

Electronic Supplementary Information (ESI†)

Fabrication of nanoscale heterostructures comprised of graphene-encapsulated gold nanoparticles and semiconducting quantum dots for photocatalysis

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Table S1 Diameter, inter-particle spacing, and density of gold (Au) nanoparticles, as-produced GNPs, and the GNPs after plasma/acid treatment patterned on the (silicon) Si substrate.

Samples	Diameter (nm)	Inter-particle spacing (nm)	Density ($10^8/\text{cm}^2$)
Au nanoparticles	47.27 ± 11.25	49.55 ± 16.85	74.51
GNPs	52.22 ± 11.33	45.14 ± 13.33	72.23
Plasma-treated GNPs	49.56 ± 12.38	46.22 ± 13.57	72.03
Acid-treated GNPs	50.62 ± 10.95	47.56 ± 14.65	70.67

Table S2 Raman peak location (cm^{-1}) and I_D/I_G for as-produced GNPs and GNPs after plasma/acid treatment.

	D band	G band	I_D/I_G
GNPs	1319.87	1602.07	1.3 ± 0.2
acid-treated GNPs	1312.56	1599.21	1.2 ± 0.1
plasma-treated GNPs	1312.56	1596.18	1.75 ± 0.25

Table S3 Binding energy (eV) chart derived from XPS study for Au nanoparticles, as-produced GNPs, plasma-treated GNPs, acid-treated GNPs, and the pristine quantum dots (QDs).

		Au nanoparticles	Plasma-treated Au nanoparticles	GNPs	Plasma-treated GNPs	Acid-treated GNPs	QDs
Au	Au 4f _{5/2}	88.27	87.50	88.23	88.47	88.20	/
	Au 4f _{7/2}	84.59	84.60	84.56	84.76	84.47	/
AuO _x	Au 4f _{5/2}	/	88.90	/	89.45	/	/
	Au 4f _{7/2}	/	85.34	/	85.74	/	/
C 1s	C-C (sp ²)	/		284.78	284.78	284.72	/
	C-C (sp ³)	/		285.30	285.26	285.15	/
	π - π	/		291.05	/	/	/
O	C-OH	/		286.75	286.91	286.45	/
	O=C-OH	/		288.81	289.14	288.71	/
	O 1s	533.21		533.24	533.26	533.32	/
QDs	Cd 3d _{5/2}	/		/	/	/	406.07
	Cd 3d _{3/2}	/		/	/	/	412.78
	Se	/		/	/	/	/
	Zn 2p _{3/2}	/		/	/	/	1022.52
QDs	Zn 2p _{1/2}	/		/	/	/	1045.76
	S 2p _{3/2}	/		/	/	/	162.75
	S 2p _{1/2}	/		/	/	/	163.94

Table S4 FTIR peak locations (cm^{-1}) for the as-produced GNPs, GNPs after plasma/acid treatment, and the GNP-QD heterostructures.

bonds	GNPs	Plasma-treated GNPs	Acid-treated GNPs	GNP (plasma-treated)-QD heterostructures	GNP (acid-treated)-QD heterostructures
C-H, C-C stretch	1510-1540	1510-1540	1510-1540	1510-1540	1510-1540
C-O-H	~1450	~1450	~1450	~1450	~1450
C=O		~1690	~1690	~1690	~1690
Amide I (C=O stretch)				~1660	~1660
Amide II (C-N stretch, N-H bend)				~1550	~1550
Amide III (C-N stretch, N-H bend)				~1240	~1240

Table S5 UV-vis spectra peak locations (nm) for Au nanoparticles, as-produced GNPs, and GNPs after acid/plasma treatment.

	Au	Graphene	Quantum dots
Au nanoparticles	500-650	/	/
GNPs	500-650	~281	/
acid-treated GNPs	500-650	~292	/
plasma-treated GNPs	500-650	~284	/
Quantum dots	/	/	~460
GNP-QD heterostructures (covalently bonded)	~580	~305	~460
GNP-QD (physically mixed)	~550	~301	~460

Fig. S1 SEM image of the GNPs after (a) plasma and (b) acid treatment. (c) Histogram showing the variation of particle diameter, inter-particle spacing, and density of the Au nanoparticles, as-produced GNPs, and GNPs after plasma/acid treatment. **Table S1** corresponds to (c).

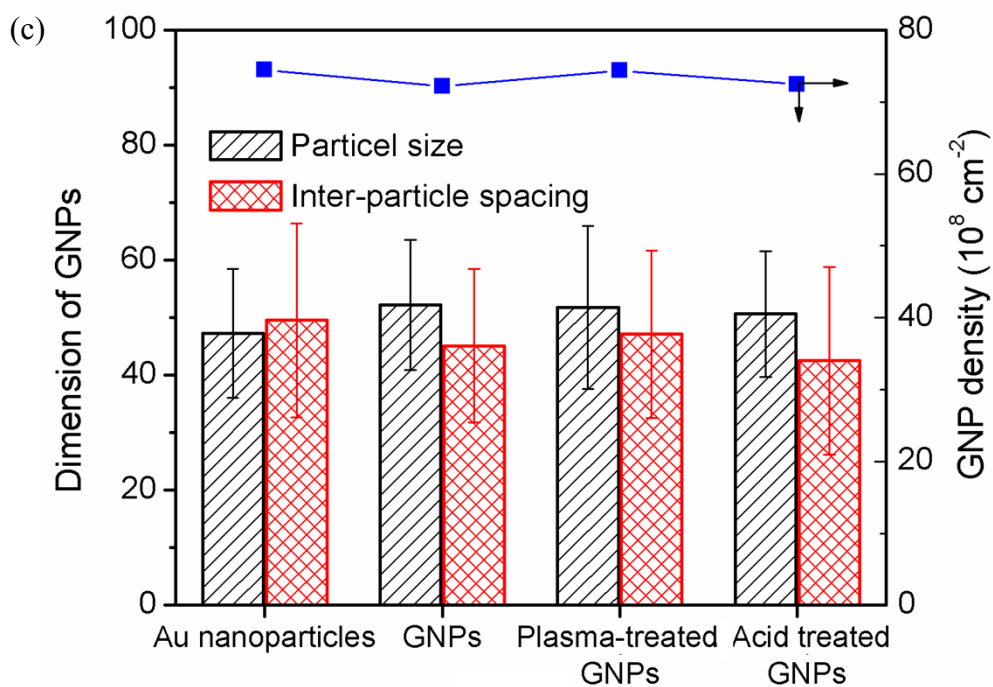
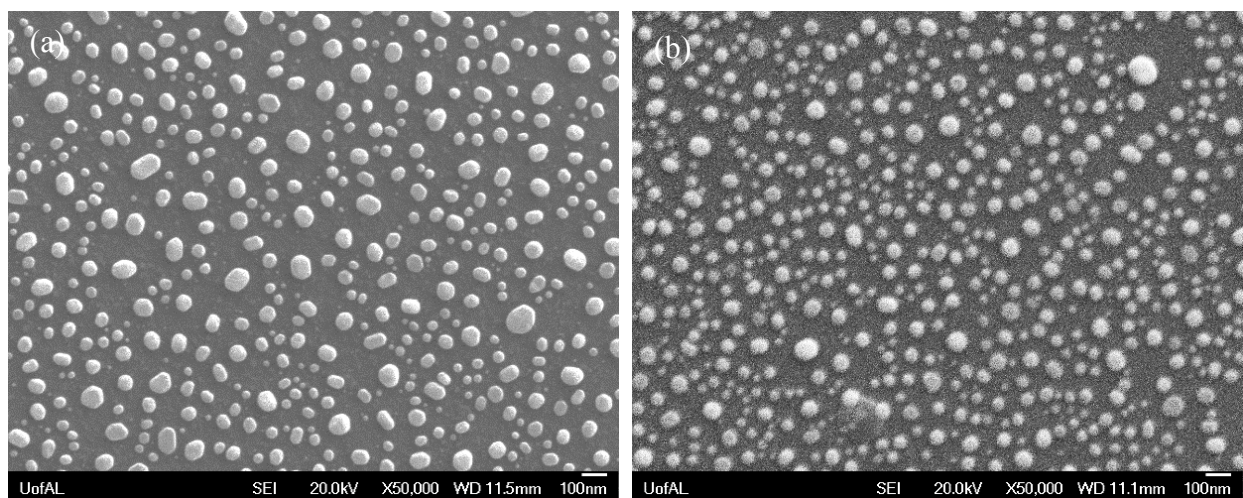


Fig. S2 XPS spectra obtained in a wide-range survey scan for the Au nanoparticles, as-produced GNPs, and GNPs after plasma/acid treatment.

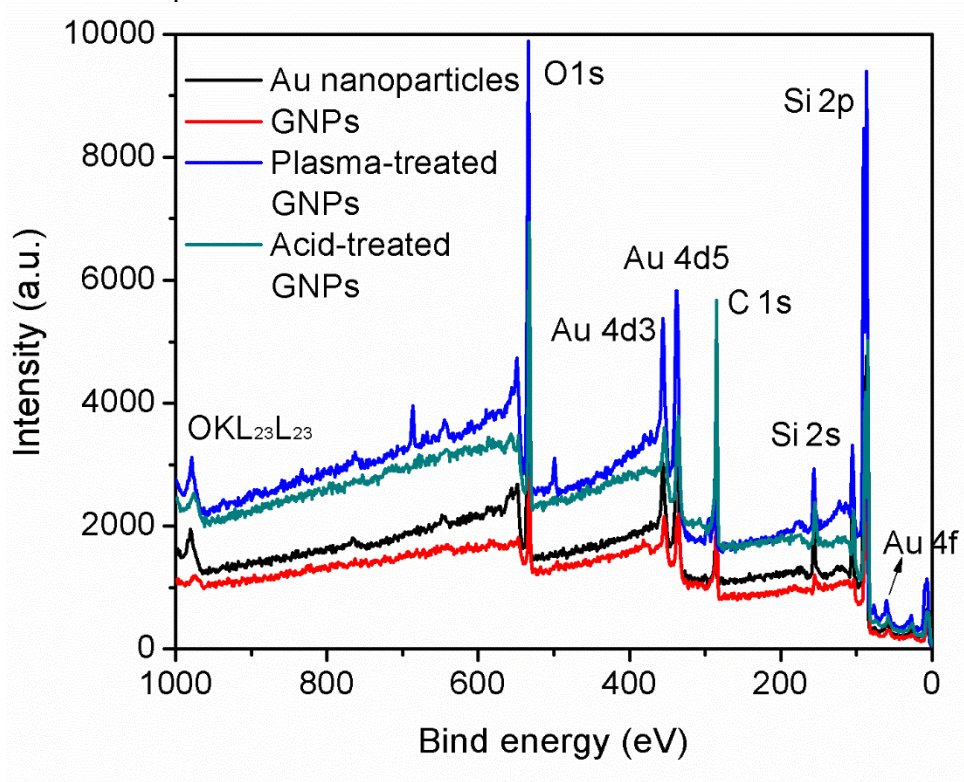


Fig. S3 Deconvoluted XPS spectra (Au 4f) for (a) Au nanoparticles, (b) plasma-treated Au nanoparticles (before GNP growth), (c) GNPs, and GNPs after (d) plasma and (e) acid treatment. *NOTE: Black scatters show the experimental spectra and the solid lines show the fitted data.*

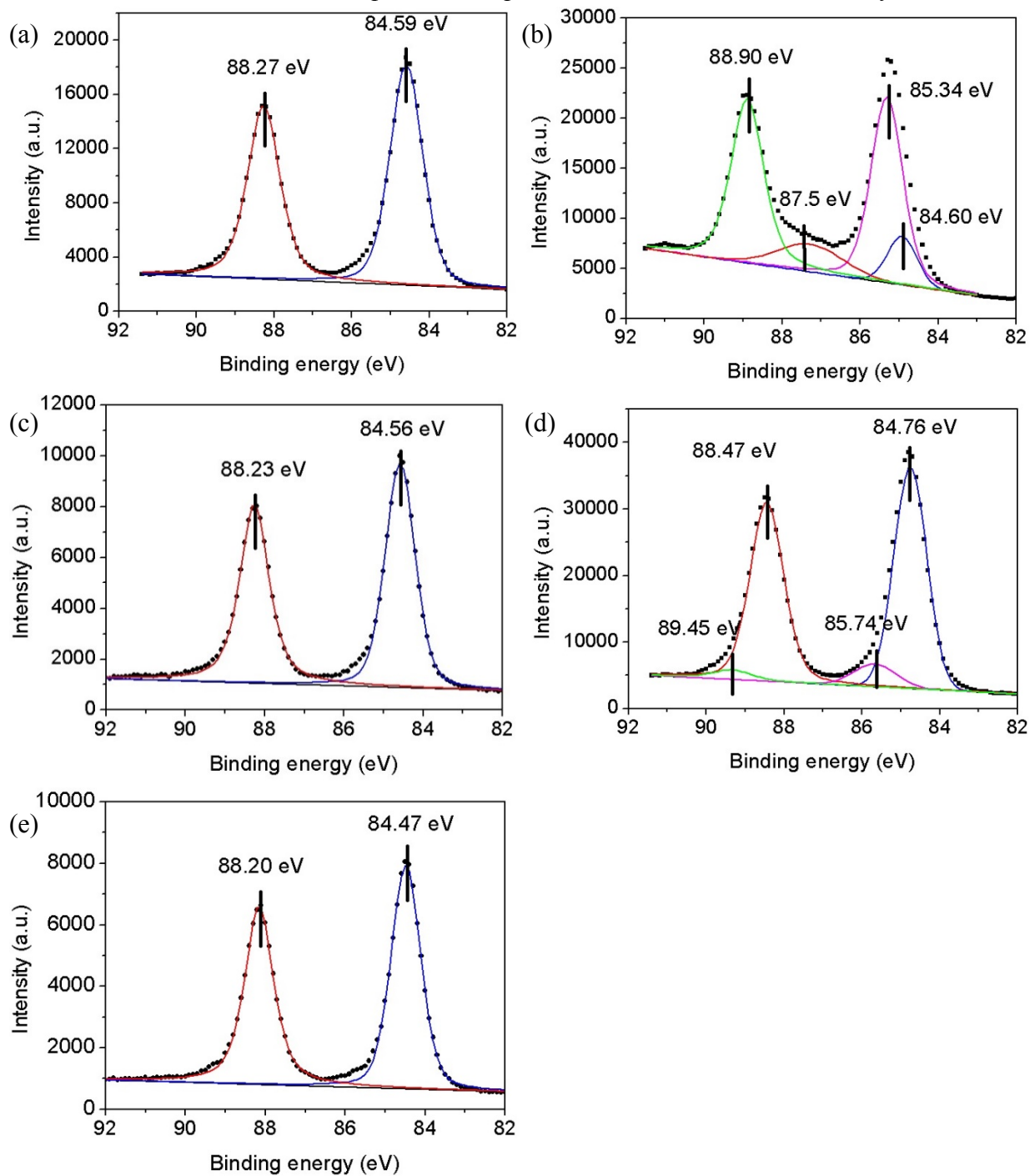


Fig. S4 TEM image of the pristine $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ quantum dots.

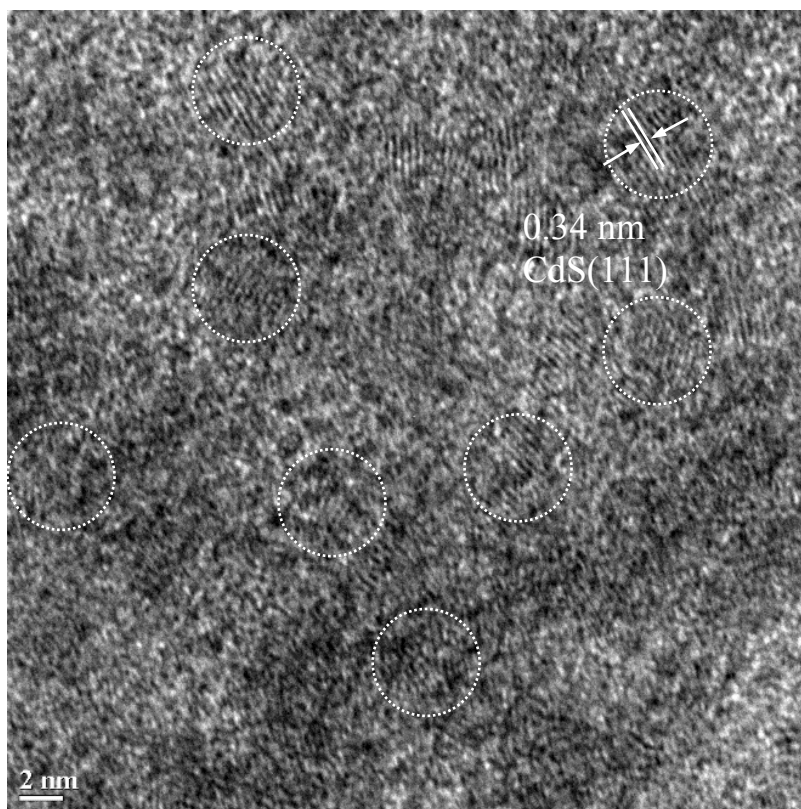


Fig. S5 XPS spectra (survey scan) of the pristine $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ quantum dots and GNP-QD heterostructures dispersed on the Si substrate. *Note: The dotted line indicate the expected peak for Se 3d.*

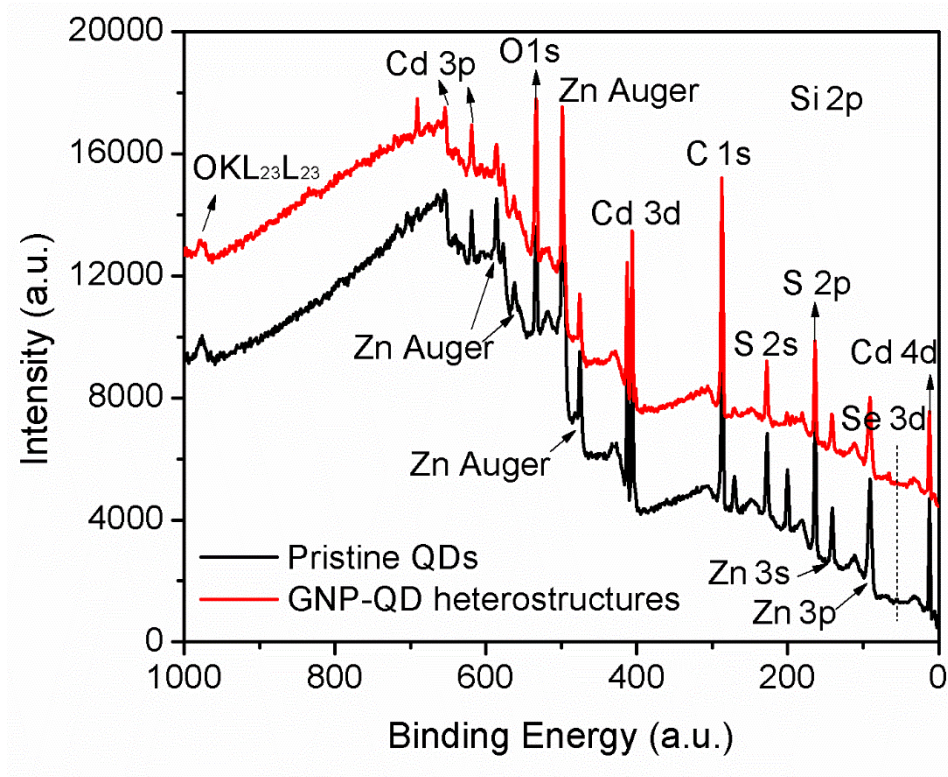


Fig. S6 Deconvoluted XPS spectra of the pristine $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ quantum dots corresponding to (a) Cd 3d, (b) Se 3d, (d) Zn 2p, (d) S 2p. *NOTE: Black scatters show the experimental spectra and the solid lines show the fitted data.*

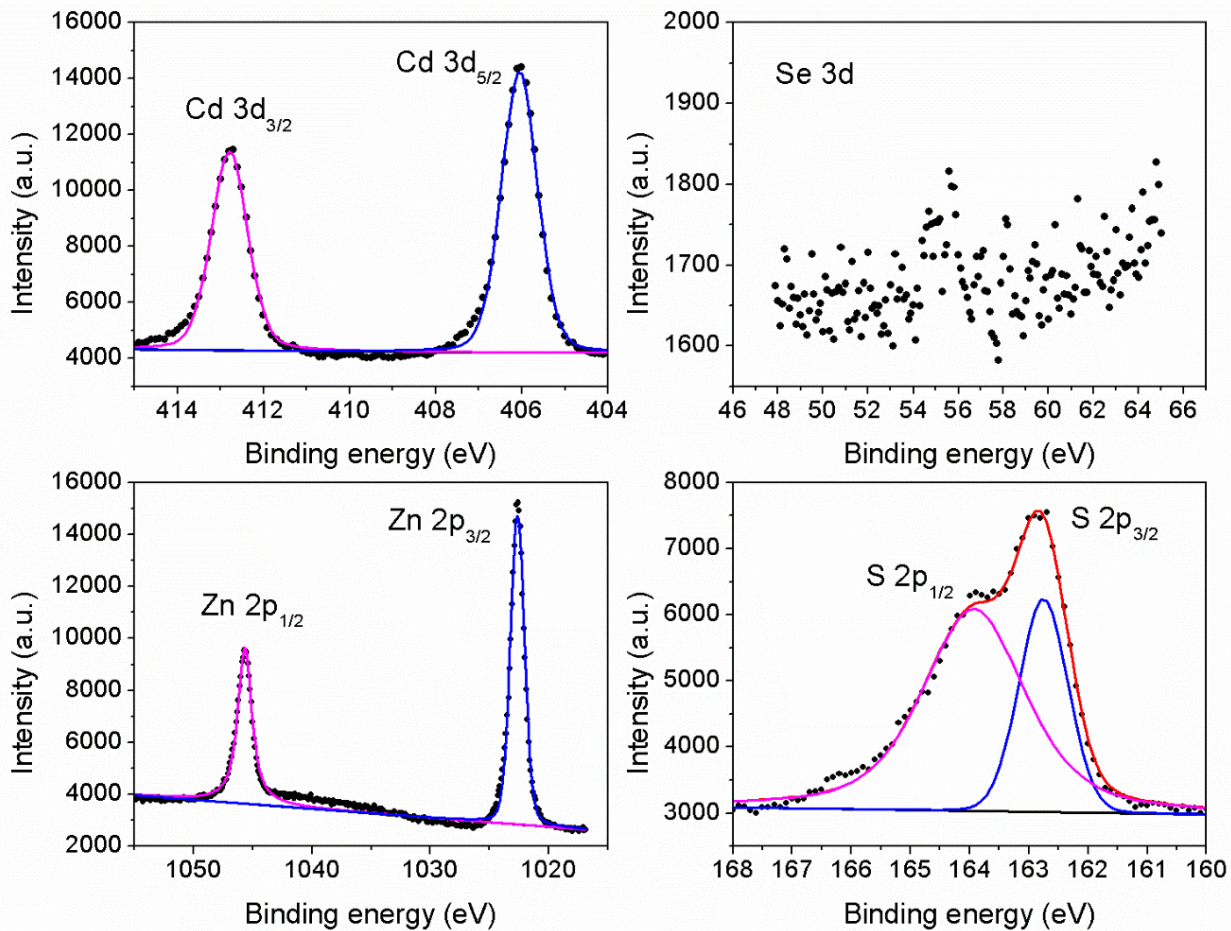


Fig. S7 Experimental (a) absorbance and (b) reflectance spectra of the pristine quantum dots dispersed on a flat white Teflon substrate. This was used to estimate the effective refractive index of the quantum dots.

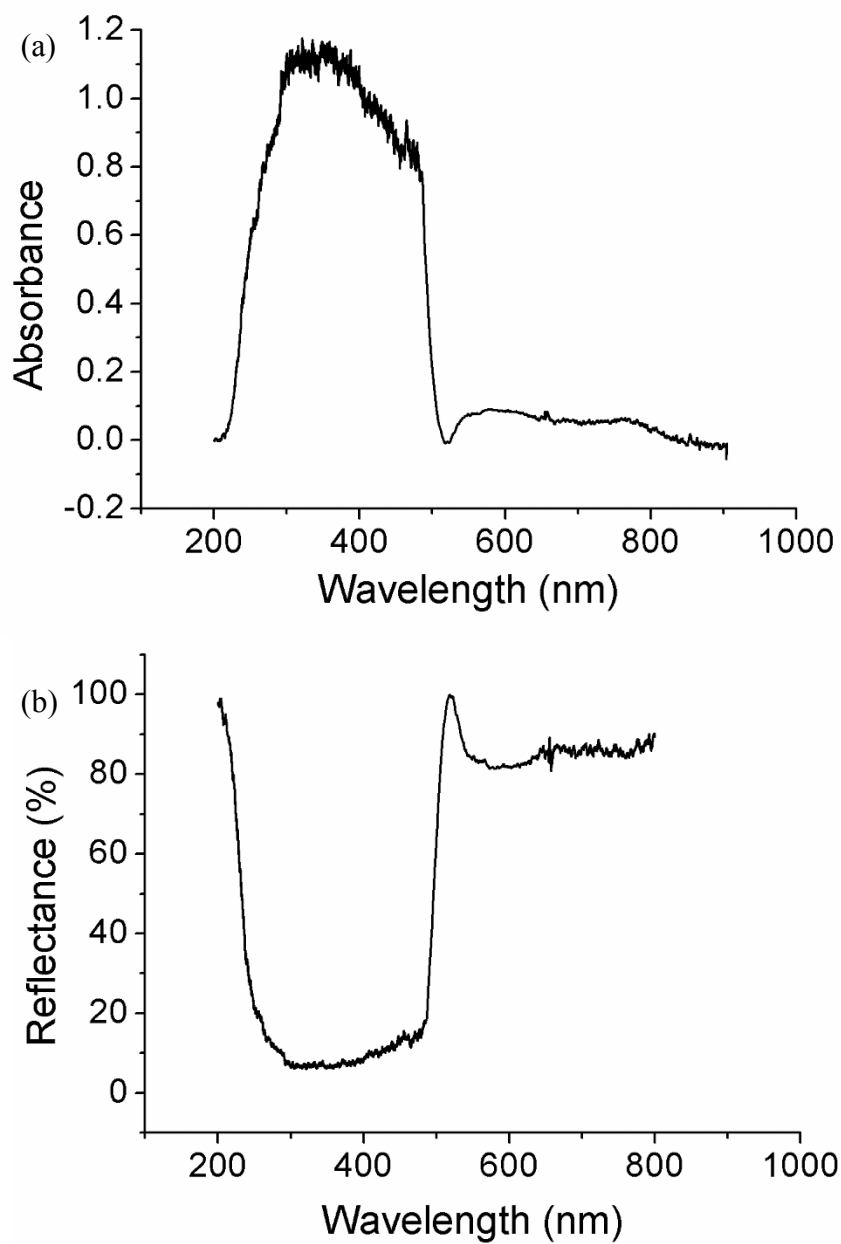


Fig. S8 Simulated (DDA method) extinction, absorbance, and scattering plots as a function of wavelength for (a) Au nanoparticles, (b) as-produced GNPs, (c) plasma-treated GNPs, and (d) GNP-QD heterostructures.

