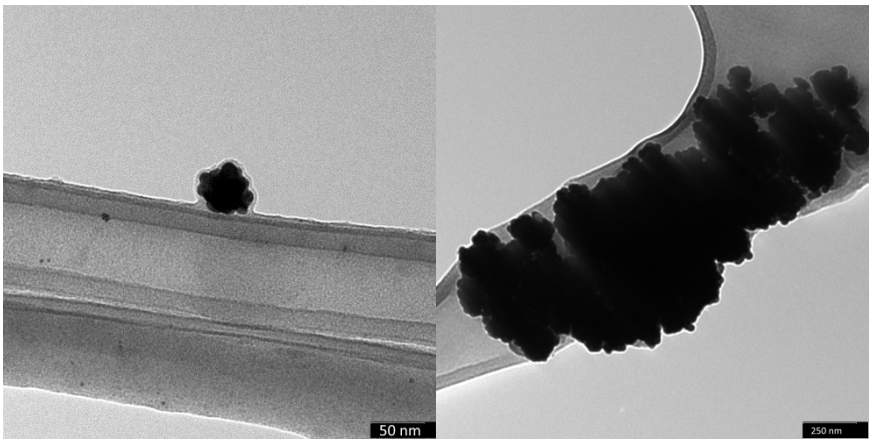


**Figure S9.** Representative TEM images of Au@pCNDs (left) and Au@pCNDs after addition of MPA (right).

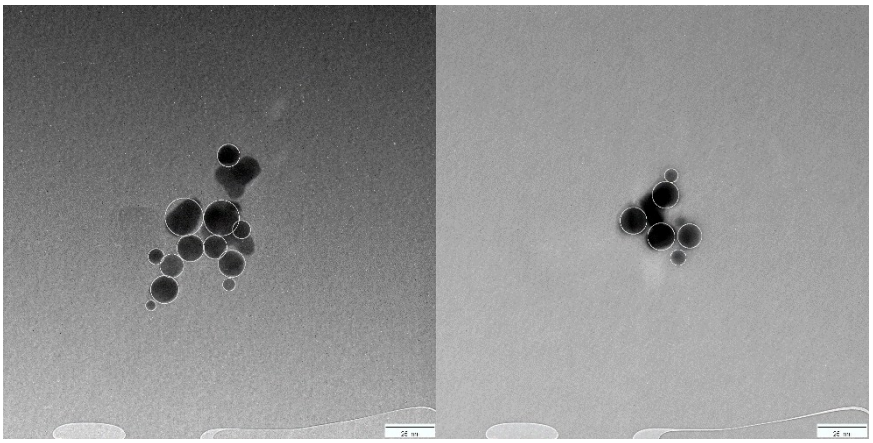

**Figure S10.** TEM images of Au@pCNDs synthesized by standard procedure and 0.75 mM $HAuCL_4$ conc.

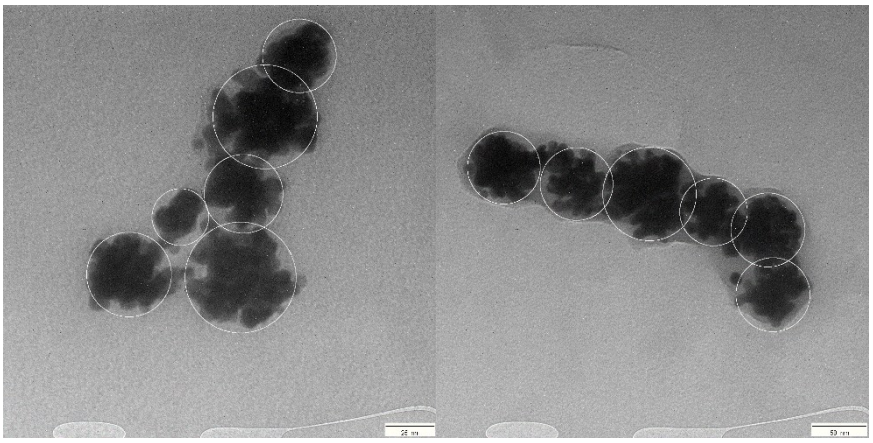

**Figure S11.** TEM images of Au@pCNDs synthesized by standard procedure and 1.00 mM $HAuCL_4$ conc.

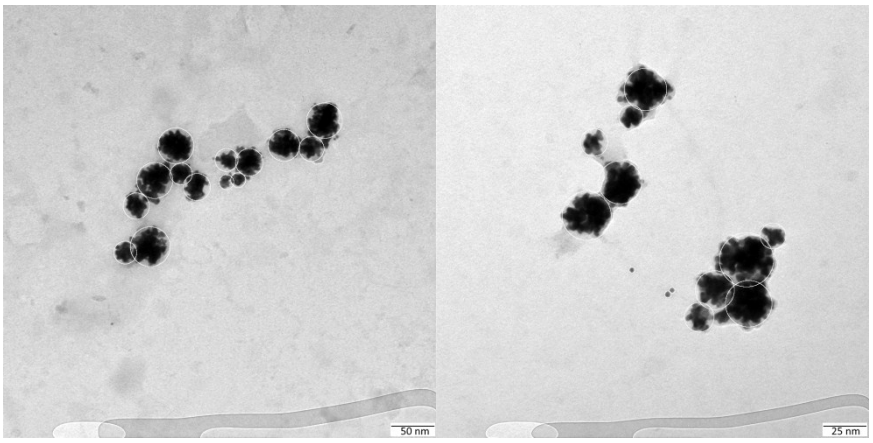


**Figure S12.** TEM images of Au@pCNDs synthesized by standard procedure and 1.25 mM $HAuCL_4$ conc.

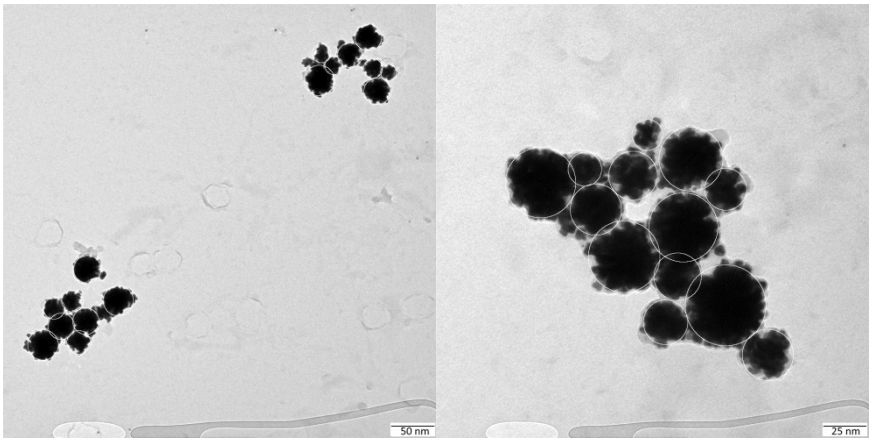


**Figure S13.** TEM images of Au@pCNDs synthesized by standard procedure and 2.00 mM $HAuCL_4$ conc.

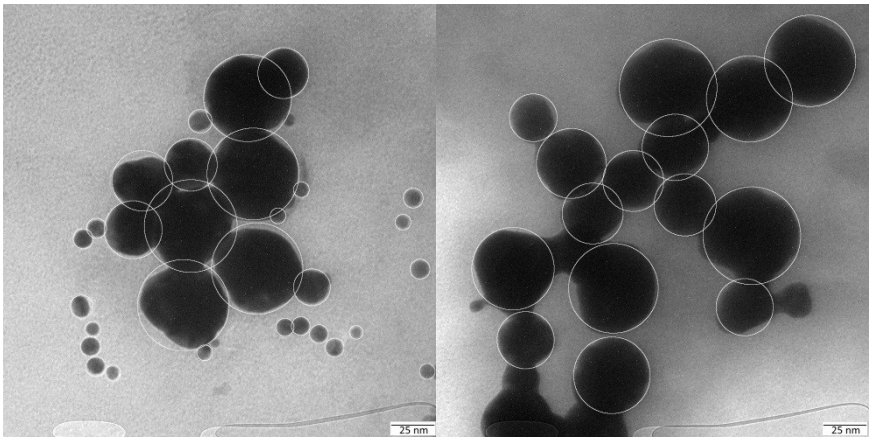


**Figure S14.** TEM images of Au@pCNDs synthesized by standard procedure and 2.50 mM $HAuCL_4$ conc.

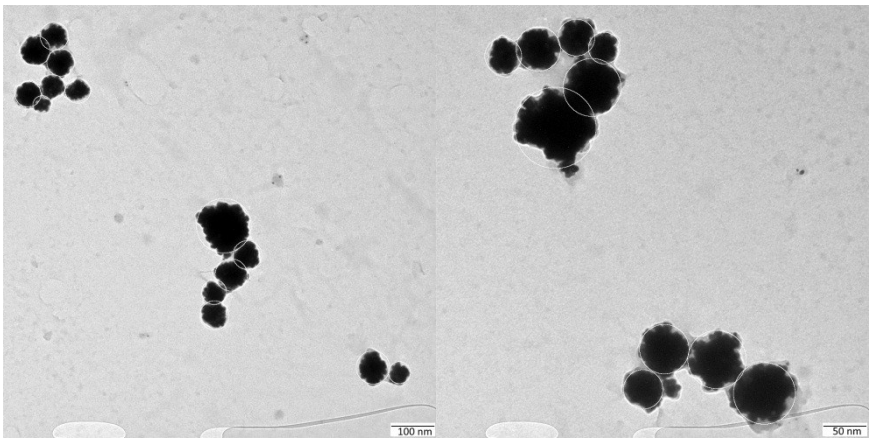


**Figure S15.** TEM images of Au@pCNDs synthesized by standard procedure and 3.00 mM $HAuCL_4$ conc.

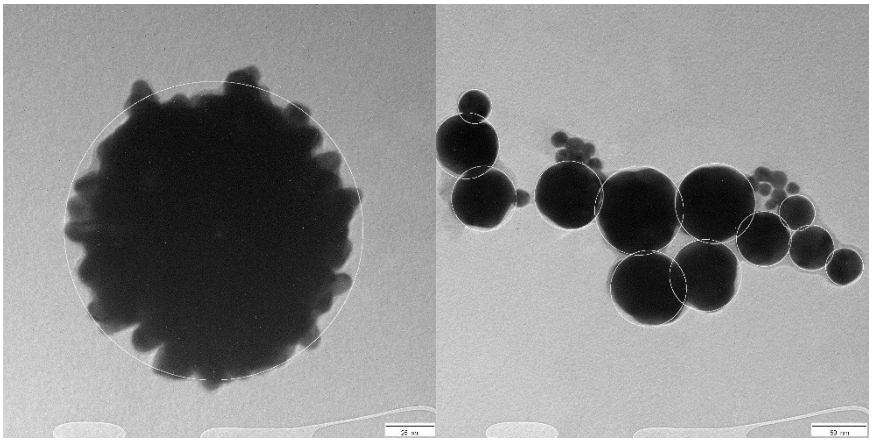

**Figure S16.** TEM images of Au@pCNDs synthesized by standard procedure and 4.00 mM $HAuCL_4$ conc.

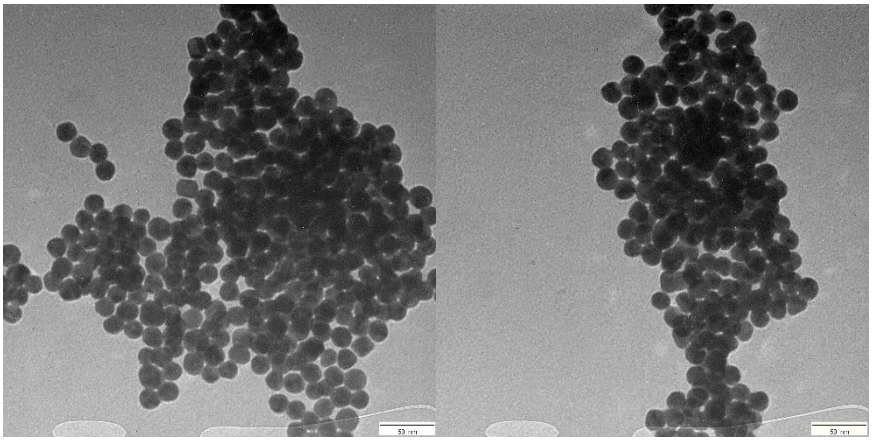

**Figure S17.** TEM images of Au@NPs synthesized by citrate reduction and 2.00 mM $HAuCL_4$ conc.

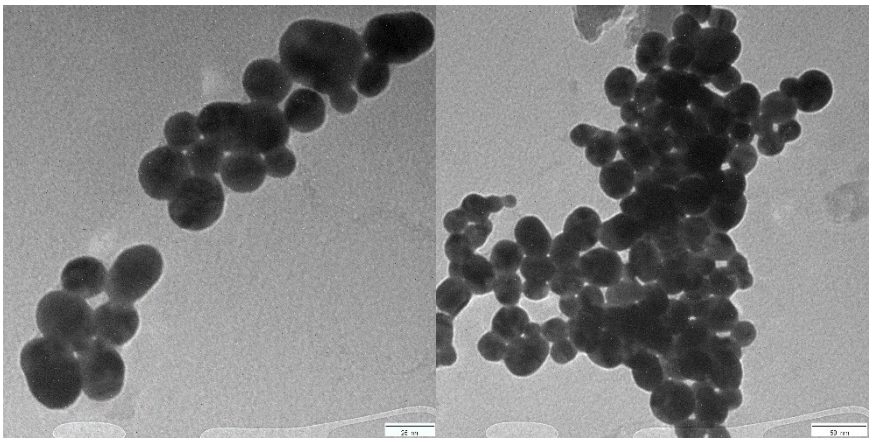

**Figure S18.** TEM images of Au@NPs synthesized by citrate reduction and 3.00 mM $HAuCL_4$ conc.

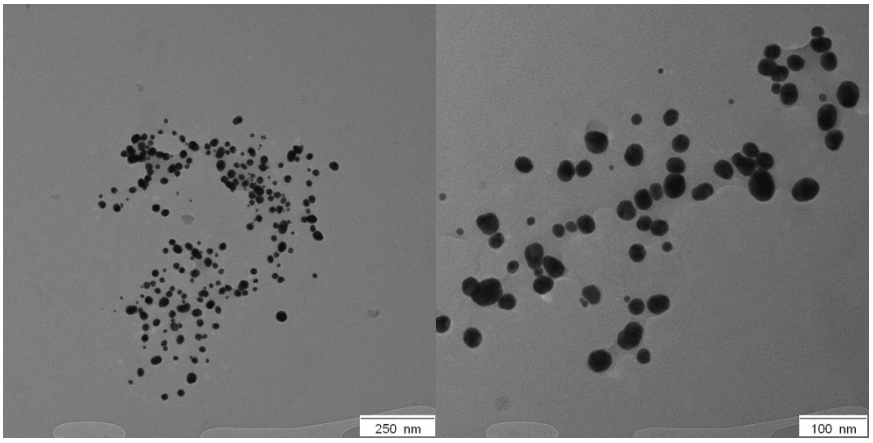


**Figure S19.** TEM images of Au@NPs synthesized by citrate reduction and 4.00 mM $HAuCL_4$ conc.

## Dynamic light scattering and Fluorescence measurements in Serum

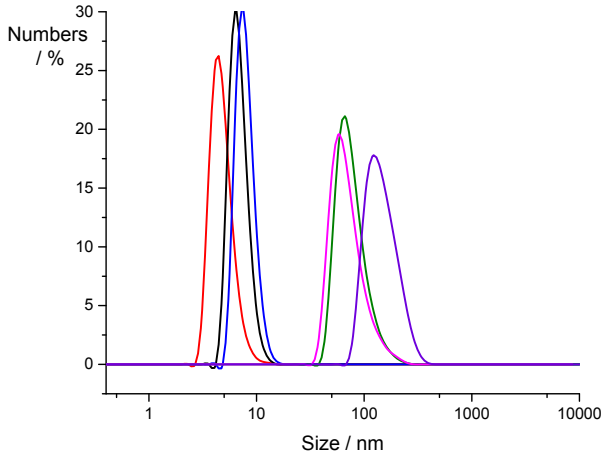


**Figure S20.** Dynamic light scattering plots of various $HAuCl_4$ (red) 0.75 mM (black) 1.00 mM (blue) 1.25 mM (green) 2.00 mM (magenta) 2.50 mM (violet) 4.00 mM in serum containing PBS

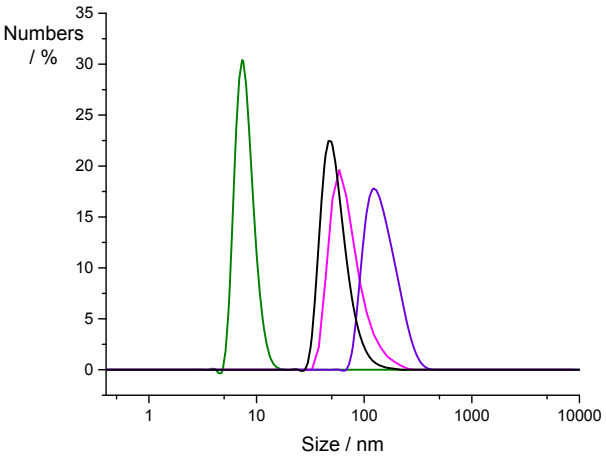


**Figure S21.** Comparison of dynamic light scattering sizes of various $HAuCl_4$ (green) 1.25 mM, (magenta) 2.50 mM and (violet) 4.00 mM to citric acid reduced/ stabilized AuNP in serum containing PBS that are used for the radiation experiments

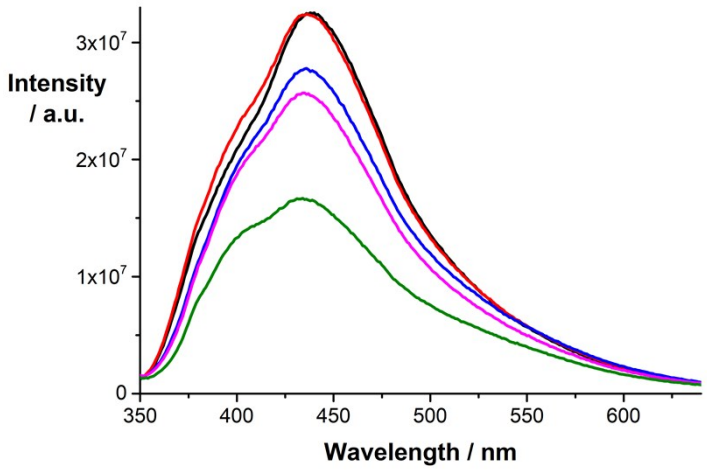


**Figure S22.** Steady state fluorescence spectra of Au@pCND in the cell medium obtained when reacting 0.06 mg/ml pCND with 1.00 (black), 1.25 (red), 2.00 (blue), 2.50 (magenta), and 4.00 (green) mM $HAuCl_4$.

## Additional Synthesis attempts

**Table S1.** Results on high concentration of precursors, here the concentration of pCND is 0.385 mM. Note: These procedures were done using a sand bath. The reactions were quenched with $H_2O$ (in batch 3 – 7 the)

| batch | $c_{pCND}$ [mg/mL] | $c_{HAuCl4}$ [mM] | ratio | $R_{time}$ [min] | $R_{temp.}$ [°C] | DLS size [nm] | TEM size [nm] | $\lambda_{max}$ [nm] |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.20 | 25 | 1:2.5 | 1 | 100 | 70-75 | 7-14 particles, 50-80 agglomerates | ~560 |
| 2[a)] | 1.20 | 50 | 1:5 | 10 | 100 | 80-85 | 57/75/92 agglomerates | ~570 |
| 3[b)] | 1.20 | 50 | 1:5 | 10 | 100 | 80-85 | no data | ~550 |
| 4[b)] | 1.20 | 25 | 1:2.5 | 10 | 100 | 90 | ~7 small particles 90-100 agglomerates | just scattering |
| 5[b)c)] | 1.20 | 100 | 1:10 | 10 | 100 | 400-600 | 2-5 a lot, 10-15 few | ~580 |
| 6[b)] | 1.20 | 200 | 1:20 | 10 | 100 | 40 | no data | ~570 |
| 7[b)] | 1.20 | 12.5 | 1:1.25 | 10 | 100 | 58 | 9-16 particles, ~60 agglomerates | ~560 |
| 8 | 1.20 | 50 | 1:5 | 30 | 100 | 90-150 | no data | just scattering |
| 9 | 1.20 | 50 | 1:5 | 10 | 60 | polydisperse | No particles observed | just scattering |
| 10[a)] | 1.20 | 50 | 1:5 | 10 | 60 | polydisperse | no data | just scattering |

[a)](MW heated) [b)] (CND preheated) [c)](pH = 10)

**Table S2.** Results on low concentration of precursors. In this procedure we are able to produce smaller nanoparticles, for example, 10-20 nm, we do not observe any correlation between precursor concentration and particle sizes. Note: Reactions were quenched in an ice bath.

| batch | $c_{pCND}$ [mg/mL] | $c_{HAuCl4}$ [mM] | ratio | $R_{time}$ [min] | $R_{temp.}$ [°C] | DLS size [nm] | TEM size [nm] | $\lambda_{max}$ [nm] |
|---|---|---|---|---|---|---|---|---|
| 11 | 0.12 | 20 | 1:20 | 10 | 100 | 12 | several homogenous particles, 60-70 | broad ~560 |
| 12 | 0.12 | 10 | 1:10 | 10 | 100 | 57 | 50-72 | ~610 |
| 13 | 0.12 | 5 | 1:5 | 10 | 100 | 19 | no data | just scattering |
| 14 | 0.12 | 20 | 1:20 | 1 | 100 | polydispers | no data | ~640 |
| 15 | 0.12 | 10 | 1:10 | 1 | 100 | 48 | 86-90 agglomerates | ~560 |
| 16 | 0.12 | 2 | 1:20 | 10 | 100 | polydispers | no data | just scattering |
| 17 | 0.006 | 2 | 1:40 | 10 | 100 | polydispers | no data | just scattering |
| 18 | 0.12 | 2 | 1:20 | 10 | 100 | polydispers | no data | ~600 |
| 19 | 0.24 | 2 | 1:10 | 10 | 100 | polydispers | no data | ~590 |
| 20 | 0.006 | 2 | 1:40 | 10 | 100 | polydispers | no data | just scattering |
| 21 | 0.12 | 2 | 1:20 | 5 | 100 | polydispers | no data | just scattering |
| 22 | 0.12 | 2 | 1:20 | 2 | 100 | polydispers | no data | ~600 |

## Radiation therapy experiments

**Table S3.** Dose modifying factor of 6, 60 and 106 nm Au@pCND, citric acid reduced/stabilized AuNP and bare pCNDs

| | DMF |
|---|---|
| pCND | 0.72 |
| Citric acid AuNP | 0.62 |
| 1.25 | 0.85 |
| 2.5 | 0.53 |
| 4 | 0.52 |