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Supporting Information for

Janus PEGylated Gold Nanoparticle: A Robust Colorimetric Probe for Sensing Nitrite Ions in Complex Samples

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EXPERIMENTAL SECTION

Materials and Instruments. Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), hydrogen peroxide (H_2O_2), and (3-aminopropyl) triethoxysilane (APTES) were purchased from Aladdin (Shanghai, China). 4-Aminobenzenthiol (4-ABT) and various buffers including phosphate buffer saline (PBS), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), and 2-(N-morpholino) ethanesulfonic acid (MES) were purchased from Heowns Biochemical Technology co., Ltd. (Tianjin, China). H_2SO_4, $NaNO_2$ and other interfering substances were purchased from Guangfu Chemical Reagent (Tianjin, China). Thiol-terminated poly (ethylene glycol) (PEG MW2000), *N*-hydroxysucinimide (NHS), thymine-1-acetic acid (T-COOH), and 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC-HCl) were purchased from Sigma Aldrich. The 96-well polystyrene plate was purchased from R&D systems. Deionized water (Milli-Q grade, Millipore) with a resistivity of 18.2 MΩ·cm was used throughout this study. The UV−vis spectra of AuNP solutions were recorded with a Hitachi U-3900 UV−vis spectrophotometer. The absorbance of AuNP solutions in 96-well plates were collected by a Synergy 2 Multi-Mode Microplate Reader (Bio-Tek Instruments, Inc.). TEM images were obtained by using a JEOL 1400 model at an accelerating voltage of 100 kV. Dynamic light scattering (DLS) was performed on a Zeta Sizer Nano ZS (Malvern Zetasizer 300HS and He/Ne laser at 632.8 nm at scattering angles of 90 at 25 ^{o}C). The Raman spectra were obtained by suspending the AuNPs in capillaries and recording on a Renishaw inVia Raman microscope (×50 objective lens with NA= 0.75, Leica)

Synthesis of 30 nm AuNPs. Gold nanoparticles with diameter of 30 nm were synthesized by means of the seed growth method, which involved two steps: First, 13 nm AuNPs were prepared with the classical method reported elsewhere.[24,32] Second, growth of the as-prepared 13 nm AuNPs. Briefly, 10 mL of 2.08 mM $HAuCl_4$ solution was added dropwise to 125 mL aqueous solution containing 1.6 M $NH_2OH{\cdot}HCl$ and 0.1 nM 13 nm AuNPs solution at vigorous stirring. After reacting for 30 min, 0.8 mL of 5 % (wt %) sodium citrate was added to the reaction solution and kept stirring for another 10 min. The resulting solution was filtered with a PES membrane (filter unit is 22 μm) to remove the large clusters and insoluble compounds. The sizes of the nanoparticles were measured to be about 30 nm by TEM analysis and the corresponding maximal absorption band was at 525 nm.

Preparation of the 4-ABT- and PEG-co-modified Janus AuNPs. A glass slide was treated with H_2SO_4 and H_2O_2 (3:1, v/v) for 30 min. After ultrasonic washing in deionized water for several times, following by ultrasonic washing in ethanol, the glass slide was immersed in the solution of APTES (10 %, v/v) for 30 min for aminosilanization. The amino-coated glass slides were then sonicated in ethanol for three times, and then in deionized water for another three times. AuNPs were adsorbed onto the glass slide by immersing the amino-coated glass slide in the solution of citrate-capped AuNPs (0.1 nM). The AuNP-coated glass slides were then immersed in the solution of 4-ABT (4-aminobenzethiol, 1 μM) for 30 min to modify the exposed side of the immobilized AuNPs with 4-ABT and then sonicated into the solution of 5 μM thiolated PEG-2000 (containing 1 ‰ Tween 20 and 2 mM K_2CO_3).

The released Au sites were taken by the PEG to produce asymmetrically functionalized AuNPs.

Preparation of thymine- and PEG- co-modified Janus AuNPs. The procedures of decorating AuNPs onto the glass slide were the same as described above. The AuNP-coated glass slide was immersed into the solution of cysteamine (1 μM) for 30 min to modify the exposed side of the immobilized AuNPs with cysteamines. Thymine-1-acetic acid (T-COOH) was treated with EDC/NHS to obtain NHS-activated thymine (NHS-CO-T). Then, the above slide was immersed in the NHS-CO-T solution (1 μM) for 4 h where the NHS-CO-T was conjugated with the immobilized cysteamine via amide bond. The resulting glass slide was then sonicated into the solution of 1 uM thiolated PEG-2000 (containing 1 ‰ Tween 20 and 2 mM K_2CO_3). The obtained solution was centrifuged and redispersed in deionized water for further use.

Detection of NO_2^-. Different concentrations of NO_2^- in various samples were mixed with 100 μL of the freshly-prepared Janus PEGylated AuNPs solutions. All the solutions were adjusted to pH 4 using HCl to facilitate the diazotization reaction. After incubation for 30 min at room temperature, the absorbance at 525 and 700 nm were measured on a microplate reader simultaneously.

Simulation of the electric field distributions on AuNPs. The simulation is performed with the RF module of COMSOL Multiphysics software. In this calculation, two physical quantities, absorption cross section (σ_{abs}) and scattering

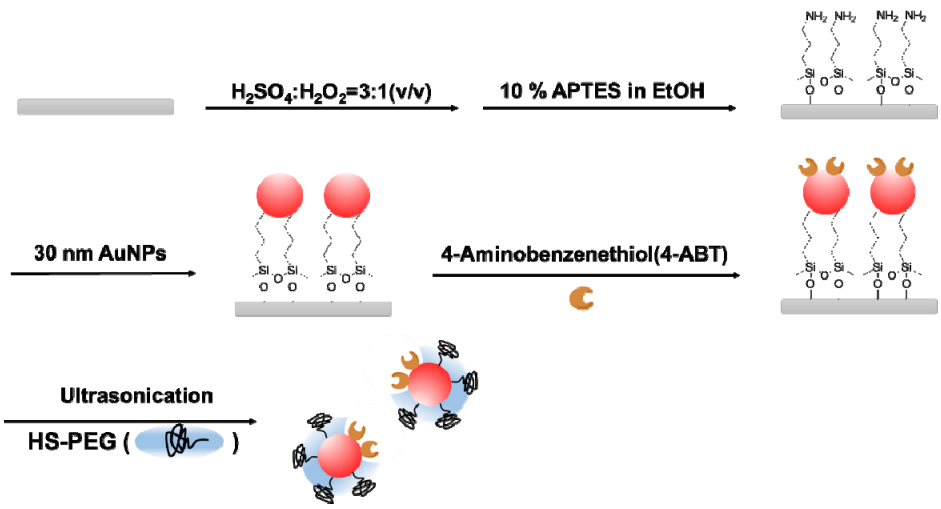
cross section (σ_{sc}), are introduced to evaluate the absorption and scattering strength of AuNPs, respectively. The absorption cross section and the scattering cross section are defined as the ratio of the power absorbed or scattered by this system (P_{abs} or P_{sc}) to the flux density (I_0) of the incident plane wave

$$\sigma_{abs} = \frac{P_{abs}}{I_0}, \quad \sigma_{sc} = \frac{P_{sc}}{I_0}, \qquad \text{(S1)}$$

The absorbed and scattered power are calculated with the following integrals,

$$P_{abs} = \iiint_V [\frac{\omega \mathrm{Im}(\varepsilon) |\mathbf{E}|^2}{2} + \frac{\omega \mathrm{Im}(\mu) |\mathbf{H}|^2}{2}] dV, \quad P_{sc} = \iint_A \mathbf{S}.\mathbf{n} dA. \qquad \text{(S2)}$$

In Eq. (S2), **E** and **H** are electric and magnetic field vectors, ω is the angular frequency of incident light, ε and μ are the dielectric constant and magnetic permeability of gold, and **S** is the Poynting vector of the scattered field. V is the region of the AuNPs, and A is a closed surface encompassing the AuNPs with **n** being the out-pointing normal vector of the surface.



Scheme S1 Schematic of the synthetic procedures of asymmetrically functionalized gold nanoparticles.

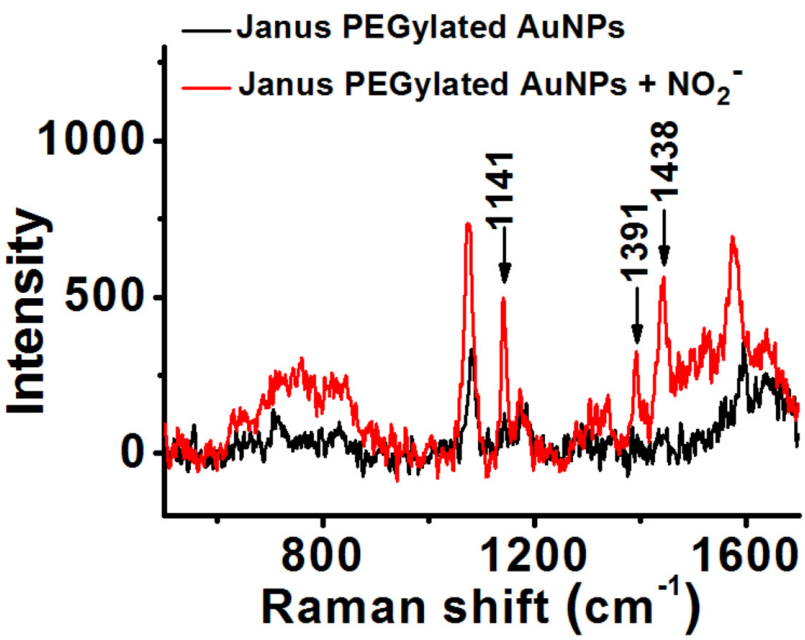


Fig. S1 Raman spectra of the Janus PEGylated gold nanoparticles (black) and those incubated with NO_2^- (red).

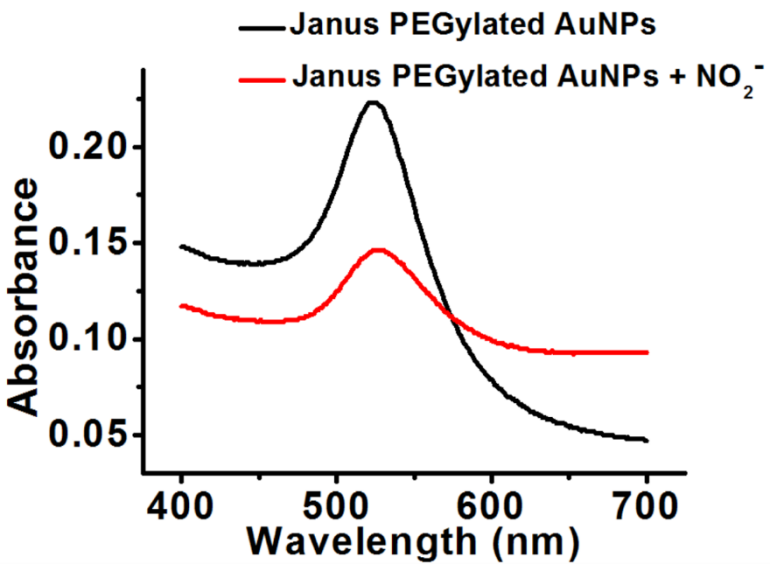


Fig. S2 UV-Vis spectra of the Janus PEGylated gold nanoparticles (black) and those incubated with NO_2^- (red).

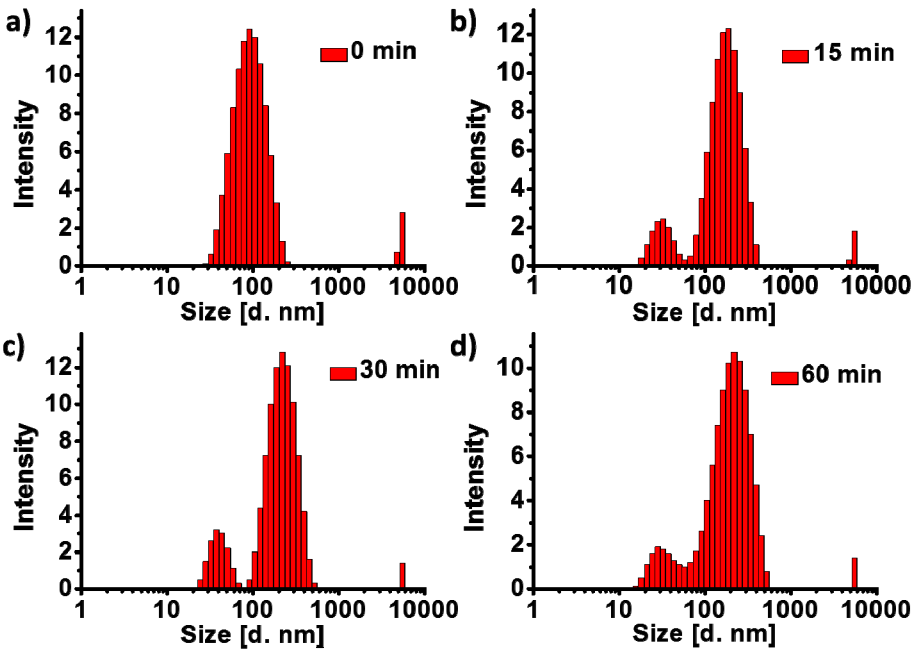


Fig. S3 Dynamic Light Scattering (DLS) of the Janus PEGylated gold nanoparticles incubated with NO_2^- for a) 0 min, b) 15 min, c) 30 min, and d) 60 min.

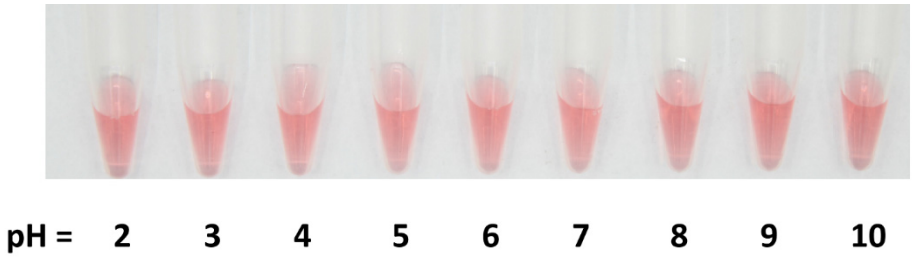


Fig. S4 Images of the Janus PEGylated gold nanoparticles dispersed in solutions with varied pH values.

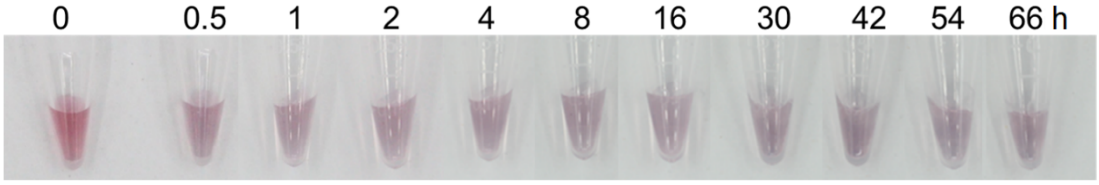


Fig. S5 Long-term signal stability of the Janus PEGylated gold nanoparticle probe for sensing NO_2^-. The signals can be maintained for several days.

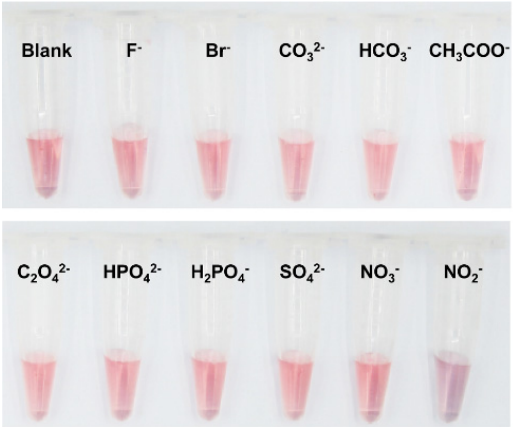


Fig. S6 Images of the Janus PEGylated AuNP solutions (0.1 nM) incubated with NO_2^- (30 μM) and various interfering anions (3 mM) respectively for 0.5 h.

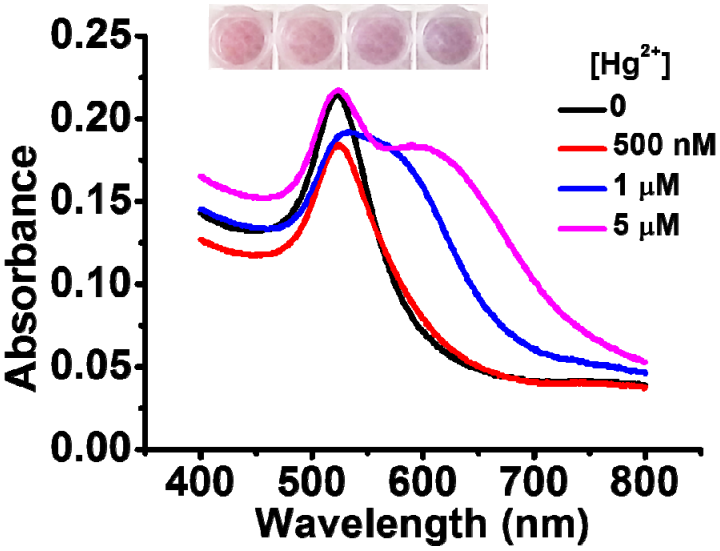


Fig. S7 UV-Vis spectra of thymine- and PEG- asymmetrically commodified gold nanoparticles incubated with various concentrations of Hg^{2+}. Inset: Images of the relevant AuNPs solutions.

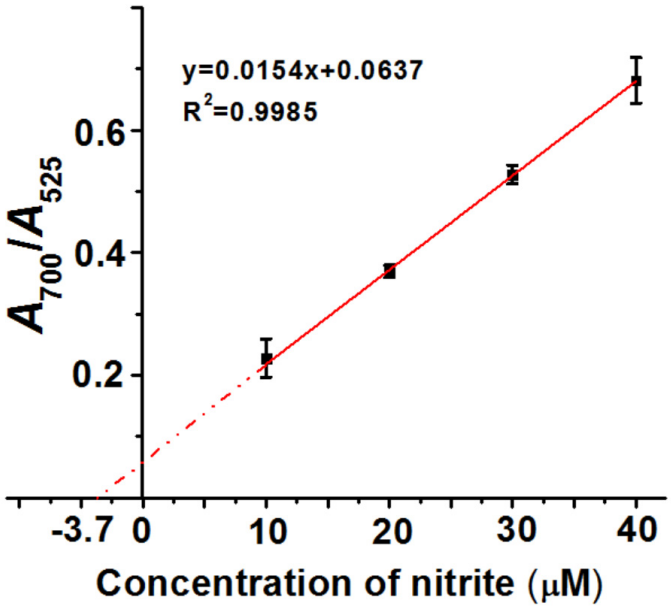


Fig. S8 Plots of A_{700}/A_{525} versus varying concentrations of NO_2^- spiked in the sausage sample. The error bars represent the standard deviations of three independent samples.