Supporting Information

Photochemistry of Ferritin Decorated with Plasmonic Gold Nanoparticles

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Figures Included

- **S1.** TEM of Ftn(1200)
- **S2.** TEM of Au/Ftn
- **S3.** Histogram of AuNP diameters in Au/Ftn heterostructures
- **S4.** UV-vis of Ftn(1200), Au/Ftn(800), Au/Ftn(1200), and Au/Ftn(2000)
- **S5.** Table of Fe loading in proteins
- **S6.** Stability of Fe(II)-ferrozine complex over time under simulated solar radiation (SSR)
- **S7.** Monitoring effect of ferrozine exposed to proteins under dark conditions
- **S8.** UV-vis of Fe(II)-ferrozine complex from proteins
- **S9.** Release of Fe(II) from Ftn(1200), Au/Ftn(800), Au/Ftn(1200), and Au/Ftn(2000) with 570 nm longpass filter
- **S10.** Release of Fe(II) from Ftn(1200), Au/Ftn(800), Au/Ftn(1200), and Au/Ftn(2000) with 625 nm longpass filter
- **S11.** TEM of AuNP synthesized via thermal method and histogram of size distrubtion
- **S12.** Release of Fe(II) from AuNP + Ftn mixture under 532 nm monochromatic laser light
- **S13.** Reduction of Cr(VI) under full and $\lambda \ge 475$ nm light in the presence of tartrate and/or Fe(II).
- **S14.** Amount of Cr(VI) reduced over time as a function of Fe loading in Au/Ftn(800), Au/Ftn(1200), and Au/Ftn(2000)



S1. TEM of Ftn(1200) (Ftn having on average 1200 Fe atoms per core) stained with 2% phosphotungstic acid; white areas are protein while dark regions within the spheres are iron oxide core.



S2. TEM of Au/Ftn where (A) and (B) are unstained images and (C) and (D) have been negatively stained with 2% phosphotungstic acid. Unstained images show larger and smaller dark spheres, which we assign as AuNP and iron ferritin cores, respectively. Stained images show white areas which are protein while dark regions are AuNP. Analysis of both unstained and stained images show an average distance between AuNP and Fe (identifiable heterostrucures) of 2.0±0.3 nm (n=20), consistent with the protein cage thickness.



S3. Histogram dispalying diameter of AuNP in Au/Ftn samples particles imaged by TEM (n= 180), where the average particle size was 7.6 ± 1.7 nm.



S4. Absorbance spectra of Au/Ftn(2000), Au/Ftn(1200), Au/Ftn(800), AuNP + Ftn(1200), and Ftn(1200), indicating postion of SPR when AuNP are present.

	[Fe] (µM)	~Fe Atoms per Ftn cage
Ftn(1200)	42.9	1200
Au/Ftn(800)	25.4	800
Au/Ftn(1200)	43.5	1200
Au/Ftn(2000)	67.0	2000

S5. Table of total Fe in photochemical reactions determined by ICP-OES and calculated Fe atoms per Ftn cage.



S6. Aqueous Fe(II), 20 uM final concentration, was added to excess Ferrozine and immediately placed in front of SSR. Intial increase is due to chelation of Fe(II) to Fz, followed by stable concentration under further irradiation.



S7. UV-vis was used to monitor potential ferrozine induced iron reduction from Ftn and Au/Ftn in the dark. Protein, tartrate, ferrozine, and Tris (standard reaction conditions) were scanned at time 0 (dark trace) and then rescanned 45 minutes later (light trace), offset for clarity. No significant increase at 562 nm was observed. All proteins show less than 1 μM Fe(II) release under these conditions.



S8. Absorbance spectra of Fe(II)-ferrozine generated by Fe(II) release under SSR. All proteins show λ_{max} located at 562 nm, consistent with Fe(II)-ferrozine complex.



S9. Release of Fe(II) from Ftn(1200), Au/Ftn(800), Au/Ftn(1200), and Au/Ftn(2000) exposed to SSR cutoff by a 570 nm longpass filter (error bars smaller than symbols).



S10. Release of Fe(II) from Ftn(1200), Au/Ftn(800), Au/Ftn(1200), and Au/Ftn(2000) exposed to SSR cutoff by a 625 nm longpass filter (error bars smaller than symbols).



S11. TEM of AuNP synthesized via thermal method in the absence of Ftn (top) and measured by particle diameter distribution (bottom). Average particle diamater was 29.6±5.7 nm.



S12. Release of Fe(II) from AuNP + Ftn(1200) heteromixture under 532 nm monochromatic laser light. Black trace is before exposreu to 532 nm laser light while the red trace is after 10 minutes of exposure. Sharp decrease in absorbance at 532 nm is caused by interaction of surface plasmon and indicent radiation.



S13. Homogenous photochemical reduction of Cr(VI) in the presence of tartrate and 10 μ M Fe(II) (no protein) exposed to SSR (\blacksquare), $\lambda \ge 475$ nm (\bullet), and dark conditions (\blacktriangle). Also shown is the reduction of Cr(VI) in the presence of tartrate (no protein, no Fe(II)) as a result of exposure to SSR (\triangleright).



S14. Reduction of Cr(VI) under SSR (A) and $\lambda \ge 475$ nm (B) in the presence of Au/Ftn(800), Au/Ftn(1200), and Au/Ftn(2000).