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Phenothiazine-Capped Gold Nanoparticles: Photochemically Assisted Synthesis and Application in Electroensing of Phosphate Ions

Sandeep Gupta,^[a] Akhilesh K. Singh,^[a] Ravish K. Jain,^[b] Ramesh Chandra,^[b] and Rajiv Prakash^{*[a]}

Dedicated to the 150th birth anniversary of Mahamana Pandit Madan Mohan Malviya Ji

We describe a green photochemical route for the synthesis of gold nanoparticles (AuNPs) using phenothiazine (PTZH) as a reductant as well as a stabilizer without any extra control (i.e. surfactant, pH, etc.). The synthesized AuNPs are characterized by using UV/Vis spectroscopy, cyclic voltammetry, and transmission electron microscopy. Furthermore, a possible mechanism for the formation of the AuNPs is proposed. This hybrid electrode material, derived from nanoscale gold particles capped with PTZH and its oxidation product, is explored for the development of a highly sensitive amperometric sensor for

phosphate ions. The electrochemistry behind the electrocatalytic sensing of phosphate is attributed to the nano-sized gold particles that are capped with PTZH and its oxidation product, which exhibit high electron-transfer kinetics through the interaction of the hybrid PTZH–AuNPs with oxygen atoms of PO_4^{3-} . The modified electrode efficiently gives an electrochemical signature of phosphate ions at a potential of -0.336 V versus AgCl/Ag and shows a linear response toward phosphate sensing, with a sensitivity of $0.794\text{ }\mu\text{A }\mu\text{M}^{-1}$ and a limit of detection of $0.022\text{ }\mu\text{M}$, at a signal-to-noise ratio of 3.

1. Introduction

The first synthesis of gold (Au) colloids was reported approximately 150 years ago by Michael Faraday, who used phosphorous to reduce Au(III).^[1] Since Faraday's pioneering work, a lot of research activity on gold nanoparticles (AuNPs) has been seen during the last three decades, because of their attractive chemical, optical, and electronic properties, as well as their biocompatibility, which render AuNPs a suitable and promising material for photoelectric devices, catalysis, electrochemical sensing, and bioimaging applications. Turkevich et al.^[2] employed a mild reducing agent (sodium citrate) to form Au colloids in aqueous solution from HAuCl_4 . Another milestone in the synthesis of AuNPs was achieved by Brust et al.^[3] The widely used Brust method consists of a biphasic system, in which a reducing agent (NaBH_4), an appropriate capping agent (long chain thiol), and a phase transfer agent (tetraoctylammonium bromide) are used to generate AuNPs. In many cases, the excess use of NaBH_4 can cause a sudden change in the pH value of the resultant solution as well as the adsorption of


unused BH_4^- onto the nanoparticle surfaces, resulting in the contamination of the surfaces of the AuNPs.

Analytical spectrophotometric determination of gold with phenothiazine (PTZH) was reported by Nemcova and Rychlovsky,^[4] who demonstrated that the reaction of Au(III) with PTZH produces a green-colored solution; however, they did not report the formation of Au nanostructures and did not utilize microscopy techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which represent the key step forward in this paper.

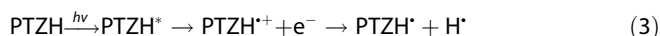
Photochemical synthesis of Au nanostructures has been reported by several research groups.^[5–7] However, to the best of our knowledge, there is no report available on the photochemical synthesis of Au nanostructures by using PTZH as a reductant as well as a stabilizer. Zhu et al.^[8] have studied the chemistry of PTZH in detail and have provided experimental evidence of its electron-transfer ability and the formation of stable radical PTZH cations, which are stable enough to be detected at room temperature by using electron paramagnetic resonance (EPR) spectroscopy. PTZH is an electron-donor compound, which has a low ionization potential and can easily form radical cations; photo-oxidation of PTZH yielding stable radical cations has been studied in detail by several research groups.^[9–14] Rodrigues et al.^[11] have also studied photochemically generated stable radical cations of PTZH by using EPR spectroscopy as well as flash photolysis studies. Photoionization of PTZH can either yield electrons and radical cations of PTZH [Eq. (1)] or PTZH and hydrogen radicals [Eqs. (2) and (3)]. These photo-

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chemically generated electrons can then be used for the reduction of HAuCl_4 .



in which PTZH , PTZH^{\cdot} , $\text{PTZH}^{\cdot+}$, e^- , H^{\cdot} represent the excited state of PTZH , the PTZH radical, the radical cation of PTZH , an electron, and a hydrogen radical, respectively.

Furthermore, our group is interested in the development of electrochemical sensors based on nanostructured materials. One of the objectives of this work was to utilize the nanoparticle-based platform for the electrocatalytic sensing of phosphate ions. The concept of modified electrode is one of the exciting developments in the field of electroanalytical chemistry. Micro-/nano-electrode ensembles have been widely used for the development of electrochemical sensors. They show several advantages over conventional macro electrodes, owing to increased mass transport, decreased influence of solution resistance, fewer electrode fouling problems, and better detection limits because of the higher ratio between the faradaic and capacitive currents.^[15,16] To the best of our knowledge, this is the first time AuNPs capped with PTZH (PTZH-AuNPs) have been employed for the electrocatalytic sensing of phosphate ions. PTZH-AuNPs are used for the modification of electrodes, and efforts have been made to develop a sensitive platform for the voltammetric detection of phosphate ions.

Dihydrogen phosphate (H_2PO_4^-) plays a key role in biological, environmental, and many industrial processes. In recent years, phosphate levels in water have significantly increased because of leaching from agricultural soils after wide use of phosphate-based commercial fertilizers, which may have an adverse effect on water quality and food quality. Therefore, detection of phosphate ions, both inorganic and organic, is important in biological, environmental, and biomedical areas. On the basis of previous literature reports, several colorimetric probes, so-called “naked-eye chemosensors”, have been developed for the detection of phosphate anions based upon the selective recognition unit, hydrogen-bonding receptors, and so forth.^[17,18] Also, great efforts have been devoted to designing hybrid-electrode materials for the detection of phosphate anions based on the modification of electrodes through electrochemical technique.^[19–21] However, we developed an amperometric technique, which is sensitive to phosphate ions,

and our method does not suffer from interference from arsenate or carbonate, which are known to limit the application of other methods of phosphate analysis.

2. Results and Discussion

2.1. Physical and Chemical Properties of PTZH-AuNPs

PTZH was selected on the basis of its unique properties and reducing capability under UV/Vis light, as well as its capability to stabilize AuNPs through interactions with the sulfur- and nitrogen-coordinating sites present in PTZH . Few amines and amino acids have the capability to reduce Au(III) as well as the ability to stabilize the nanoparticles through weak covalent and weak electrostatic interaction between gold and nitrogen atoms.^[22,23] Also, it is well known that thiol-based ligands stabilize AuNPs through Au-S interactions.^[3] Although PTZH and its products do not have long chain structures, they can stabilize AuNPs through coordination with the nitrogen and sulfur site present within their structures. This is because of the planar radical-cation-structure formation after oxidation, owing to the large aromatic resonance stabilization, which has been well studied by both theoretical and experimental observations.^[8,24]

In the present work, HAuCl_4 was reduced photochemically by PTZH . A series of color changes were noticed during the course of the reaction, as shown in Figure 1. Also, we studied the time-dependent UV/Vis spectra of nanoparticle formation with respect to the addition of Au(III) to PTZH solution, as shown in Figure S1 in the Supporting Information, which reveals that the absorption increases with increasing reaction time. The corresponding TEM images are shown in Figure S2 in the Supporting Information.

The formation of AuNPs was ascertained by the characteristic surface plasmon resonance (SPR) band of the AuNPs, which appeared in the UV/Vis absorption spectrum at approximately 526 nm. The UV/Vis spectrum of PTZH shows two absorption bands at 273 and 332 nm, as shown in Figure S3 in the Supporting Information. The PTZH spectrum does not show any absorption in the range 400–750 nm, whereas the AuNPs exhibit a distinct absorption band approximately 526 nm, corresponding to SPR band of AuNPs as shown in Figure 2a. AuNPs can also be characterized by using cyclic voltammogram.^[25]

The cyclic voltammogram of AuNPs on an indium–tin oxide (ITO) electrode surface in 0.5 M H_2SO_4 electrolyte is shown in Figure 2b. The characteristic Au surface oxidation and the corresponding oxide reduction confirms that the ITO surfaces were modified with AuNPs.^[26] The TEM image shown in Fig-

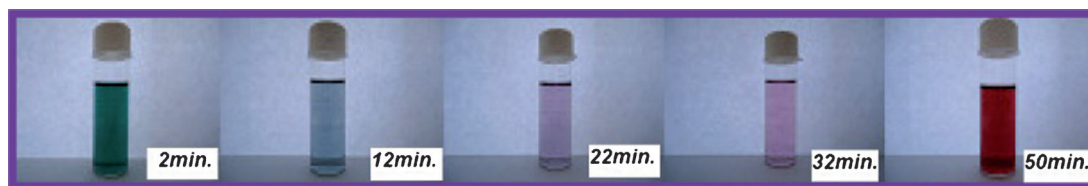


Figure 1. The colorless solution of PTZH turned to green within 1–2 min after addition of Au(III) . The green reaction mixture faded within 10 min, and then it turned light violet to light pink within another 10 min, and finally wine-red after 40–50 min.

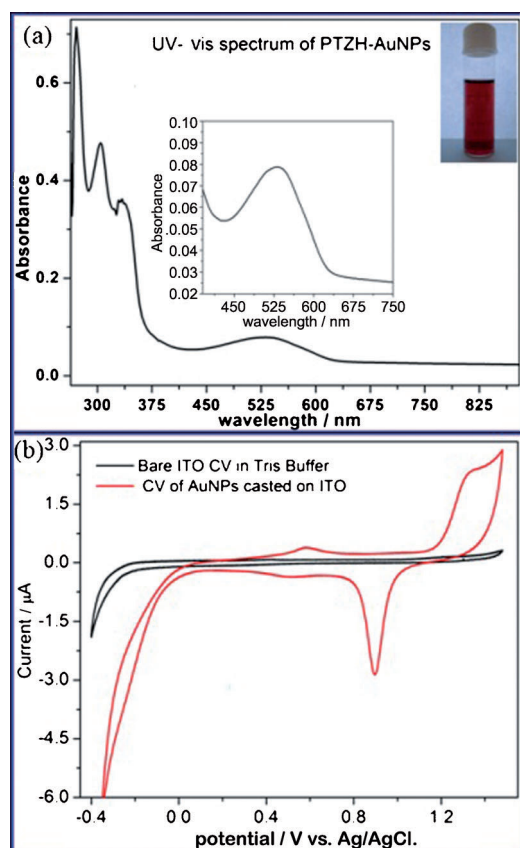


Figure 2. a) UV/Vis spectrum of PTZH-AuNPs [insets: macroscopic appearance of the AuNPs (photo) and zoom-view UV/Vis spectrum of the SPR band of Au]. b) Cyclic voltammograms of bare ITO and PTZH-AuNPs-modified ITO electrodes in Tris buffer.

Figure 3a reveals that the average particle size of AuNPs is approximately 45 nm and the corresponding size distribution of AuNPs is shown in Figure 3c. The Scherrer ring of the selected area electron diffraction (SAED) pattern obtained for the AuNPs, as shown in Figure 3b, can be indexed as the (111), (200), (220), and (311) planes of a face-centered cubic lattice of Au atoms. On the basis of previous literature reports, we propose that HAuCl_4 is reduced to form Au(II), which disproportionates to Au(III) and Au(I). Furthermore, Au(I) is reduced to metallic Au(0), leading to the formation of AuNPs, as shown in Figure 3d.^[5,8]

Fourier-transform infrared (FTIR) spectroscopy (Figure 4) was used to characterize the particles, and some major changes occur to the bands assigned to PTZH upon formation of PTZH-AuNPs, as shown in the highlighted spectra in the region of 400–2000 cm^{-1} . The FTIR spectrum of PTZH was assigned from the literature;^[27] this shows angle bending of $\delta(\text{C-S})$, asymmetric angle bending of $\delta(\text{C-S-C})$, angle bending of $\delta(\text{C-N})$, symmetric stretching of $\nu_s(\text{C-N-C})$, and asymmetric stretching of $\nu_{as}(\text{C-N-C})$, which appear at 441.3, 511.2, 897.2, 1251.2, and 1262.3 cm^{-1} , respectively. In the FTIR spectrum of PTZH-AuNPs, these peaks are observed at 430.7, 497.2, 863.5, 1224.2, and 1242.3 cm^{-1} , respectively. The shift of these peaks to lower wavenumbers indicates a decrease in the bond strength of C-S as well as C-N in the PTZH-AuNPs. The de-

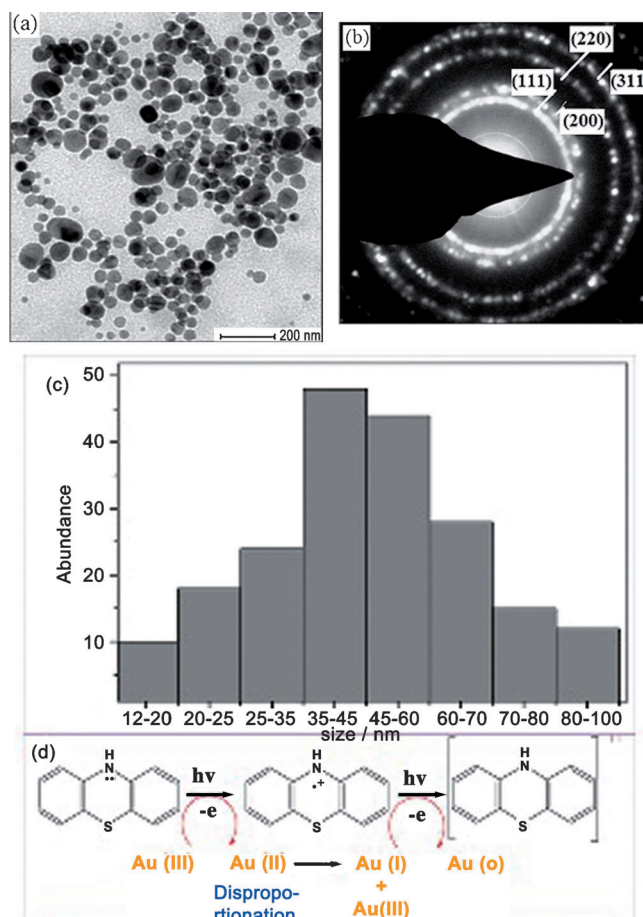


Figure 3. a) TEM image and b) SAED pattern of the AuNPs. c) Size distribution of PTZH-AuNPs and d) the reaction scheme for the photochemical formation of AuNPs.

crease in the assigned stretching frequencies is attributed to the transfer of electron density from the S and N atoms to Au atom, resulting in electrostatic interactions between S or N atoms and AuNPs.^[22,23] With this experimental FTIR result, it is assumed that the AuNPs are co-adsorbed on the PTZH surface through electrostatic interaction with S and N atoms.

2.2. Electroensing of Phosphate Ions

PTZH-AuNPs can be used as modifiers of electrode surfaces because of some of their characteristics, such as they are less soluble in water, so that leaching of material from the electrode surface can be avoided and can be easily adsorbed on Au surface through interaction with sulfur and nitrogen. The majority of modified AuNP interfaces are based on the affinity between thiols and gold (i.e. the S-Au interaction) or the amine to gold atom (N-Au) interaction.^[15–16,28] Cyclic voltammetric responses of the polycrystalline Au electrode and the electrode modified with PTZH-AuNPs were examined by using 0.1 mM $\text{Fe}(\text{CN})_6^{4-/3-}$ in Tris buffer solution. A significant increase in the peak current was observed for the same amount of $\text{Fe}(\text{CN})_6^{4-/3-}$ for the modified electrode compared to the unmodified polycrystalline Au electrode, as shown in Figure 5,

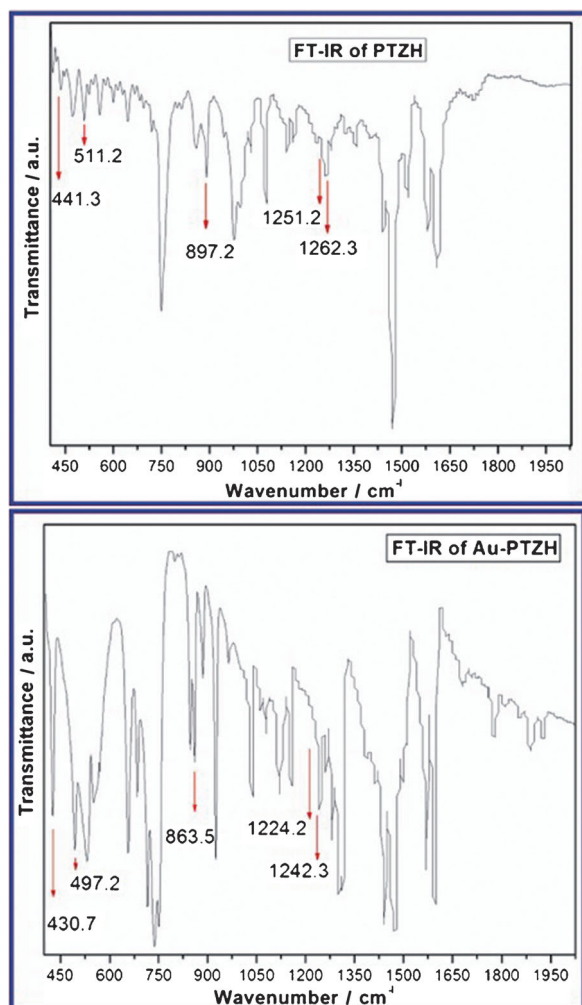


Figure 4. FTIR spectrum of PTZH (top) and PTZH-AuNPs (bottom).

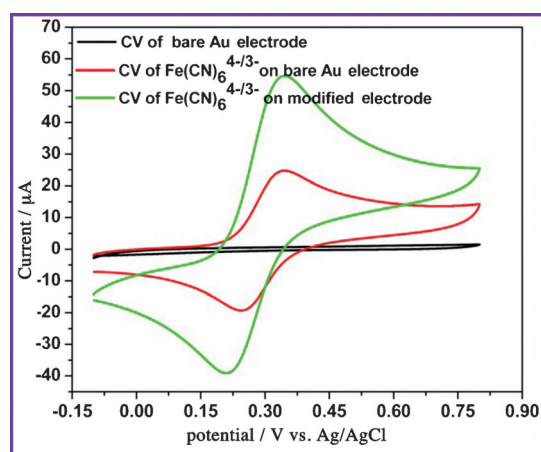


Figure 5. Cyclic voltammograms for a bare Au electrode in blank buffer, and both the bare and modified electrodes in buffer containing the $\text{Fe}(\text{CN})_6^{4-/3-}$ redox couple.

indicating that the electrode modified with PTZH-AuNPs favors the electron-transfer reaction. The catalytic efficiency of nano-sized materials mainly depends on 1) the surface-to-

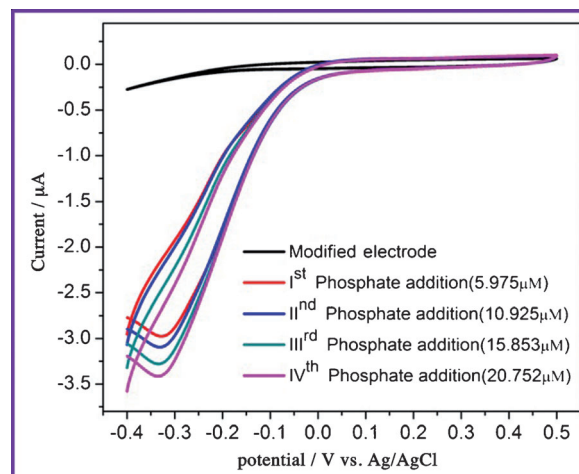


Figure 6. Cyclic voltammograms for the successive addition of phosphate in 0.1 M tris buffer at pH 7.2.

volume ratio of the material and 2) the electronic interactions between the material and the analyte. Nanoparticles are very different from their bulk counterparts, because the catalytic activity originates from their quantum-scale dimensions.^[28–30]

The PTZH-AuNP-modified electrode did not show any redox peaks in the potential window -0.4 to $+0.5$ V versus Ag/AgCl in the blank sample. We selected particular potential window regions in which there are no other redox peaks of the material. However, well-defined voltammetric responses were obtained for successive additions of phosphate, as shown in Figure 6. Upon successive addition of phosphate, a substantial increase in the peak current reflects a fast electron-transfer reaction on the PTZH-AuNPs-modified electrode, owing to the high catalytic effect of the nanostructured platform. In order to verify this, we modified the electrode surfaces with citrate-stabilized AuNPs and PTZH alone. Thereafter, we performed two sets of experiments in which the response of phosphate addition towards both of these modified electrodes was assessed, and it was found that no clear peak appears with an increasing concentration of analyte, as shown in Figure S4 in the Supporting Information. The specific catalytic activity originates from the hybrid material, that is, PTZH-AuNPs, and not from the AuNPs or the PTZH alone. Furthermore, the electrochemistry behind the electrocatalytic sensing of phosphate is attributed to the catalytic effect of the nano-sized gold particle capped with PTZH and its oxidation product, which exhibit high electron-transfer kinetics through the interaction of AuNPs with the oxygen atoms of PO_4^{3-} .^[17,18] The proposed schematic representation of the nanostructured platform of the PTZH-AuNPs for modified electrode is shown in Figure 7.

For the amperometric study, a fixed reduction potential of -0.336 V versus AgCl/Ag was chosen from the cyclic voltammetry studies, and aliquots of phosphate were injected into a stirred supporting electrolyte solution. A systematic change in the current was noticed after each addition of phosphate into the supporting electrolyte solution, and a steady-state response was attained within 2–3 s. After the fourth standard addition of phosphate, equal quantities of $0.03 \mu\text{M}$ of carbonate

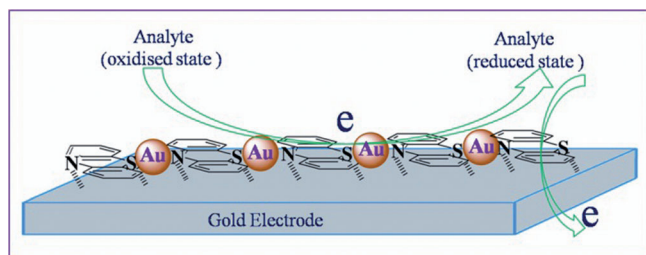


Figure 7. Nano-integrated platform of the PTZH-AuNPs as a modified electrode.

and arsenate were added sequentially, and their influence on the current response was noted. However, it can be seen from Figure 8a that the added interfering anions (carbonate and arsenate) had no effect on the chronoamperometric current. The sensing platform is, therefore, highly sensitive and showed a linear response towards phosphate addition, with a sensitivity and limit of detection of $0.794 \mu\text{A} \mu\text{M}^{-1}$ and $0.022 \mu\text{M}$, respectively, and the signal-to-noise ratio was 3, as shown in the chronoamperometric calibration plot in Figure 8b.

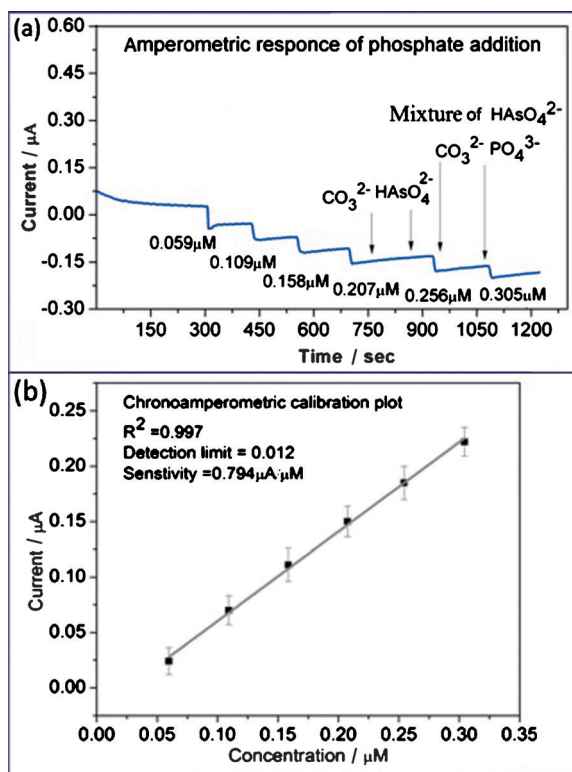


Figure 8. a) Amperometric response at an applied potential of -0.336 V versus Ag/AgCl for the successive addition of phosphate in 0.1 M Tris buffer at pH 7.2 under stirred conditions. b) The corresponding standard addition calibration plot of chronoamperometric current versus phosphate concentration.

The PTZH-AuNPs-modified electrode was further tested for sensing phosphate in commercially available fertilizer samples. We kept all of the measurement conditions the same as they were in the test with standard additions of phosphate. Cyclic

voltammograms and the corresponding chronoamperometric calibration plot for the real samples (commercially available phosphate fertilizer) are shown in Figure S5 of the Supporting Information, which indicated that the modified electrode is also highly selective for phosphate analysis in real samples. The amperometric experiments were repeated four times with the modified electrode and the experiments were highly reproducible. The mean deviation of the current values was within 8%. A detailed investigation into the mechanism of the electrocatalysis of the modified electrode, to achieve low detection limits and electroanalytical determination of phosphate in biological systems, is likely to be addressed in our future studies.

3. Conclusions

Photochemically assisted formation of novel AuNPs by using PTZH is reported, and its application in the amperometric sensing of phosphate ions is demonstrated in standard samples as well as in a commercial fertilizer. The sensing platform is highly sensitive and shows a linear response towards standard phosphate additions, with a sensitivity and limit of detection of $0.794 \mu\text{A} \mu\text{M}^{-1}$ and $0.022 \mu\text{M}$, respectively. The method described in this work offers the selective, sensitive, enzyme-free electroanalytical determination of phosphate. This may also be practical for field-deployable onsite measurements, in which the practical use of costly equipment, such as inductively coupled plasma optical emission spectrometers and other large-scale instruments, is not possible. It is believed that the publication of this work will strongly promote the fast development of the electrocatalytic applications and chemistry of PTZH and its analogues.

Experimental Section

Materials

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich), PTZH (Sigma-Aldrich), ITO plates (Asahi Beer Optical Ltd, Japan), ethanol (99.5%), and sodium dihydrogen phosphate (Merck Germany) were used as received, unless otherwise mentioned. The glassware used in the preparation of the AuNPs was cleaned with freshly prepared aqua regia (3:1 HCl/ HNO_3) and rinsed comprehensively with ultrapure millipore water ($18.2 \text{ M}\Omega \text{ cm}$) before use. (Caution: aqua regia is a powerful oxidizing agent and it should be handled with extreme care.)

Tris buffer (pH 7.2) was prepared from 0.1 M tris(hydroxymethyl)amino methane. The pH value was adjusted with 0.1 M HCl. Commercially available phosphate fertilizer (Parry's super phosphate, P = 16%, Coromandel International Limited) was used for real-sample analysis. A stock solution of the fertilizer sample ($10 \mu\text{M}$ phosphate) was prepared by dissolving the fertilizer (0.046 g) in water (50 mL) and diluting accordingly. Deaerated Tris buffer (pH 7.2) was used as a supporting electrolyte in the electroanalytical detection of phosphate.

Synthesis of AuNPs

In a typical synthesis, HAuCl_4 ($20 \mu\text{L}$, 5 mM) was mixed with continuously stirred PTZH solution (21 mM). PTZH is insoluble in water, but it is soluble in ethanol; therefore, an aqueous ethanolic solu-

tion (15: 85 v/v) was prepared to dissolve the PTZH. The entire reaction content was then irradiated by using a 100 W sun lamp with a spectral output of > 360 nm. The glass vial was kept at a distance of 12 cm from the light source to avoid heating the solution.

Amperometric Sensing of Phosphate Ions

A polycrystalline Au electrode with a geometrical surface area of 0.031 cm^2 was used as the substrate for the fabrication of the nanostructured platform. The thoroughly cleaned polycrystalline Au electrode was soaked in an ethanolic solution of PTZH–AuNPs for 6 h for the formation of a nanoparticle assembly on the electrode surface. The assembled PTZH–AuNPs on the gold surface were examined by taking field-emission SEM images, as shown in Figure S6 in the Supporting Information. The reduction potential, that is, -0.336 V versus Ag/AgCl was chosen for the amperometric analysis of phosphate ions under optimized conditions, and aliquots of phosphate were injected into a stirred supporting electrolyte (pH 7.2 tris buffer) solution. A systematic change in the current was noticed after each addition of phosphate into the supporting electrolyte solution.

Instrumentation

UV/Vis absorption spectra were recorded by using a Lambda-25 PerkinElmer (Germany) spectrophotometer with a quartz cuvette having optical path length of 1 cm. The microscopic views of the samples were examined by using a transmission electron microscope (Tecnai G2, 20 FEI Corporation Netherlands) operating at 200 kV. A few microliters of the colloidal AuNP suspension was dropped onto carbon-coated copper grids (obtained from Pelco International, USA) and allowed to dry, then the fabricated electrode modified with AuNPs was examined by using SEM recorded with a JEOL JEM 6700F field-emission scanning electron microscope. FTIR studies of PTZH and PTZH–AuNPs were carried out by using a Nicolet Thermo Scientific 6700 (Germany). Cyclic voltammetry and amperometric analysis of the modified electrode were performed by using an Autolab potentiostat–galvanostat (PG-STAT, 302, Netherlands) with computer-controlled GPES software. A conventional three-electrode system, consisting of the modified electrode as the working electrode, Pt foil as the counter electrode, and Ag/AgCl as the reference electrode, was used for all of the electrochemical measurements. Neutral tris buffer (pH 7.2) was used as the supporting electrolyte and the scan rate was kept at 50 mVs^{-1} for each measurement.

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Keywords: electrocatalysis • electrochemistry • gold nanoparticles • phenothiazine • sensors

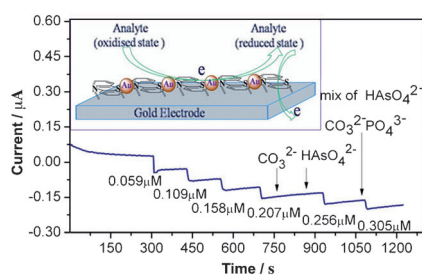
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ARTICLES

Top hat: Gold nanoparticles (AuNPs), formed through a photochemically assisted process by using phenothiazine (PTZH), stabilize themselves through electrostatic interactions with sulfur and nitrogen atoms. This hybrid electrode material can be used to modify electrodes for electrochemical sensing and catalysis, which can be used for the fabrication of sensing devices. We demonstrate the electrocatalytic activity of AuNPs capped with PTZH for the electrochemical sensing of phosphate ions.



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Phenothiazine-Capped Gold Nanoparticles: Photochemically Assisted Synthesis and Application in Electrochemical Sensing of Phosphate Ions

