Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

Controllable coating and reshaping of gold nanorods with tetracyanoquinodimethane

Jaedeok Lee, Hyoseong Lee, Collins Kiguye, Cheongwon Bae and Juyeong Kim*

Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University, Jinju 52828, South Korea

*To whom correspondence should be addressed. Email: chris@gnu.ac.kr

Materials and Methods

Figures S1-S8

Table S1

References

Materials and Methods

Section 1. Chemicals

Sodium borohydride (99%, $NaBH_4$, Sigma-Aldrich), L-ascorbic acid (BioXtra, 99%, $C_6H_8O_6$, Sigma-Aldrich), gold(III) chloride trihydrate (99.9%, $HAuCl_4 \cdot 3H_2O$, Sigma-Aldrich), gold(III) chloride trihydrate (≥49.0%, $HAuCl_4 \cdot 3H_2O$, Sigma-Aldrich), silver nitrate (99.0%, $AgNO_3$, Sigma-Aldrich), cetyltrimethylammonium bromide (99.9%, $C_{19}H_{42}BrN$, Sigma-Aldrich), sodium iodide (99.999%, NaI, Sigma-Aldrich), 7,7,8,8-tetracyanoquinodimethane (98%, $C_{12}H_4N_4$, Sigma-Aldrich), hexadecylpyridinium chloride monohydrate (98%, $C_{21}H_{38}ClN \cdot H_2O$, TCI), hexadecyltrimethylammonium chloride (95%, $C_{19}H_{42}ClN$, TCI), potassium bromide (99%, KBr, Sigma-Aldrich), sodium hydroxide (99.99%, NaOH, Sigma-Aldrich), lithium iodide (99.9%, LiI, Sigma-Aldrich), ethyl ether (99.0%, $C_4H_{10}O$, Daejung) and acetonitrile (99.8%, CH_3CN, Daejung) were purchased and used without further purification. All glassware was treated with aqua regia (a mixture of HCl and HNO_3 with a volume ratio of 3:1), thoroughly rinsed with water, and dried immediately before use. Nanopure water (18.2 MΩ·cm at 25 ℃) purified by a Merck Millipore Direct Q3 UV Water Purification System was used for all washing and solution preparation.

Section 2. Synthesis of gold nanoparticles

2.1. Nanorods

Gold nanorods were prepared according to a literature method.[1,2] To synthesize gold seeds first, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (10 mM, 125 μL, 99.9%) was added to 5 mL of 100 mM cetyltrimethylammonium bromide (CTAB) and mixed well. While the mixture was stirred vigorously at 1150 rpm, an ice-cold $NaBH_4$ (10 mM, 300 μL) was injected quickly into the solution. It was stirred for 1 min, and the solution was aged at 30 ℃ for 20 min. Then, aqueous solutions of $HAuCl_4 \cdot 3H_2O$ (10 mM, 10 mL, 99.9%), $AgNO_3$ (10 mM, 1.8 mL) and ascorbic acid (100 mM, 1.14 mL) were added in sequence into 200 mL of 100 mM CTAB in a 250 mL flask while stirred mildly at 30 ℃. The gold seed solution (240 μL) was added to the mixture while it was stirred at 500 rpm, and the solution was left undisturbed for 2 h. After that, the brown solution was divided into six 50 mL centrifuge tubes, and they were centrifuged at 8000 rpm for 15 min. Supernatant was removed as much as possible, and ~36 mL of 50 mM CTAB was added to the concentrated solution combined from the six centrifuge tubes. The solution was centrifuged at 8000 rpm for 15 min. Supernatant was removed as much as possible, and 5 mL of 50 mM CTAB was added to the concentrated solution and mixed well in a 15 mL centrifuge tube. Note that there could be slight deviation on the gold nanorod dimension from batch to batch. In the main text, the gold nanorods (length = 52.2 ± 3.4 nm and width = 13.5 ± 0.9 nm) used in the reaction time study (Fig. 2a-c) were slightly smaller than those (length = 55.0 ± 3.3 nm and width = 15.4 ± 1.4 nm) used in the aging time study (Fig.1 and Fig. 2d-f). We did not observe any significant effect on the tetracyanoquinodimethane (TCNQ) coating from such dimensional difference.

2.2. Nanospheres

Gold nanospheres were obtained by etching gold nanorods.[1,2] Gold nanorods (4.8 mL) with an extinction of ~49

prepared in Section 2.1 was mixed well with 113.8 mL of 50 mM CTAB in a 250 mL flask at 40 ℃. While the solution was stirred at 300 rpm, an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (10 mM, 949 μL, 99.9%) was added to the mixture. It was stirred at 200 rpm for 4 h. After that, the light red solution was divided into six 15 mL centrifuge tubes and centrifuged at 10000 rpm for 45 min. Supernatant was removed as much as possible, and 5 mL of 100 mM hexadecylpyridinium chloride monohydrate (CPC) was added into each concentrated solution and mixed well. They were centrifuged at 10000 rpm for 30 min. Supernatant was removed as much as possible, and all concentrated solutions were combined and stored in 5 mL of 100 mM CPC. The UV-visible spectrum of the gold nanospheres has a highest peak at 523 nm with an extinction of ~1.

2.3. Nanocubes

Gold nanocubes were prepared by a seeded growth method.[1,2] Aqueous solutions of KBr (100 mM, 500 μL), $HAuCl_4 \cdot 3H_2O$ (10 mM, 100 μL, 99.9%) and ascorbic acid (100 mM, 150 μL) were added in sequence into 5 mL of 100 mM CPC in a 20 mL vial and mixed well. Then, gold nanospheres (100 μL) with an extinction of ~1 prepared in Section 2.2 was added to the mixture and left undisturbed for 1 h. It was centrifuged at 5000 rpm for 8 min. Supernatant was removed as much as possible, and 5 mL of 50 mM CTAB was added and mixed well. It was centrifuged at 3750 rpm for 8 min. Supernatant was removed as much as possible, and it was stored in 5 mL of 50 mM CTAB. The UV-visible spectrum of the gold nanocubes has a highest peak at 550 nm with an extinction of ~1.2.

2.4. Nanoprisms

Gold nanoprisms were prepared by a seedless method.[3] Aqueous solutions of hexadecyltrimethylammonium chloride (CTAC, 100 mM, 1.6 mL), $HAuCl_4 \cdot 3H_2O$ (2.54 mM, 80 μL, ≥49.0%), NaI (10 mM, 75 μL) and NaOH (100 mM, 20 μL) were added in sequence into 8 mL of deionized water in a 20 mL vial and mixed well. Then, aqueous solutions of ascorbic acid (64 mM, 80 μL) and NaOH (100 mM, 10 μL) were added in sequence into the mixture and mixed well for ~2 s. The solution was left undisturbed for 8 min and centrifuged at 6000 rpm for 8 min. Supernatant was removed as much as possible, and 9 mL of deionized water was added and mixed well. The solution was centrifuged at 4000 rpm for 8 min. Supernatant was removed as much as possible, and it was mixed with 3 mL of deionized water. For purification to separate nanoprisms from spherical impurities, an aqueous solution of CTAC (200 mM, 5.57 mL) was added into the as-prepared prism solution and mixed well. The CTAC concentration was adjusted to 130 mM to induce depletion attraction of the nanoprisms. The mixture was left undisturbed overnight until it turned purple. Supernatant was gently removed as much as possible, and the sediment at the bottom of the centrifuge tube was mixed with 0.5 mL of deionized water. The green solution was transferred to a new 15 mL centrifuge tube, mixed with 1 mL of deionized water and 1.5 mL 100 mM CTAC (final CTAC concentration = 50 mM for storage). The UV-visible spectrum of the gold nanoprisms has a highest peak at 665 nm with an extinction of ~0.9.

Section 3. TCNQ coating

3.1. Synthesis of Li(TCNQ)

Li(TCNQ) was synthesized according to a literature method.[4,5] TCNQ (1.02 g) was refluxed in 100 mL of dry acetonitrile at 90 ℃ under nitrogen. LiI (2.00 g) was refluxed in 5 mL of dry acetonitrile at 90 ℃ under nitrogen. While the two solutions were refluxed, the LiI solution was transferred into the TCNQ solution through a Teflon tubing. The mixture was stirred for 5 min under nitrogen and cooled down to room temperature. It was filtered and washed with acetonitrile and ethyl ether. Purple-green powder was collected and dried under vacuum overnight. Yield: 0.90 g (85%). Anal. Calcd (Found) for $C_{12}H_4N_4Li$: C, 68.27 (68.92); H, 1.91 (1.90); N, 26.54 (27.39)

3.2. TCNQ coating procedure

An aqueous solution of 200 μM Li(TCNQ) was prepared by dissolving 0.0106 g of Li(TCNQ) in 250 mL of deionized water. The TCNQ solution was wrapped with an aluminum foil to prevent from light exposure and left undisturbed for two days. Due to the high concentration of Li(TCNQ), yellow crystals were formed during the aging time and the solution turned blue. The yellow crystals were separated by centrifugation at 10000 rpm for 3 min before the reaction with gold nanorods. The purified blue solution was stored under dark.

To coat gold nanorods with TCNQ, the high CTAB concentration of the gold nanorod solution was first reduced. The gold nanorod solution (473 μL) in 50 mM CTAB was diluted with 8.53 mL of 50 mM CTAB. The diluted solution was centrifuged at 8000 rpm for 10 min. Supernatant was removed as much as possible, and 9 mL of deionized water was added and mixed well. It was centrifuged at 8000 rpm for 10 min, and supernatant was removed down to ~20 μL. The concentrated gold nanorod solution (20 μL) was injected rapidly into 5 mL of the TCNQ solution in a 20 mL vial while stirred at 600 rpm. The solution turned from bright blue to dark blue, and it was stirred for 4 h. After that, the solution was centrifuged at 7000 rpm for 3 min. Supernatant was removed as much as possible, and 1 mL of deionized water was added to the concentrated solution. The UV-visible spectrum of the TCNQ-coated gold nanorods has a highest peak at 783 nm.

The CTAB concentration effect (Fig. S3) was performed by adjusting the final CTAB concentration in the mixture between the TCNQ solution and the gold nanorods to 100 μM and 500 μM, respectively. The other procedures were fixed the same as mentioned in the previous paragraph.

The TCNQ coating on different gold nanoparticle shapes (Fig. S8) was performed the same as mentioned above with different particle concentrations (nanocubes = 0.32, nanoprisms = 1.03 and nanospheres = 0.17 in extinction). Also, centrifugation speed was adjusted the same as used in each particle synthesis (Section 2).

Section 4. Characterisation

A FEI Tecnai 12 transmission electron microscope with a LaB_6 emitter at 120 kV and a FEI Tecnai TF30ST transmission electron microscope with a ZrO/W(100) Schottky emitter at 300 kV were used for nanoparticle characterisation. Samples with uncoated gold nanoparticles were prepared by centrifugation in order to reduce the surfactant concentration to ~0.5 mM and to increase the particle concentration, and 10 μL was dropped on a transmission electron microscopy (TEM) grid (Electron Microscopy Sciences, CF400-CU) and dried for 2 h at an

ambient condition before TEM imaging. For TCNQ-coated nanoparticles, 10 μL of as-prepared product solution was dropped on a TEM grid and dried under vacuum for 30 min.

A UV-3600 Plus UV-VIS-NIR Spectrophotometer (Shimadzu Corporation) with a quartz cuvette (path length = 1 cm) was used for measuring extinction of nanoparticles in the solution phase. Solid samples (Fig. 1f) were measured using a UV-2600 UV-VIS Spectrophotometer (Shimadzu Corporation). TCNQ-coated gold nanorods in deionized water was centrifuged at 7000 rpm for 3 min. Supernatant was removed, and the wet product was dried under vacuum overnight. The dried product was mixed with KBr, measured in the UV-2600 UV-VIS Spectrophotometer. Uncoated gold nanorods were prepared via the same preparation method.

A Horiba Jobin-Yvon LabRAM HR800 Raman Spectrophotometer was used to measure vibrational frequency of the TCNQ coating layers (Fig. 1g). Samples were prepared as mentioned in the previous paragraph without KBr and placed on a slide glass for the measurement. A Malvern Zetasizer Nano ZS was used to measure zeta potentials. To remove any remaining ions after the reaction, samples were centrifuged one more time and dispersed in deionized water before the measurement.

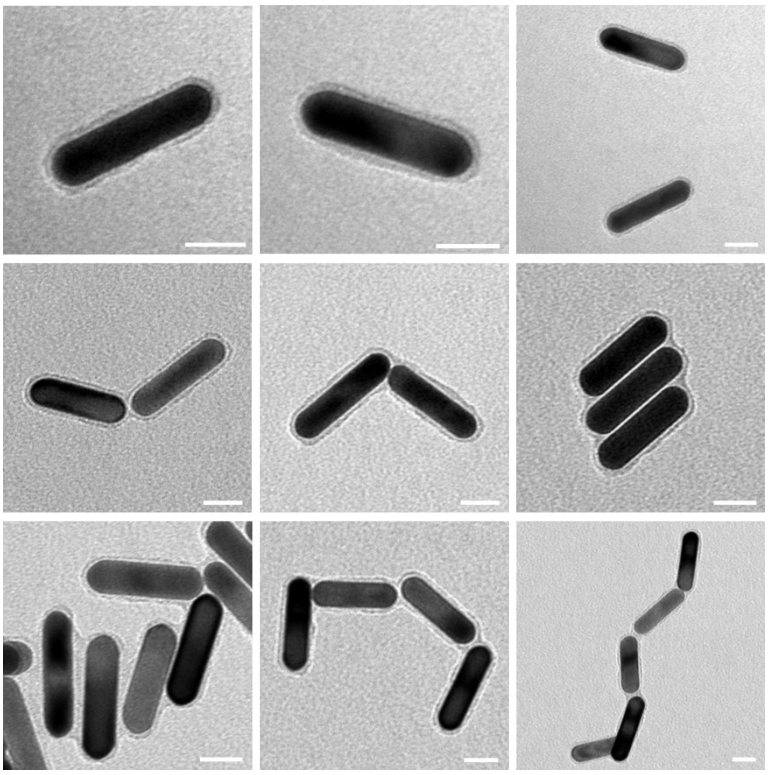

Figure S1. TEM images of TCNQ-coated gold nanorods. The coating was performed with 2-day aged TCNQ solution. Scale bars: 20 nm.

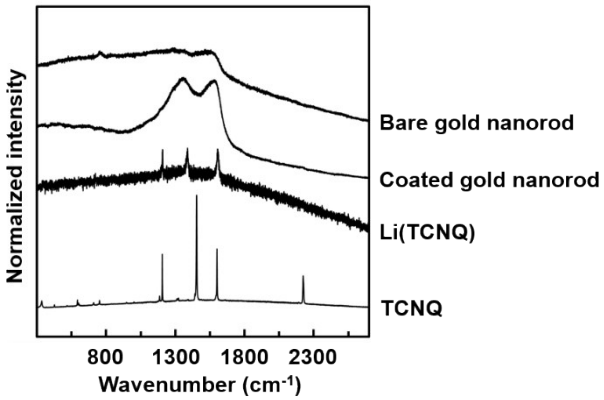

Figure S2. Raman spectra of TCNQ, Li(TCNQ), TCNQ-coated gold nanorods and bare gold nanorods. All spectra are normalized for simplicity.

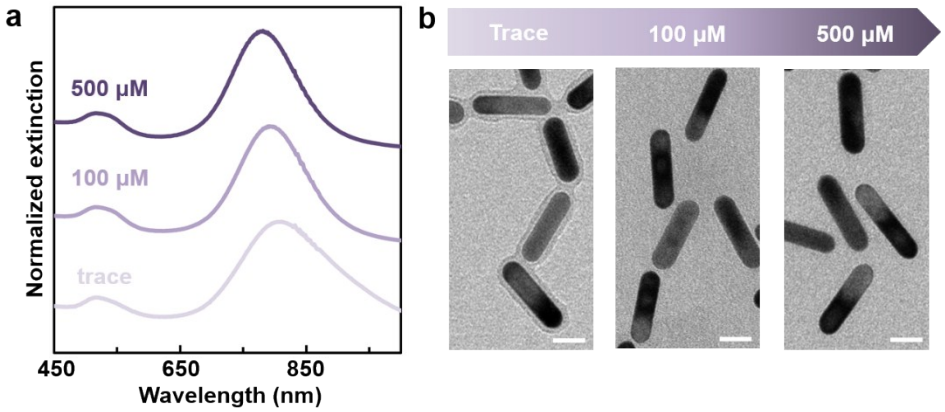

Figure S3. (a) UV-visible spectra of gold nanorods after reaction with Li(TCNQ) in the presence of CTAB (trace, 100 µM and 500 µM). All spectra are normalized for simplicity. (b) Representative TEM images of gold nanorods after reaction with Li(TCNQ) in the presence of CTAB (trace, 100 µM and 500 µM). Scale bars: 20 nm.

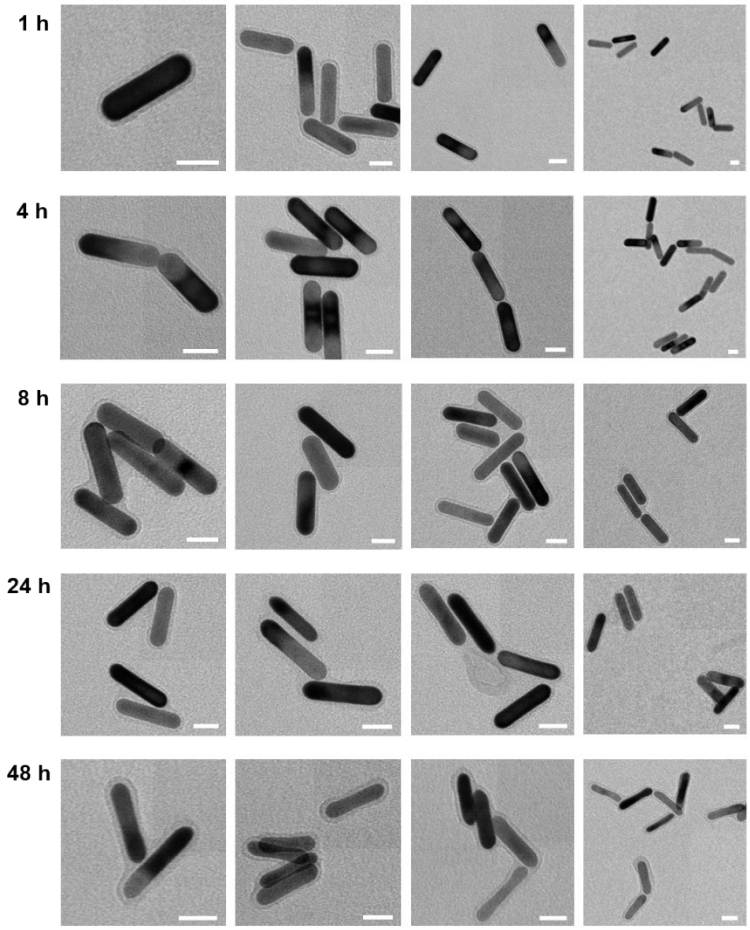

Figure S4. TEM images of TCNQ-coated gold nanorods at different reaction times (1 h, 4 h, 8 h, 24 h and 48 h). Scale bars: 20 nm.

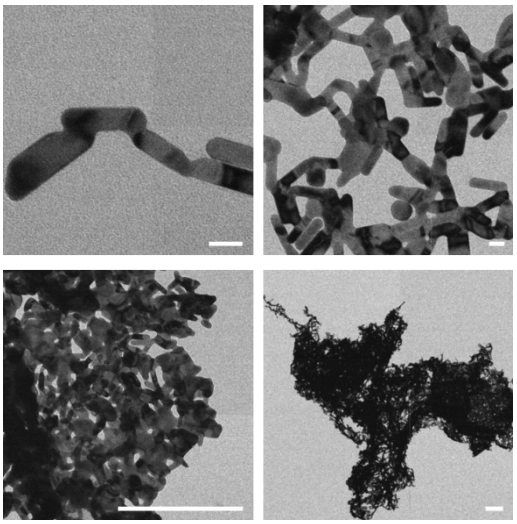

Figure S5. TEM images of gold nanorods after stirred for 48 h without Li(TCNQ). Scale bars: 20 nm (upper row) and 300 nm (bottom row).

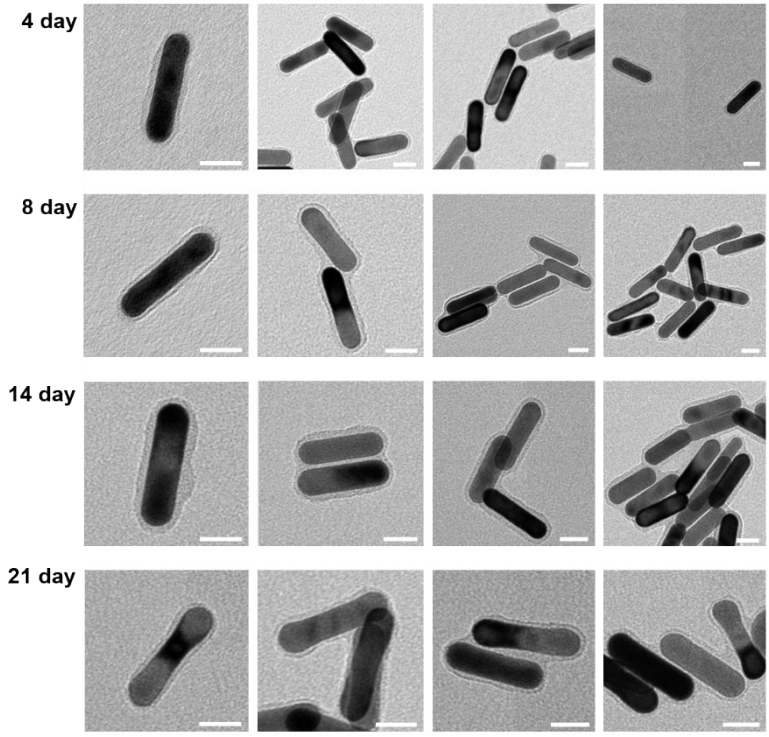

Figure S6. TEM images of TCNQ-coated gold nanorods after reaction with Li(TCNQ) aged for 4 day, 8 day, 14 day and 21 day. Scale bars: 20 nm.

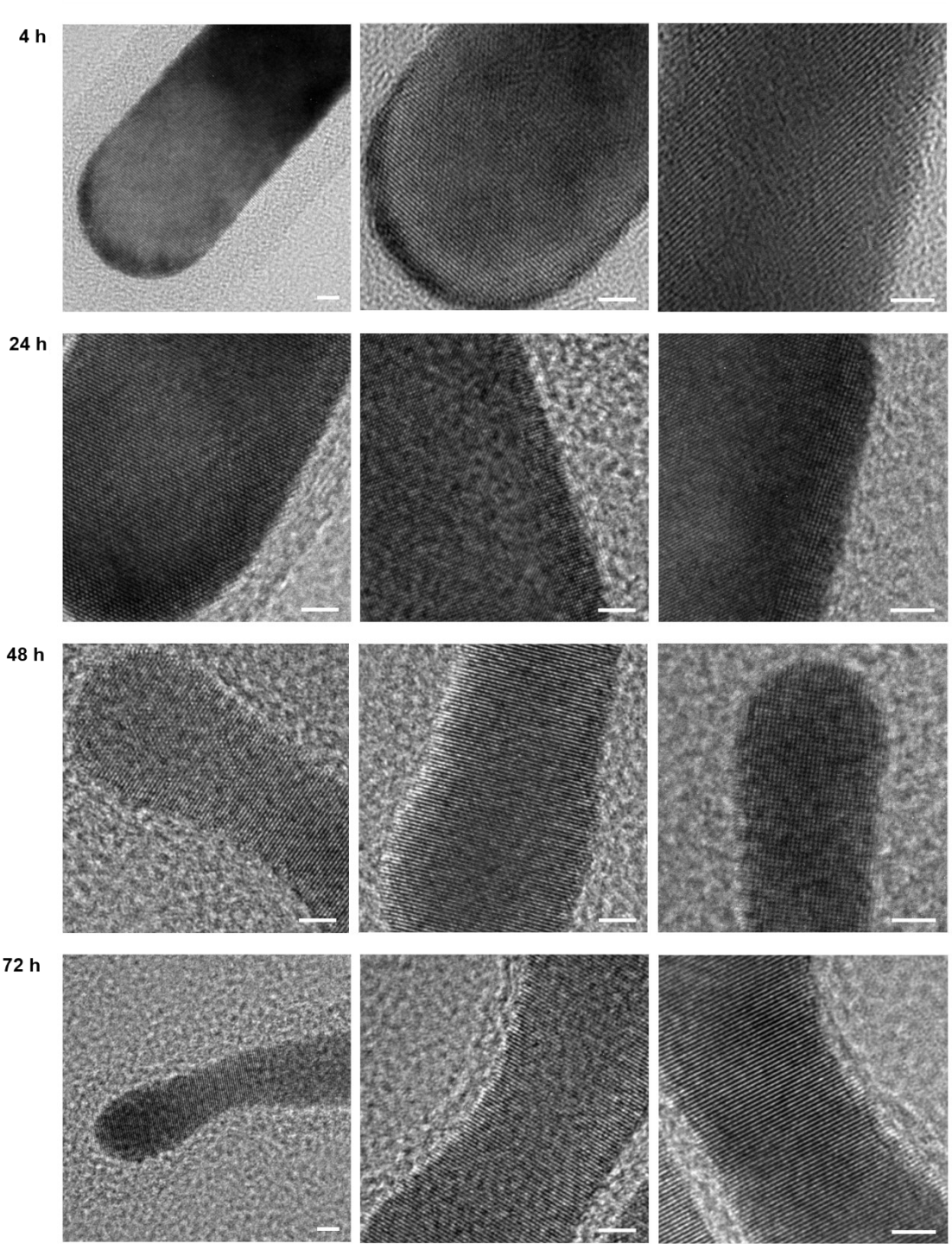

Figure S7. High-resolution TEM images of TCNQ-coated gold nanorods at different reaction times (4 h, 24 h, 48 h and 72 h). Scale bars: 2 nm.

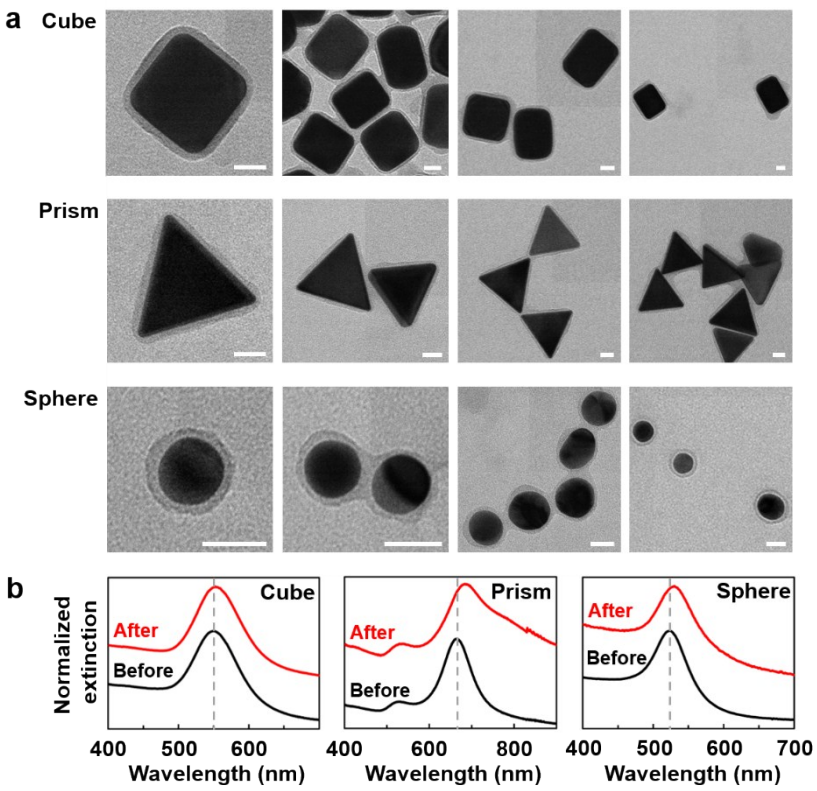

Figure S8. (a) TEM images of TCNQ-coated gold nanocubes, nanoprisms and nanospheres. (b) UV-visible spectra of gold nanocubes, nanoprisms and nanospheres before (black) and after (red) the TCNQ coating. All spectra are normalized for simplicity. The dotted grey lines are a guide to the eye. Scale bars: 20 nm.

Table S1. Zeta potential measurements of uncoated gold nanorods and TCNQ-coated gold nanoparticles.

Sample name	Zeta potential (mV)
Gold nanorods in 0.1 μM CTAB	53.1
TCNQ-coated gold nanorods	-24.5
TCNQ-coated gold nanocubes	-33.5
TCNQ-coated gold nanoprisms	-38.7
TCNQ-coated gold nanospheres	-38.9

References

1 M. N. O'Brien, M. R. Jones, K. A. Brown and C. A. Mirkin, *J. Am. Chem. Soc.*, 2014, **136**, 7603.

2 J. Kim, X. Song, A. Kim, B. Luo, J. W. Smith, Z. Ou, Z. Wu and Q. Chen, *Macromol. Rapid Commun.*, 2018, **39**, 1800101.

3 J. Kim, X. Song, F. Ji, B. Luo, N. F. Ice, Q. Liu, Q. Zhang and Q. Chen, *Nano Lett.*, 2017, **17**, 3270.

4 L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, 1962, **84**, 3374.

5 J. Kim, A. Silakov, H. P. Yennawar and B. J. Lear, *Inorg. Chem.*, 2015, **54**, 6072.