

Electronic Supplementary Information

Mechanistic insights into the photocatalytic properties of metal nanoclusters/graphene ensembles. The role of light on the reduction of 4-nitrophenol

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EXPERIMENTAL SECTION

General

All solvents and reagents were purchased from Aldrich and used without further purification unless otherwise stated. Steady state electronic absorption spectra were recorded on a Perkin-Elmer (Lambda 19) UV–Vis spectrophotometer. Steady state emission spectra were recorded on a Fluorolog-3 JobinYvon-Spex spectrofluorometer (model GL3-21). The light source used was a 500 W Xenon lamp, which was positioned 20 cm away from the reactor. Scanning transmission electron microscopy (STEM) analysis was performed on a JEOL JEM-2100F electron microscope equipped with double JEOL Delta spherical aberration correctors operated at an electron accelerating voltage of 60 kV. For the analysis, the samples were dropped onto a molybdenum microgrid coated with a holey amorphous carbon film. Energy dispersive X-ray spectroscopy (EDX) measurements were carried out using double JEOL Centurio detectors installed to the electron microscope.

Synthesis of M_{NCs}

Ag_{NCs}. The preparation of Ag_{NCs} was based on previously reported methods.¹⁻³ In a typical experiment, α -lipoic acid (19 mg, 0.09 mmol) was dissolved in HPLC grade H₂O (14 mL) were placed into a flask. Subsequently, NaBH₄ (7.0 mg, 0.18 mmol) was added dropwise under stirring until the solution became transparent (15 min). Afterwards, aqueous AgNO₃ (700 μ L, 25 mM) was added into the reaction mixture while stirring and the solution turned into dark red. To this mixture, an excess of a freshly prepared aqueous NaBH₄ (10 mg to 2 mL water) was added dropwise and a dark brown solution developed. The flask was wrapped with aluminium foil to minimize the influence of light. A bright orange solution obtained after 4-5 hours stirring at room temperature, indicating the completion of the Ag_{NCs} growth. The as-prepared Ag_{NCs} were stored in dark.

Au_{NCs}. The preparation of Au_{NCs} was adapted from previously described synthetic procedures.⁴⁻⁵ Typically, α -lipoic acid (6.2 mg, 30 μ mol) was dissolved in HPLC grade H₂O (20 mL), in which the pH was previously adjusted to 11 with aqueous NaOH (1M). Then, addition of an aqueous HAuCl₄ (4.2 mg in 200 μ L water) was followed and the reaction was stirred until the reaction mixture became colourless. Afterwards, a freshly prepared aqueous NaBH₄ (0.8 mg to 400 μ L water) was added dropwise and the solution

color immediately turned into brown. The reaction proceeded for 16 hours at room temperature and the solution colour changed from dark brown into pale brown indicating the effective growth of Au_{NCS}.

Functionalization of graphene

Initially, graphite powder was oxidized following a modified Hummers and Offeman's method.⁶ Then, oxidized graphene (20 mg) was activated by treatment with SOCl₂ (6 mL) at 70 °C for 24 hours under nitrogen atmosphere. After that period, the excess SOCl₂ was evaporated under reduced pressure and the remaining solid was washed with dry THF under nitrogen to remove residual SOCl₂. Afterwards, *N*-tert-butoxycarbonyl-2,2'-(ethylenedioxy)bis-(ethylamine) (300 mg) was added in dry THF (5 mL) and the reaction mixture was refluxed for 3 days. After that period, the reaction mixture was filtered over a PTFE membrane filter (0.2 μm pore size) and extensively washed with CH₂Cl₂ for several times to remove organic residues and dried at room temperature overnight under vacuum. Next, the material was dispersed in dry CH₂Cl₂ and treated with gaseous HCl to cleave the *N*-tert-butoxycarbonyl moieties and liberate free amine units. After a period of 24 hours, the solvent was evaporated to dryness and the solid material was washed with CH₂Cl₂ and dried to yield water-dispersible ammonium functionalized graphene *f*-G.

Preparation of M_{NCS}/*f*-G ensembles

An aqueous solution of M_{NCS} was titrated with aqueous *f*-G (1 mg/mL) and the formation of Ag_{NCS}/*f*-G and Au_{NCS}/*f*-G ensembles was verified by electronic absorption and fluorescence emission spectroscopy assays.

Catalytic reduction of 4-nitrophenol

In a typical experiment, 4-nitrophenol (20 μL, 3.6 mM), 42 μL Au_{NCS}/*f*-G (5:2 volume ratio) were dissolved in 3 mL water and excess NaBH₄ (10 mg) was introduced to the quartz cuvette under stirring. The progress of the reaction was monitored by UV-Vis absorption at different time intervals.

References

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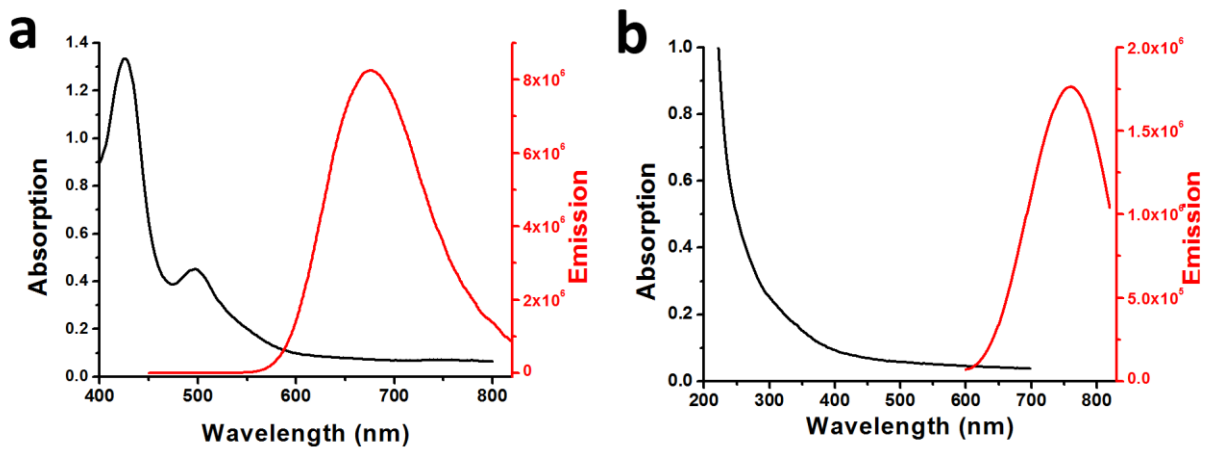


Figure S1. UV-Vis and photoluminescence spectra of (a) Ag_{NCs} (excitation wavelength 430 nm), and (b) Au_{NCs} (excitation wavelength 420 nm).

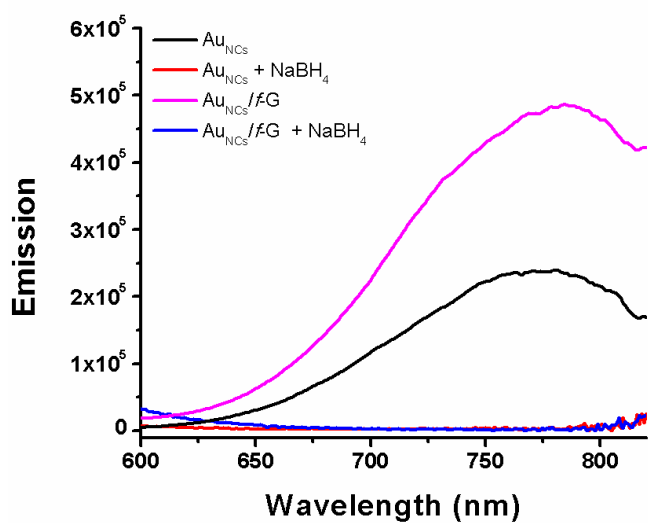


Figure S2. Photoluminescence spectra of Au_{NCS} (black) and $\text{Au}_{\text{NCS}}/f\text{-G}$ ensembles (pink) with and without NaBH_4 (red and blue), respectively. For the acquisition of the spectrum for $\text{Au}_{\text{NCS}}/f\text{-G}$ ensemble (pink) an additional $100\mu\text{L}$ Au_{NCS} was added to the stock quenched dispersion.

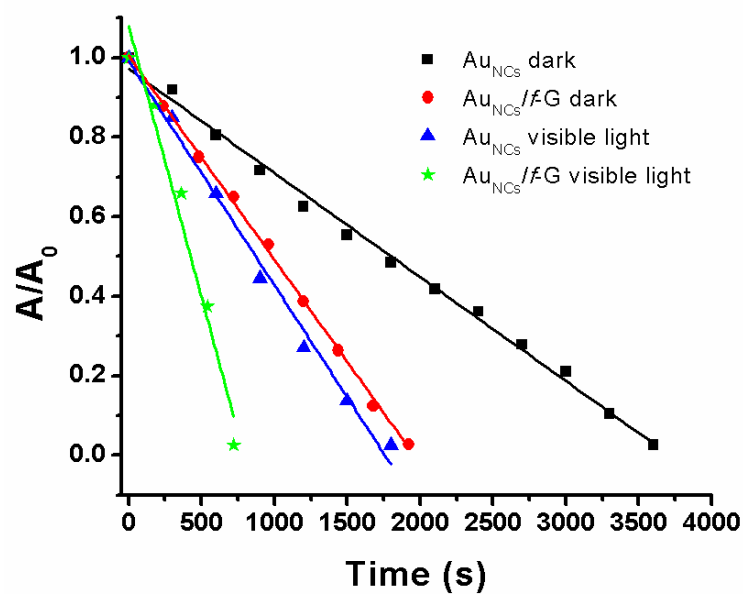


Figure S3. Kinetics for the reduction of 4-nitrophenol to 4-aminophenol, in the presence of bare Au_{NCs} (black, blue) and $Au_{NCs}/f-G$ (red, green) in the dark and under visible light illumination conditions, respectively, as monitored from the nitrophenol peak at 400 nm.

Table S1. Collective data known in literature for Au/graphene-based catalysts for the reduction of 4-nitrophenol (4-NP) to 4-animophenol in the absence and presence of light irradiation.

Reference	Metal Content	Graphene Content	NaBH ₄ quantity	4-NP	4-NP/Au (% w/w)	Photo catalysis	Mechanism	Time (min)	<i>k</i> (s ⁻¹)
This work	0.003 mg Au	0.012 mg	10 mg	0.1 mg	3%	YES	Zero-order	12	6.0x10 ⁻⁴ ^a
This work	0.003 mg Au	0.012 mg	10 mg	0.1 mg	3%	NO	Zero-order	32	1.4x10 ⁻³ ^a
<i>J. Mater. Chem.</i> 2012, 22 , 8426-8430.	0.024 mg Au	0.076 mg	0.076 mg	0.039 mg	61%	NO	Pseudo-first	12	3.17x10 ⁻³
<i>Catal. Sci. Technol.</i> 2011, 1 , 1142-1144.	0.14 mg Au	-	6.05 mg	0.97 mg	14%	NO	Pseudo-first	27	0.002
<i>Catal. Sci. Technol.</i> 2011, 1 , 1142-1144.	0.14 mg Au	0.5 mg	6.05 mg	0.97 mg	14%	NO	Pseudo-first	18	0.003
<i>ACS Appl. Mater. Interfaces</i> 2012, 4 , 5472-5482.	12 mg AuNPs	1.32 g	18.915 mg	0.0974 mg	12320%	NO	Pseudo-first	5	0.14x10 ⁻³
<i>RSC Adv.</i> 2016, 6 , 35945-35951.	0.5 mg Au	2.8 mg	0.1135 mg	0.21 mg	238%	NO	Pseudo-first	7	9.87x10 ⁻³
<i>RSC Adv.</i> 2016, 6 , 64028-64038.	4.78 mg Au	-	47 mg	0.347 mg	1377%	NO	Pseudo-first	39	N/A
<i>RSC Adv.</i> 2016, 6 , 64028-64038.	4.78 mg Au	25 mg	47 mg	0.347 mg	1377%	NO	Pseudo-first	18	0.003
<i>Pol. J. Chem. Tech.</i> 2016, 18 (4), 47-55.	8 mg Au	8 mg	7.566 mg	0.417 mg	1918%	NO	Pseudo-first	50	0.4x10 ⁻³
<i>Pol. J. Chem. Tech.</i> 2016, 18 (4), 47-55.	8 mg Ag	8 mg	7.566 mg	0.417 mg	1918%	NO	Pseudo-first	50	0.7x10 ⁻³
<i>Appl. Surf. Sci.</i> 2016, 389 , 1050-1055.	1.64 mg Au + 0.89 mg Ag	-	0.075 mg	1.95 mg	130%	NO	Pseudo-first	6	3.47x10 ⁻³
<i>Appl. Surf. Sci.</i> 2016, 389 , 1050-1055.	1.64 mg Au + 0.89 mg Ag	0.83 mg	0.075 mg	1.95 mg	130%	NO	Pseudo-first	6	6.83x10 ⁻³

^a The reaction rate coefficient is expressed in M s⁻¹.