Electronic Supplementary Material

Amalgamated gold-nanoalloys with enhanced catalytic activity for the detection of mercury ions (Hg^{2+}) in seawater samples

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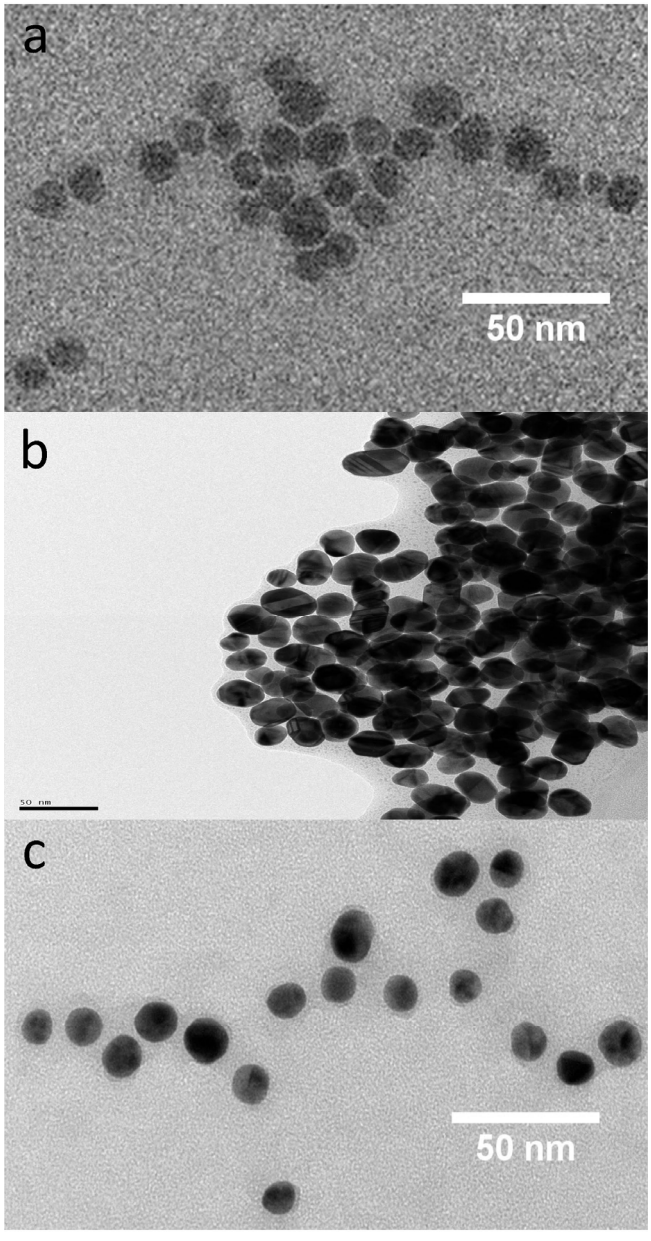

Figure S1 Transmission electron microscopy (TEM) images of (a) stable bare-AuNP and (b) aggregated AuNPs, in the presence of dH_2O and 0.5 M NaCl, respectively (c) OEG-functionalised AuNPs. Scale bar: 50 nm.

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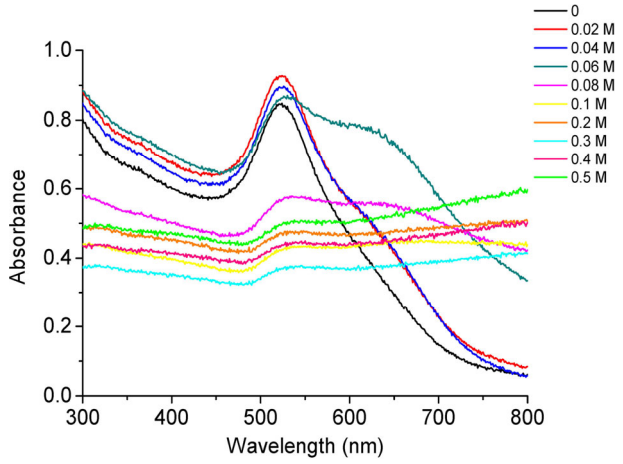


Figure S2 UV-vis spectra of AuNP (average diameter ~13-20 nm) treated with different NaCl concentrations (0-0.5 M).

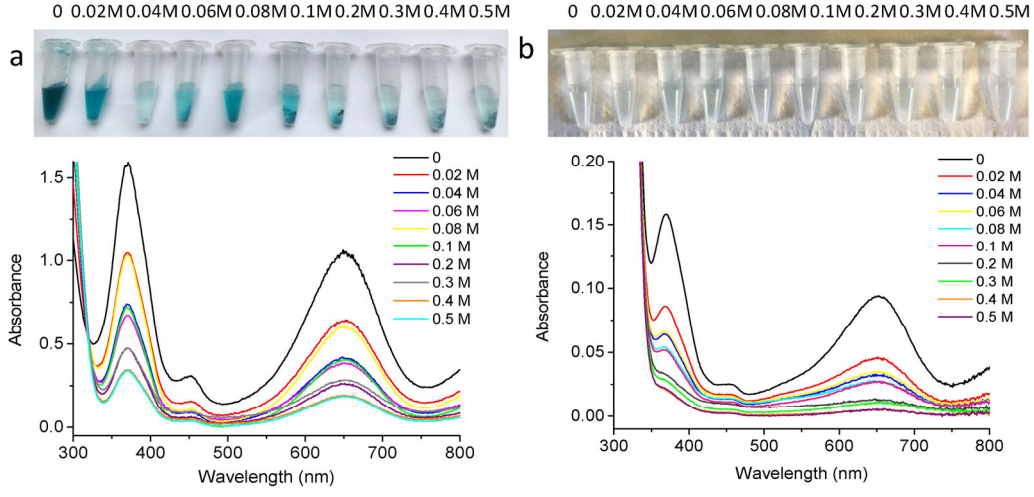
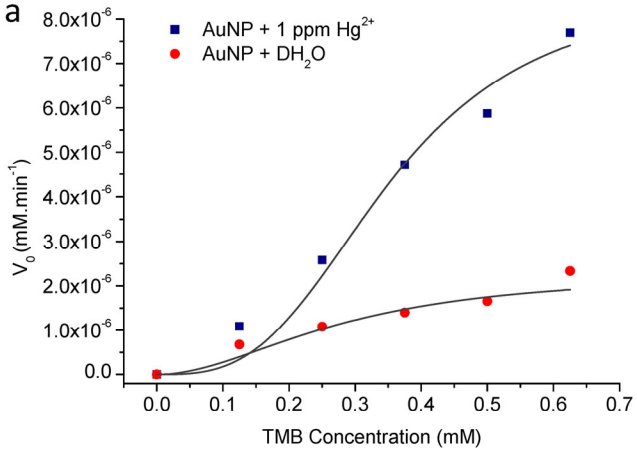


Figure S3 The effect of NaCl on AuNP peroxidase-like activity. (a, top) colour photograph of aggregated AuNPs after treatment with NaCl. The samples were centrifuged, subsequently the AuNP pellet was collected and resuspended in dH_2O and mixed with TMB/2% H_2O_2. (a, below) corresponding UV-vis spectra illustrating the peroxidase-like activity of aggregated particles after centrifugation. (b, top) colour photograph of the supernatant removed from the centrifuged particles mixed with TMB/2% H_2O_2. (b, below) corresponding UV-vis spectra showing the peroxidase-like activity of the supernatant.



b

Catalyst	Concentration (M)	V_{max} (M.min^{-1})	K_M (mM)	k_{cat} (min^{-1})	k_{cat}/K_M (mM^{-1}.min^{-1})	Catalytic yield
AuNP + 1 ppm Hg^{2+}	1.05E-09	7.70E-06	0.3537	7.33E+03	2.07E+04	100.0%
AuNP + DH_2O	1.05E-09	2.34E-06	0.2842	2.23E+03	7.84E+03	37.8%

Figure S4 Michaelis-Menten kinetic analysis to confirm how the catalytic properties of the bare-nanozyme differs in the absence and presence of Hg^{2+} (1 ppm). (a) Typical Michaelis-Menten curve illustrating the initial velocity (V_o) of the reaction after 10 min. The concentration of H_2O_2 was fixed at 590 mM (6%), and that of TMB was varied. (b) Comparison of Michaelis-Menten steady-state parameters illustrating Michaelis constant (K_m), maximum reaction rate (V_{max}), catalytic constant (K_{cat}) and catalytic efficiency (K_{cat}/K_m) of bare-AuNP in the absence and presence of Hg^{2+} (1 ppm).

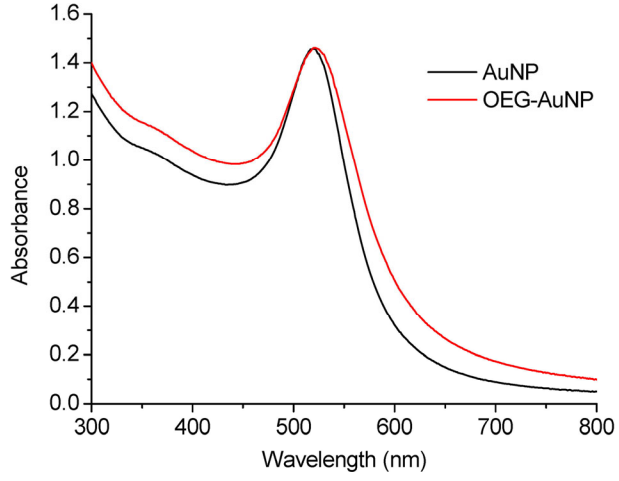


Figure S5 UV-vis analysis of bare-AuNP and OEG-AuNP. The results demonstrate the typical absorption peak of AuNPs at 519 nm (black line), and a shift in wavelength to 522 nm for OEG-AuNP (red line). This further supports that the AuNPs are successfully functionalised with OEG due to the increase in refractive index.

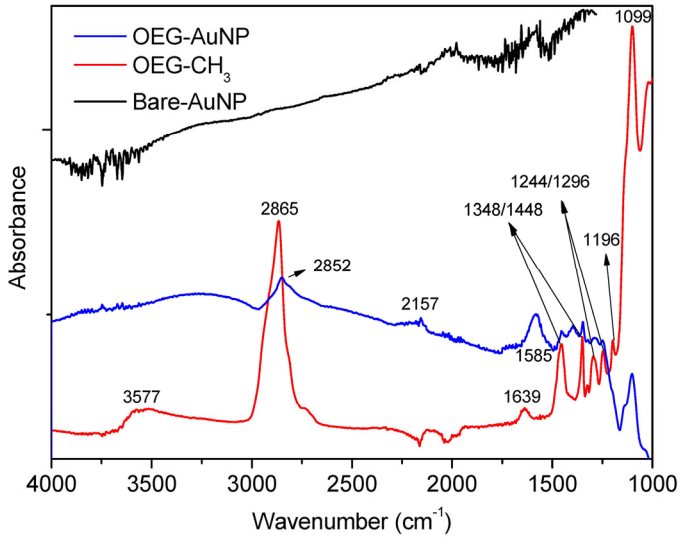


Figure S6 Characterisation of OEG-AuNP using Fourier-transform infrared spectroscopy (FTIR). Spectra for bare-AuNP (red line), OEG-CH_3 molecule (red line) and OEG-functionalised AuNP (blue line).

FTIR was conducted to characterise the successful functionalisation of AuNPs with OEG. As inorganic materials the citrate-capped AuNPs do not provide a FTIR spectrum (black line). However, the FTIR spectra of OEG-functionalised AuNPs exhibit bands that are similar to that of pure OEG. As found previously [S1], the band which exists at 1099 cm^{-1} are from the C-O-C bending bands of the OEG, of which the frequency appears to diminish after the thiolated OEG functionalises onto the surface of the AuNP. The bands at 1196 cm^{-1} correspond to the C-O stretching bands of the OEG-thiol and do not exist in the OEG-AuNP spectra. Bands at 1244 cm^{-1} and 1296 cm^{-1} are in relation to the asymmetric and symmetric scissoring (bending) of the alkyl chain (CH_2), whilst the bands at 1348 cm^{-1} and 1448 cm^{-1} correspond to C-H bending from the methyl group (CH_2 and CH_3) [S2]. The frequency of these bands is also diminished after the OEG is functionalised to the surface of the AuNP. The band at 1639 cm^{-1} corresponds to the C=O stretch for the free OEG-thiol (red line). These bands do not exist in the spectra of OEG-functionalised AuNPs, however this band shifts to a lower wavenumber (1585 cm^{-1}) in the spectra of OEG-AuNPs [S3], suggesting that the C=O band is strongly disrupted when the OEG-thiol anchors onto the surface of the AuNP through strong Au-S bonds. The band at 2157 cm^{-1} in the spectrum of OEG-AuNP (blue line) indicates the presence of a C≡C bond, thus confirming that the OEG-thiol has functionalised to the AuNP surface through strong covalent bonds (Au-S). The bands at 2865 cm^{-1} and 2852 cm^{-1} correspond to the asymmetric and symmetric stretching of the alkyl chain for pure OEG-thiol and OEG-AuNP, respectively. These bands are also shifted to a lower wavenumber, and may be due to the formation of new hydrogen bonds. The bands at 3577 cm^{-1} are due to the O-H vibrations of alcohol and trapped water molecules, of which the band frequency is also reduced in the spectra of OEG-AuNP [S1]. Overall, the functionalisation of AuNPs with OEG was successful as verified by the FTIR results.

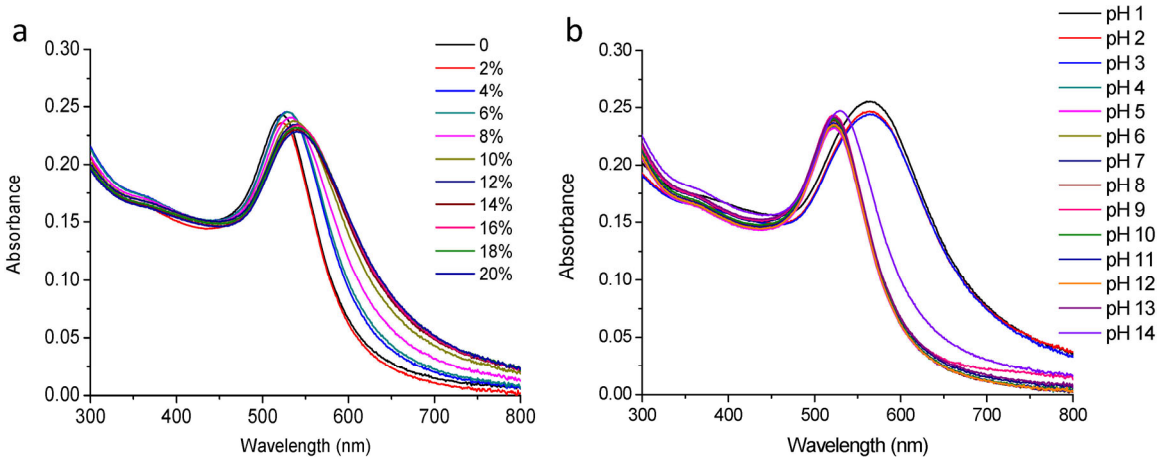


Figure S7 Full wavelength spectra to examine the stability of AuNP functionalised with OEG in the presence of (a) 0-20% NaCl and (b) PBS buffer pH 1-14.

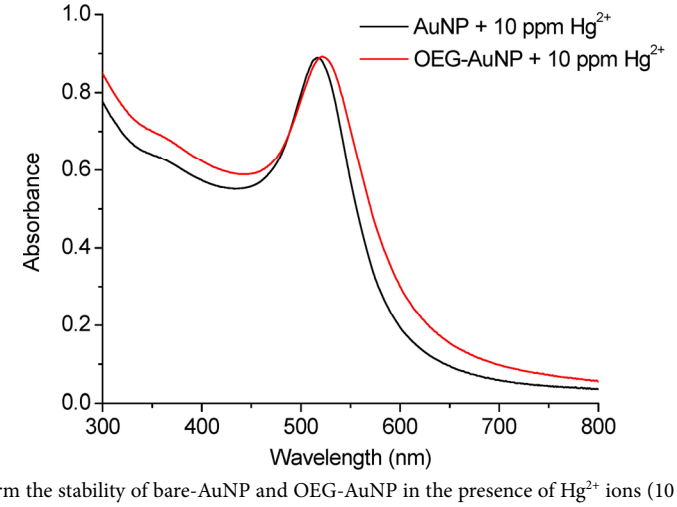


Figure S8 UV-vis analysis to confirm the stability of bare-AuNP and OEG-AuNP in the presence of Hg^{2+} ions (10 ppm). As the colorimetric response is based on the nanozyme activity, it was important to confirm that the AuNP size or aggregation state was not affected by the presence of Hg^{2+}. The results confirm that the stability of bare-AuNP and OEG-AuNP remains unaffected by the presence of Hg^{2+}.

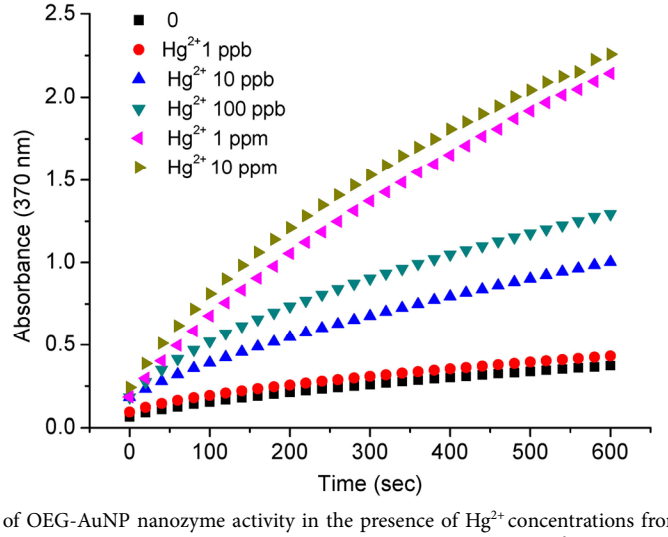


Figure S9 Scanning kinetic analysis of OEG-AuNP nanozyme activity in the presence of Hg^{2+} concentrations from 0-10 ppm, 1.25 mM TMB and 6% H_2O_2, over 10 min. From the results we were able to confirm the hypothesis that in the presence of Hg^{2+}, the nanozyme activity of OEG-AuNP could be recovered, and therefore be exploited to develop a colorimetric sensor for Hg^{2+} in complex water samples.

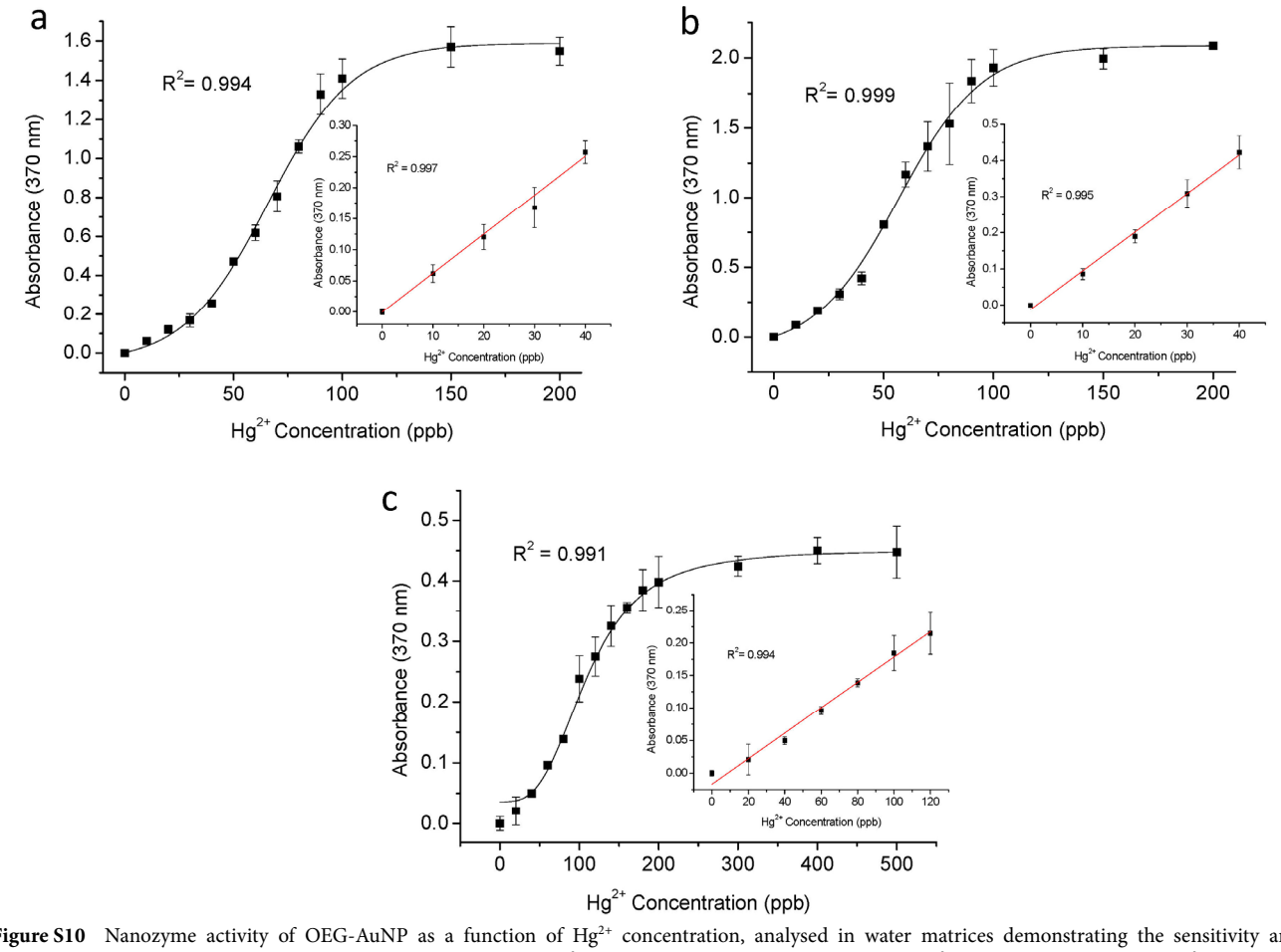


Figure S10 Nanozyme activity of OEG-AuNP as a function of Hg^{2+} concentration, analysed in water matrices demonstrating the sensitivity and applicability of the assay. Inset is the linear relationship between Hg^{2+} concentrations spiked in (a) tap water (R^2=0.997), (b) bottled water (R^2=0.995) and (c) saline solution (R^2=0.994) and the enhancement of nanozyme activity witnessed by OEG-AuNPs after 10 min incubation.

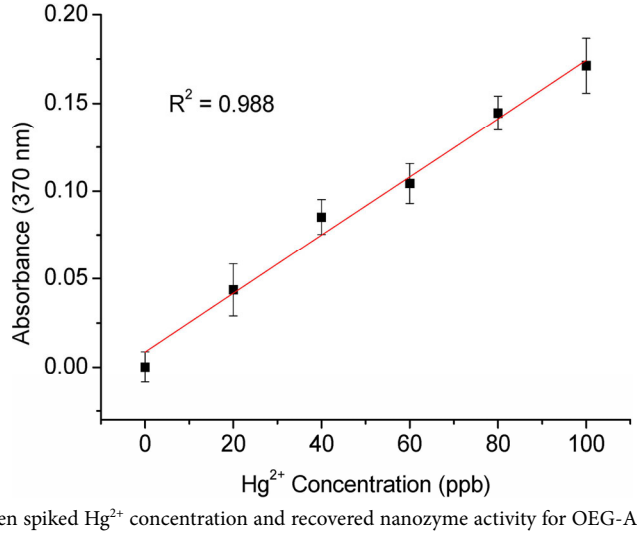


Figure S11 Linear relationship between spiked Hg^{2+} concentration and recovered nanozyme activity for OEG-AuNP analysed in a coastal seawater Hg^{2+} Certified Reference Material (CRM).

Supplementary References

[S1] Cao, C.; Sim, S.J. Preparation of highly stable oligo(ethylene glycol) derivatives-functionalized gold nanoparticles and their application in LSPR-based detection of PSA/ACT complex. *J. Nanosci. Nanotechnol*. **2007**, *7*, 3754-3757.

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[S3] Jiang, G.; Wang, L.; Chen, W. Studies on the preparation and characterization of gold nanoparticles protected by dendrons. *Mater. Lett*. **2007**, *61*, 278-283.