

# Supporting Information

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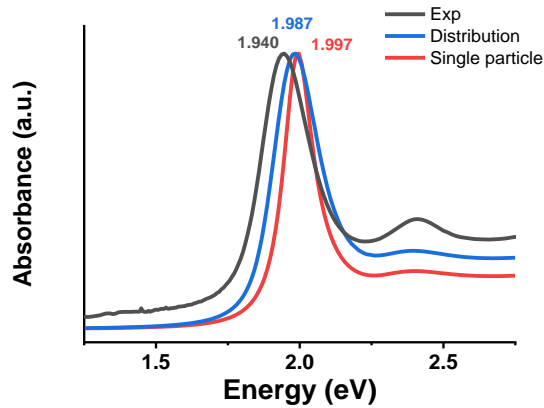


Figure S 1: Experimental LSPR spectrum (black line) of GNB particles with absorption maximum at 639 nm (i.e. 1.940 eV) compared with full-EM theoretical spectra computed using the full ensemble of the GNBs in the sample (blue line) and the an average single-particle model (red line). Both longitudinal and transverse components of LSPR absorption are computed to show proper comparison with the experimental spectrum.

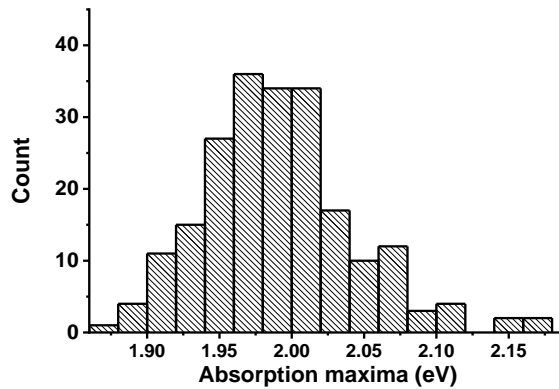


Figure S 2: Histogram representation of LSPR absorption maxima distribution for the full ensemble spectrum reported in Fig. S1

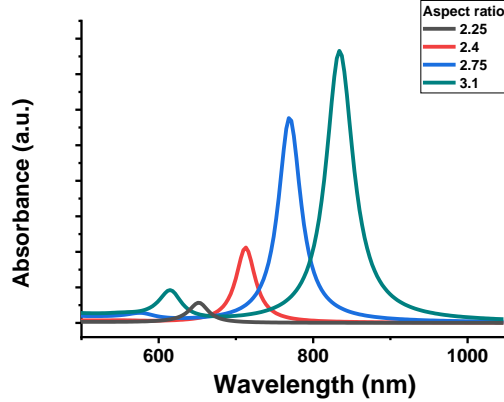


Figure S 3: Simulated absorption electronic spectra of GNBs featuring the various ARs reported in (a), including AR=2.25 (in dark gray), AR=2.40 (in red), AR=2.75 (in blue), AR=3.10 (in green), computed with the BEM approach and using the BCS model, showing the AR-dependent shifting of plasmon resonance and the increase of absorption intensity with the GNB size.

Table S 1: Comparison between full-EM simulations of different GNBs' models and experimental LSPR absorption maxima.

$w$ (nm)	11	15	22	25
$AR_{id}$	3.6	3.6	3.6	3.6
$AR$	2.25	2.4	2.75	3.1
Tip truncation	38%	27%	19%	11%

	Energies (eV)#			
EXP*	1.94 [640nm]	1.76 [705nm]	1.60 [775nm]	1.48 [840nm]
DDA*	1.84 (-0.10)	1.79 (+0.03)	1.60 (+0.00)	1.49 (+0.01)
BPS	1.83 (-0.11)	1.66 (-0.10)	1.53 (-0.07)	1.40 (-0.08)
BCS	1.91 (-0.03)	1.74 (-0.02)	1.61 (+0.01)	1.49 (+0.01)
BCF	1.88 (-0.06)	1.82 (+0.06)	1.67 (+0.07)	1.52 (+0.04)

\*from literature, see main text.

#experimental values in nm (in square brackets); deviations from experiments (in brackets)

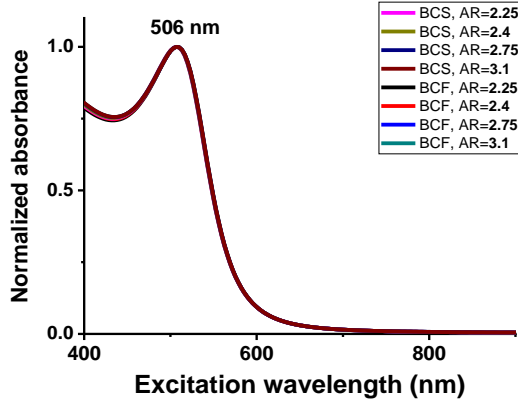


Figure S 4: Normalized absorption spectra polarized along the transverse axis for the four analyzed aspect ratios for both shapes 2 and 3 (bicone A and B). The peak at 506 nm is the transverse surface plasmon resonance. Here the absorption intensity was normalized to show how the size of the base and the shape of the tip do not influence the TSPR energy. The absorption at 506 nm is in very good agreement with the experimental value measured around 500 nm.

Table S 2: Geometrical parameters of GNBs extracted from TEM images reported in previous experimental work.

LSPR Abs. max.	$w$ (nm)	$AR$	$AR_{id}$	Tip truncation %
GNBs in Ref. <sup>1</sup>				
677	$18.1 \pm 0.9$	$2.39 \pm 0.10$	$3.67 \pm 0.24$	35%
698	$20.1 \pm 0.9$	$2.46 \pm 0.13$	$3.82 \pm 0.27$	34%
732	$36.3 \pm 2.0$	$2.73 \pm 0.13$	$3.86 \pm 0.29$	29%
GNBs in Ref. <sup>2</sup>				
639	$34.3 \pm 1.4$	$1.84 \pm 0.14$	$3.25 \pm 0.27$	44%
650	$36.7 \pm 2.6$	$2.08 \pm 0.14$	$3.16 \pm 0.51$	34%
650	$23.0 \pm 0.9$	$1.97 \pm 0.09$	$3.77 \pm 0.20$	48%
714	$21.9 \pm 0.8$	$2.78 \pm 0.09$	$4.38 \pm 0.24$	36%
787	$26.3 \pm 1.0$	$3.12 \pm 0.12$	$4.54 \pm 0.30$	31%

## References

- (1) Sánchez-Iglesias, A.; Winckelmans, N.; Altantzis, T.; Bals, S.; Grzelczak, M.; Liz-Marzán, L. M. High-Yield Seeded Growth of Monodisperse Pentatwinned Gold Nanoparticles through Thermally Induced Seed Twinning. *Journal of the American Chemical Society* **2017**, *139*, 107–110.
- (2) Chateau, D.; Desert, A.; Lerouge, F.; Landaburu, G.; Santucci, S.; Parola, S. Beyond the Concentration Limitation in the Synthesis of Nanobipyramids and Other Pentatwinned Gold Nanostructures. *Applied Materials & Interfaces* **2019**, *11*, 39068–39076.