SUPPORTING INFORMATION

Preparation of modified oligonucleotides and AuNP modified with DNA

The modified oligonucleotides were prepared according to standard phosphoramidite chemistry using a DNA synthesizer (ABI 3400, Applied Biosystems) with Glen Research reagents. The synthesized oligonucleotides were detached from the CPG support in concentrated aqueous ammonia at room temperature, then deprotected by heating the solution at 60 °C for 8 hours. After removal of the ammonium solution, the residue was purified by reverse-phase HPLC using an ODS column (4.6 × 150 mm) using a linear gradient of 50 mM ammonium formate and CH_3CN. The thiol groups were attached to the 5'-end of DNA using a thiol modifier. The PDI-conjugated DNAs were prepared according to our previous procedures.[1] As a spacer molecule for the counterpart of the PDI molecule, a propyl linker was introduced to the complementary stands.

Freshly-prepared oligonucleotides modified with a thiol group at the 5'-terminus (1000 eq per particle)[2,3] were added to an aqueous solution of gold nanoparticles (20 nm, 1.2 nM) purchased from BBInternational. The solution was incubated for 16 hr at 50 ºC, then the concentration of NaCl was increased up to 1.0 M and incubated for 40 hr at 50 ºC. After the conjugation, the AuNP conjugates were centrifuged and precipitated to remove any unreacted DNA contained in the supernatants. The precipitates were then resuspended in a 20 mM Na phosphate buffer containing 100 mM NaCl and 0.01% SDS.

Preparation of AuNP-coated electrodes through DNA hybridization

Gold working electrodes (0.02 mm^2 in area, BAS) were sequentially polished with 0.3 and 0.05 μm alumina powders (MicroPolish, Buhler) and electrochemically etched in 1 M sulfuric acid. The freshly-cleaned electrodes were derivatized with DNA by treatment in a solution of 20 mM phosphate buffer (pH 7.0) and 100 mM NaCl (E-buffer) containing the thiol-modified DNA (10 μM) for 12 hours at room temperature. After washing the electrodes in 10 mM Tris buffer, the electrodes were backfilled with 1 mM of 6-mercapto-1-hexanol in Tris buffer for 30 min to prevent any undesired adsorption. The electrodes were then immersed in a solution of gold nanoparticles modified with complementary DNA in E-buffer for 12 hours to prepare the gold nanoparticle-covered electrodes. After extensive washing of the electrode with E-buffer, the color of the electrode surface remained red, confirming the adsorption of the AuNPs on the surface through DNA hybridization (Figure S1).

Photocurrent measurements were immediately performed after washing with E-buffer (two times) in the presence of sodium ascorbate which served as a sacrificial electron donor. The photocurrent intensity was measured upon irradiation by a Xe lamp (MAX-302, Asahi Spectra) equipped with a band-pass filter from 460 nm to 600 nm with an interval of 20 nm. The intensity was calibrated based on the intensity of the light source to obtain the photocurrent action spectrum. The current intensity was obtained at a bias voltage of −0.1 V vs Ag/AgCl using the electrochemical analyzer (ALS, model 630C).

Quantification of surface coverage with AuNP

Surface modification with AuNP through DNA hybridization showed a color change from gold to red, indicating that the surface was covered with the AuNPs. For quantification, the AuNP-covered electrodes were incubated with hot water to promote the dehybridization and recover the AuNP on the surface (Figure S2). After the incubation at 80 °C for 12 hours, UV/vis absorption measurements were carried out to estimate the surface coverage by the AuNPs. Based on the absorption intensity at 520 nm for the AuNP plasmon and extinction coefficient for 20 nm AuNP ($\varepsilon = 9.406 \times 10^8$ $M^{-1}cm^{-1}$), surface coverage was estimated to be approximately 80 %.

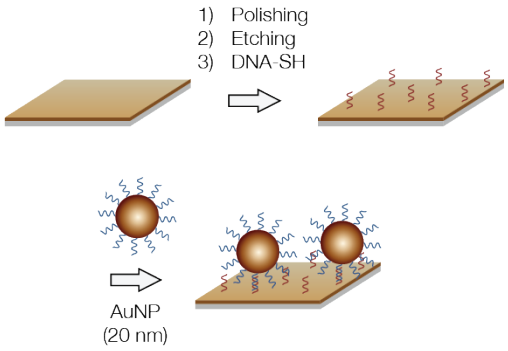

Figure S1. Preparation of the electrode covered with a monolayer of AuNP on the surface through DNA hybridization and release of AuNP by heat-induced dehybridization.

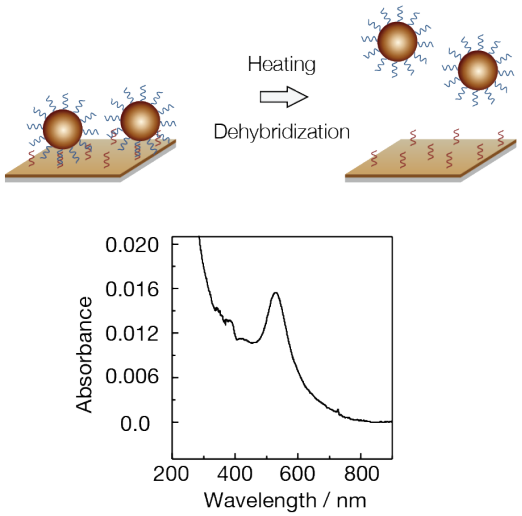

Figure S2. Detachment of AuNPs by heat-induced dehybridization and UV/vis absorption of recovered AuNPs.

REFERENCES

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3) K. Sato, K. Hosokawa and M. Maeda, *J. Am. Chem. Soc.*, 2003, **125**, 8102.