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Colorimetric assay of heparin in plasma based on the inhibition of oxidase-like activity of citrate-capped platinum nanoparticles

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A B S T R A C T

We report citrate-capped platinum nanoparticles (Pt NPs) as oxidase mimetics for effectively catalyzing the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB), 2,2'-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid), dopamine, and methylene blue in the presence of O₂. To confirm oxidase-like activity of citrate-capped Pt NPs, their activity toward oxygen reduction reaction was studied using cyclic voltammetry and rotating ring-disk electrode method. The results obtained showed that Pt NP NPs can catalyze the oxidation of organic substrates to the colored product and the reduction of oxygen to water through a four-electron exchange process. Because the aggregation of Pt NPs can inhibit their oxidase-like activity and protamine can recognize heparin, we prepared the protamine-modified Pt NPs through direct adsorption on the surface of citrate-capped Pt NPs. The electrostatic attraction between heparin and protamine-stabilized Pt NPs induced nanoparticle aggregation, inhibiting their catalytic activity. Therefore, the lowest detectable heparin concentrations through UV-vis absorption and by the naked eye were estimated to be 0.3 and 60 nM, respectively. Moreover, the proposed system enabled the determination of the therapeutic heparin concentration in a single drop of blood.

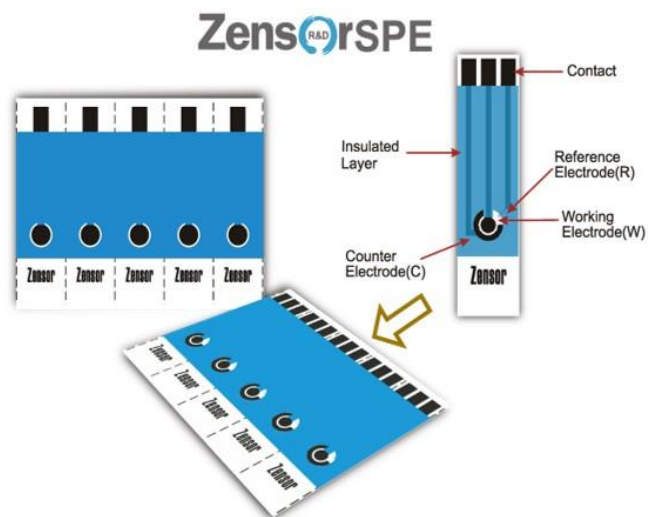
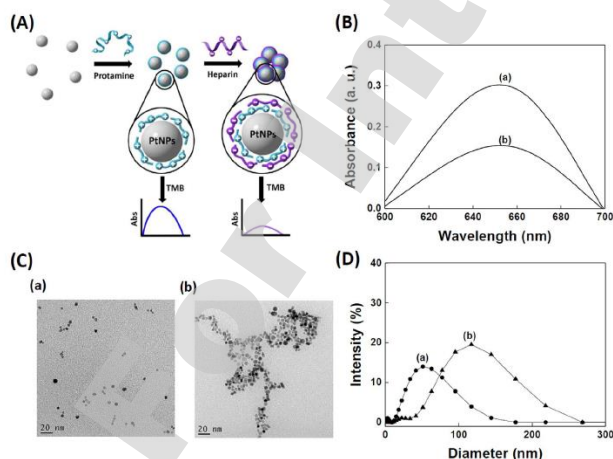


Fig. 3. Protamine-modified Pt NPs for heparin sensing. (A) Illustration of NP aggregation-induced inhibition of oxidase-like activity of protamine-modified Pt NPs. (B) Absorption spectra of a solution of 0.1 mM TMB upon the addition of (a) protamine-modified Pt NPs and (b) protamine-modified Pt NPs and 100 nM heparin. (C) TEM images and (D) DLS spectra of protamine-modified Pt NPs in the (a) absence and (b) presence of 10 µM heparin. (A-D) The reaction condition performed in 50 mM sodium acetate (pH 4.0) at ambient temperature for 15 min.

Aggregation-Induced Electrochemiluminescence of Platinum(II) Complexes

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Supporting Information

ABSTRACT: We report the electrochemiluminescence properties of square-planar Pt(II) complexes that result from the formation of supramolecular nanostructures. We define this new phenomenon as aggregation-induced electrochemiluminescence (AIECL). In this system, self-assembly changes the HOMO and LUMO energies, making their population accessible via ECL pathways and leading to the generation of the luminescent excited state. Significantly, the emission from the self-assembled system is the first example of electrochemiluminescence (ECL) of Pt(II) complexes in aqueous solution having higher efficiency than the standard, Ru(bpy)₃²⁺. The finding can lead to a new generation of bright emitters that can be used as ECL labels.

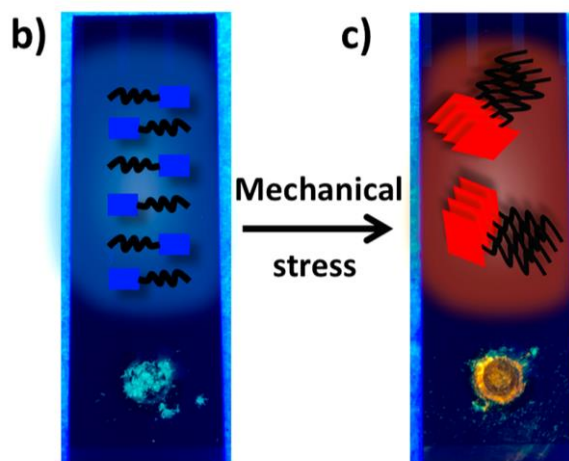
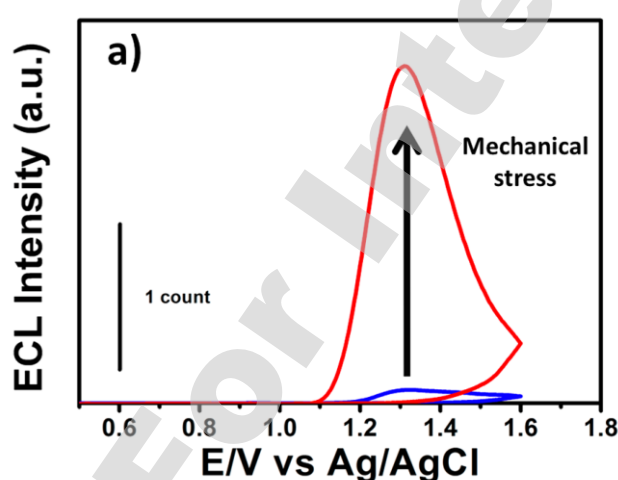
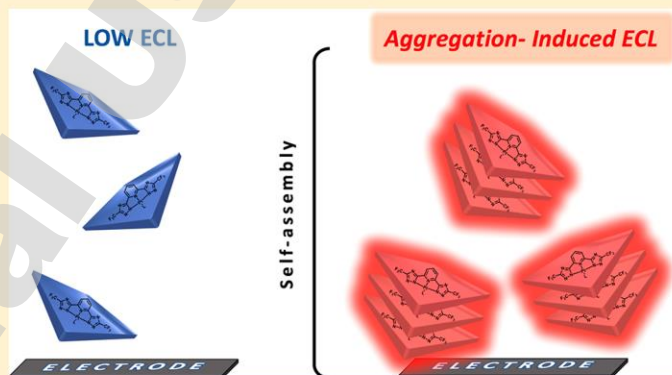


Figure 3. (a) ECL emission recorded during a cyclic voltammetry at a scan rate of 0.2 V s⁻¹ in 0.1 M LiClO₄ water solution of Pt-PEG physically transferred onto SPE before (blue trace) and after (red trace) mechanical stress using 10 mM Na₂C₂O₄ as co-reactant; photographs of luminescence of Pt-PEG onto SPE under a bench-top UV lamp (365 nm) and cartoons showing the principle of its mechanochromism (b) before and (c) after grinding with a pestle.

UV-Light-Induced Improvement of Fluorescence Quantum Yield of DNA-Templated Gold Nanoclusters: Application to Ratiometric Fluorescent Sensing of Nucleic Acids

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Supporting Information

ABSTRACT: The use of DNA as a template has been demonstrated as an effective method for synthesizing different-sized silver nanoclusters. Although DNA-templated silver nanoclusters show outstanding performance as fluorescent probes for chemical sensing and cellular imaging, the synthesis of DNA-stabilized gold nanoclusters (AuNCs) with high fluorescence intensity remains a challenge. Here a facile, reproducible, scalable, NaBH₄-free, UV-light-assisted method was developed to prepare AuNCs using repeats of 30 adenosine nucleotides (A₃₀). The maximal fluorescence of A₃₀-stabilized AuNCs appeared at 475 nm with moderate quantum yield, two fluorescence lifetimes, and a small amount of Au⁺ on the surface of the Au core. Results of size-exclusion chromatography revealed that A₃₀-stabilized AuNCs were more compact than A₃₀. A series of control experiments showed that UV light played a dual role in the reduction of gold-ion precursors and the decomposition of citrate ions. A₃₀ also acted as a stabilizer to prevent the aggregation of AuNCs. In addition, single-stranded DNA (ssDNA) consisting of an AuNC-nucleation sequence and a hybridization sequence was utilized to develop a AuNC-based ratiometric fluorescent probe in the presence of the double-strand-chelating dye SYBR Green I (SG). Under conditions of single-wavelength excitation, the combination of AuNC/SG-bearing ssDNA and perfectly matched DNA emitted fluorescence at 475 and 525 nm, respectively. The formed AuNC/SG-bearing ssDNA enabled the sensitive, selective, and ratiometric detection of specific nucleic acid targets. Finally, the AuNC-based ratiometric probes were successfully applied to determine specific nucleic acid targets in human serum.

KEYWORDS: gold nanoclusters, DNA, UV light, fluorescence, ratiometric sensor

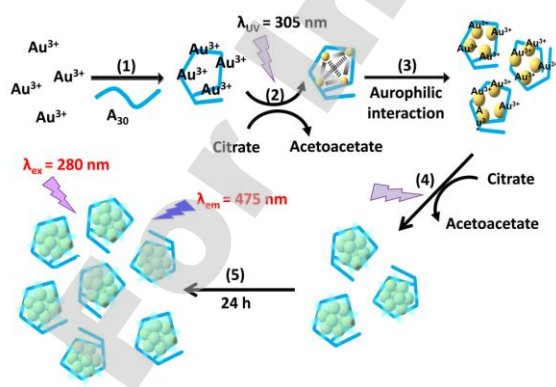
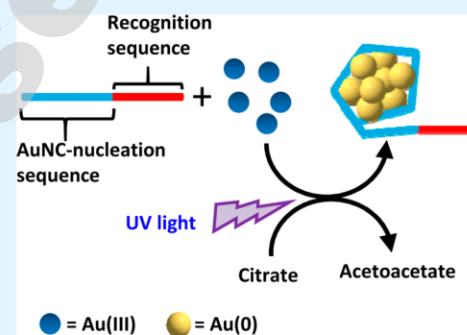
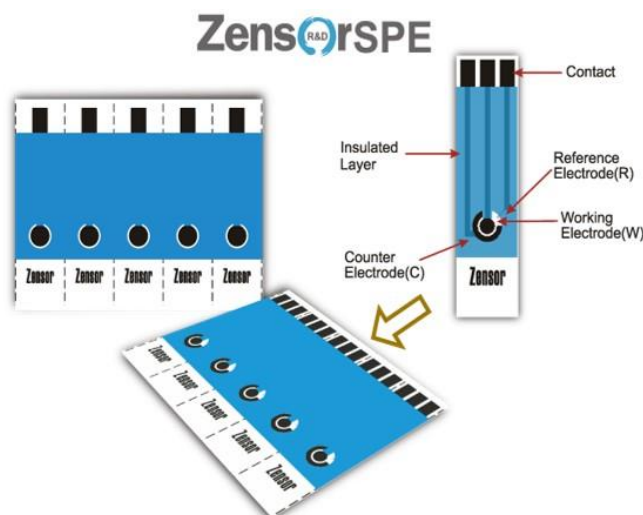


Figure 4. Step-by-step illustration of the procedure for UV-light-mediated synthesis of A₃₀-stabilized AuNCs in the presence of sodium citrate.



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Surface-enhanced Raman scattering-active desert-rose-like Ag mesoparticles prepared using cyclic voltammetric methods†

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Desert-rose-like Ag mesoparticles were deposited on a screen-printed carbon electrode substrate through a cyclic voltammetric process in aqueous AgNO_3 containing Au nanoparticles. The prepared mesoparticles were characterized using scanning electron microscopy, energy dispersive X-ray spectroscopy, surface-assisted laser desorption/ionization mass spectrometry, X-ray photoelectron spectroscopy, and high-resolution X-ray diffractometry. In addition, the potential for applying these mesoparticles in surface-enhanced Raman scattering (SERS) was investigated. The prepared mesoparticles exhibited a more intense SERS signal (34.3 times) than did irregularly shaped Ag particles because of their extremely intense local electromagnetic fields. The enhancement factor of 4-mercaptobenzoic acid molecules on these mesoparticles was approximately 10^5 . Furthermore, SERS spectra of 4,4'-dimercapto-azobenzene, 5,5'-dithiobis-2-nitrobenzoic acid, and Cy3 dye modified DNA were obtained using these mesoparticles; moreover, hot spots for most of the enhanced SERS signals were easily obtained. The thermal stability and aging behaviour of the prepared Ag mesoparticles were higher than those of irregularly shaped Ag particles.

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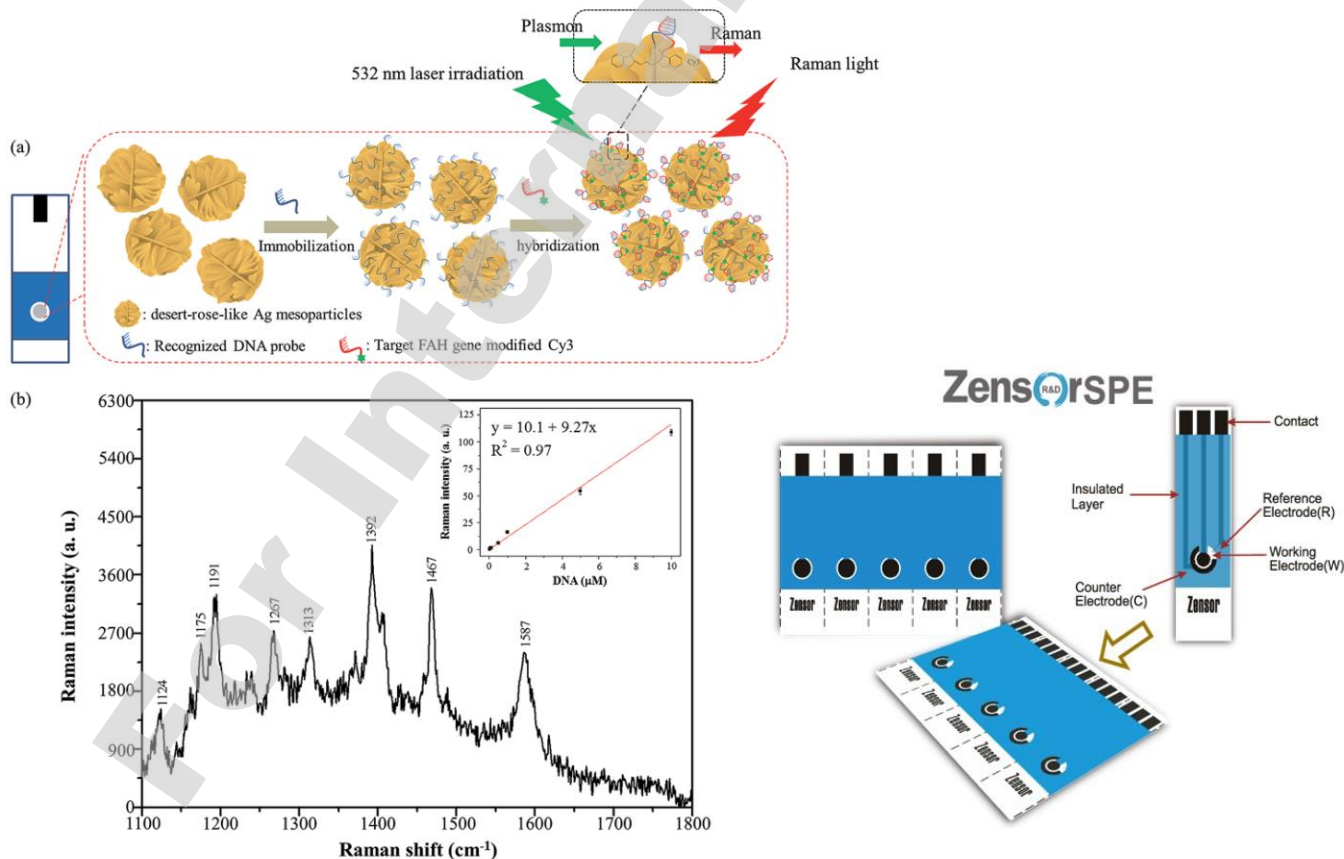
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Fig. 4 Demonstration of DNA sensing. (a) Schematic of DNA immobilization and hybridization on the desert-rose-like Ag mesoparticles. (b) Raman spectra of Cy3 obtained using a target single-stranded DNA (FAH gene) attached to the desert-rose-like Ag mesoparticles. Inset: plots of Raman signal intensity versus DNA concentration.



Electrogenerated Chemiluminescence Detection in Paper-Based Microfluidic Sensors

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ABSTRACT: This paper describes the first approach at combining paper microfluidics with electrochemiluminescent (ECL) detection. Inkjet printing is used to produce paper microfluidic substrates which are combined with screen-printed electrodes (SPEs) to create simple, cheap, disposable sensors which can be read without a traditional photodetector. The sensing mechanism is based on the orange luminescence due to the ECL reaction of tris(2,2'-bipyridyl)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$) with certain analytes. Using a conventional photodetector, 2-(dibutylamino)-ethanol (DBAE) and nicotinamide adenine dinucleotide (NADH) could be detected to levels of $0.9 \mu\text{M}$ and $72 \mu\text{M}$, respectively. Significantly, a mobile camera phone can also be used to detect the luminescence from the sensors. By analyzing the red pixel intensity in digital images of the ECL emission, a calibration curve was constructed demonstrating that DBAE could be detected to levels of $250 \mu\text{M}$ using the phone.

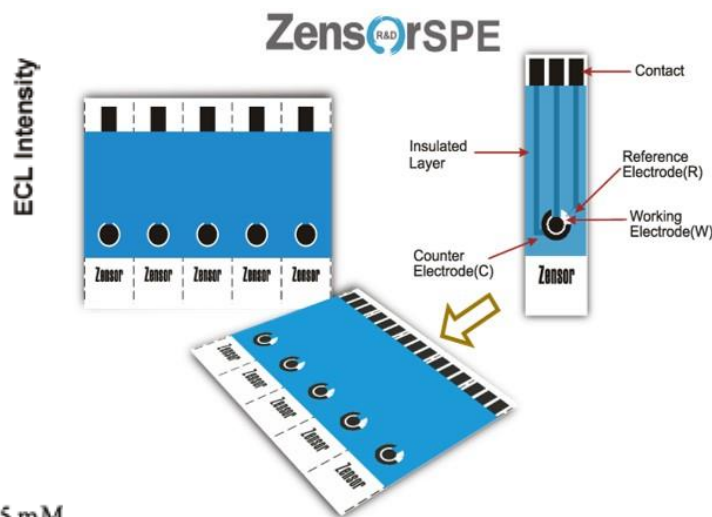
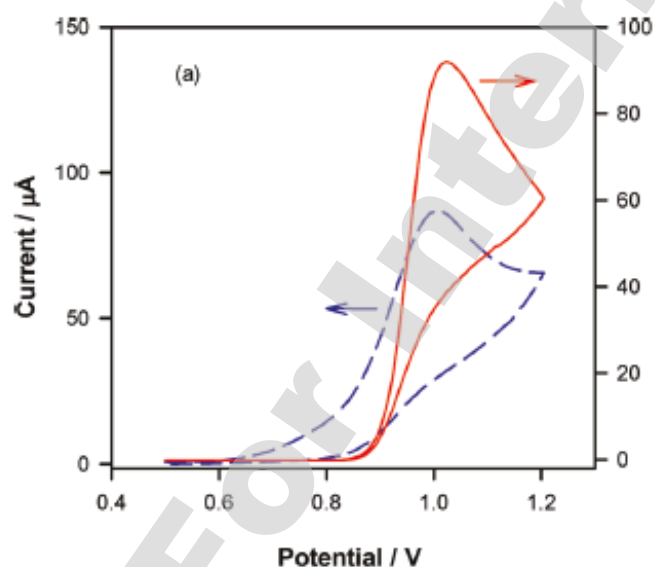
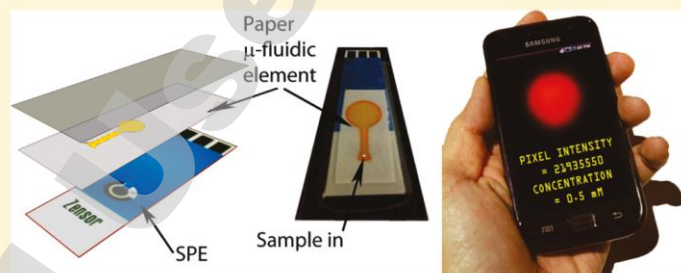


Figure 3. Typical sensor responses for (a) 5 mM DBAE and (b) 5 mM NADH in pH 7.5 0.1 M phosphate buffer. The voltammetric (current)



Photoelectrocatalytic Oxidation of *o*-Phenols on Copper-Plated Screen-Printed Electrodes

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A novel and sensitive detection method based on photoelectrocatalytic oxidation of *o*-diphenols was demonstrated on a copper-plated screen-printed carbon electrode (designated CuSPE) in pH 8 phosphate buffer solution. The *o*-diphenols can be detected amperometrically through electrochemical oxidation at a low applied potential of -0.1 V versus Ag/AgCl, where the CuSPE is much less subject to interfering reactions. The mechanism that induces good selectivity of the CuSPE is explained in terms of the formation of a cyclic five-member complex intermediate ($\text{Cu}^{\text{II}}-\text{o}$ -quinolate). A prototype homemade flow through cell design is described for incorporating the photoelectrode and light source. Electrode irradiation results in a large increase in anodic current. The oxidative photocurrents produced by irradiation increase with light intensity presumably because of the formation of semiconductor Cu_2O . The principle used in this study has an opportunity to extend into various research applications.

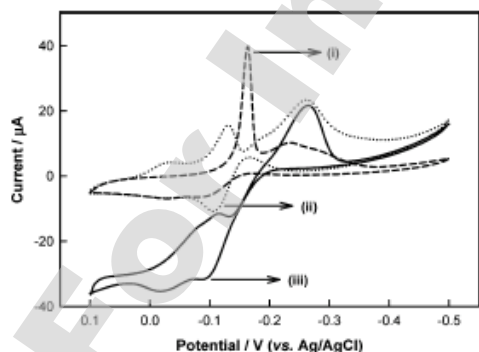


Figure 3. Cyclic voltammograms of the CuSPE in (i) blank pH 8 PBS without electrode irradiation, (ii) blank pH 8 PBS with electrode irradiation, and (iii) pH 8 PBS contained 2 mM CA with electrode irradiation. CV conditions: scan from $+0.1$ to -0.5 V at a scan rate of 5 mV/s.

