Effect of Morphology on Ultrafast Carrier Dynamics In Asymmetric Gold-iron oxide Plasmonic Heterodimers

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Supporting information

(i) Morphology of gold-iron oxide heterodimers

An interesting feature of our gold-iron oxide heterodimers is that the gold domains are embedded in a thin iron oxide shell (thickness about ~1nm). This feature can be evidenced by leaching away the gold from the heterodimers using iodine, and recording TEM images, as shown in Figure 1S for dumbbell like and rod-like structures.[1,2]

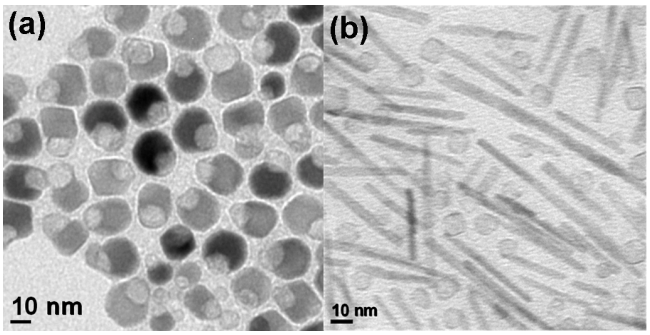

Figure S1 TEM images of dumbbell-like (a) and rod-like heterodimers, after the gold domain has been leached away.

(ii) Charge Transfer in gold nanocrystals

We simulated the effect of charge transfer on the static and dynamic spectra of gold nanocrystals, using a simple model based on the Mie theory.[3] The dielectric constant of gold was approximated by a sum of two contributions: an intraband one, which describes the response of the free electrons, and an interband one.[3,4] The reduction of the free electron density, caused by charge transfer, affects the dielectic constants in several ways. For simplicity, we took into account only the variation of the plasma frequency and of the Fermi energy. We neglected the effect of the reduced electron screening on the electron-electron scattering, because it mainly affects the width of the localized surface plasmon resonance, and not its central frequency. The results of the simulation are shown in Figure S2. In the top panel we reported the simulated static absorption spectrum of 10nm gold nanocrystals (blue curve, obtained by fitting real data) and the simulated curve after artificially reducing the electron density by 5% (green curve). In the bottom panel we reported the simulated transient absorption spectra, obtained

by assuming a 5 fold increase of the electron temperature and a 30% increase of the free electrons damping constant.[4]

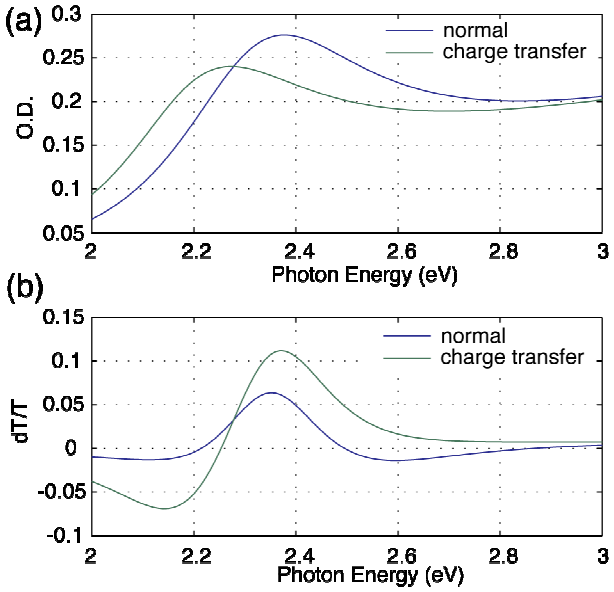

Figure S2. Simulation of the effect of reduced free electron density on the static (a) and transient (b) absorption spectra of a 10nm gold nanocrystal.

As it can be seen in Figure 1S, a reduction of the free electron density causes a red-shift of the static surface plasmon resonance and a blue-shift of the positive peak of the transient spectrum. It can also be noted that the low-enery negative peak of the transient spectrum becomes more prominent, as a result of the frequency shift.

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(3) Inouye, H.; Tanaka, K.; Tanahashi, I.; Hirao, K. Physical Review B 1998, 57, 11334–11340.

(4) Comin, A.; Korobchevskaya, K.; George, C.; Diaspro, A.; Manna, L. *Nano letters* **2012**, *12*, 921–6.