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Highly Sensitive Colorimetric Sensing of Mercury (II) Ions by Green Synthesized Gold Nanoparticles

K. O. Sodeinde[1,3], E. O. Dare[2], A. A. Lasisi[2], O. S. Ayanda[1,4], S. M. Nelana[4], E. B. Naidoo[4], O. S. Lawal[1], and N. Revaprasadu[3]

[1]*Nanoresearch Unit,*
Department of Industrial Chemistry,
Federal University Oye-Ekiti,
Oye-Are Road
Ekiti State, Nigeria
[2]*Department of Chemistry,*
Federal University of Agriculture,
Abeokuta, Ogun State, Nigeria
[3]*Department of Chemistry,*
University of Zululand,
Private Bag X1001,
KwaDlangezwa 3886, South Africa
[4]*Department of Chemistry,*
Vaal University of Technology,
Vanderbijlpark 1900, South Africa

In this study, a rapid, simple and green method for sensing mercury (II) ions in aqueous solutions based on the shift in the localized surface plasmon resonance of biosynthesized gold nanoparticles (Au NPs) using *Chrysophyllum albidum* aqueous extract is developed. Au NPs biosynthesis is via microwave-assisted method. From the kinetic studies, the first-order rate constant value of $8.89 \cdot 10^{-5}$ s^{-1} is obtained. Red shift in surface plasmon band of Au NPs from 520–540 nm to around 650 nm in a concentration-dependent manner is observed in the presence of Hg^{2+} ions. The limit of detection and percentage recovery are 0.001 mg/L and 89–93%, respectively. Sensing capacity of the method is successfully applied to Iju river water samples. This novel method shows excellent sensitivity and selectivity for Hg^{2+}, and it can be applied to the determination of Hg^{2+} in water samples.

В цьому дослідженні розроблено швидку, просту та нешкідливу методу визначення йонів Меркурію (II) у водних розчинах на основі зміщення в резонансі локалізованих поверхневих плазмонів наночастинок золота (Au-НЧ), біосинтезованих з використанням водного екстракту *Chrysophyllum albidum*. Біосинтеза Au-НЧ здійснюється за допомогою мікрохвильової ме-

тоди. З кінетичних досліджень одержано значення константи швидкости першого порядку $8{,}89 \cdot 10^{-5}$ $с^{-1}$. Червоне зміщення смуги поверхневого плазмону Au-НЧ від 520–540 нм до приблизно 650 нм, залежно від концентрації, спостерігається у присутності йонів Hg^{2+}. Границя виявлення й процентне відновлення складають 0,001 мг/л і 89–93% відповідно. Чутлива здатність методи успішно застосовується до проб води річки Іджу. Ця нова метода демонструє відмінну чутливість і селективність для Hg^{2+}, і її можна застосовувати для визначення Hg^{2+} у пробах води.

В этом исследовании разработан быстрый, простой и безвредный метод определения ионов ртути (II) в водных растворах на основе смещения в резонансе локализованных поверхностных плазмонов наночастиц золота (Au-НЧ), биосинтезированных с использованием водного экстракта *Chrysophyllum albidum*. Биосинтез Au-НЧ осуществляется с помощью микроволнового метода. Из кинетических исследований получено значение константы скорости первого порядка $8{,}89 \cdot 10^{-5}$ $с^{-1}$. Красное смещение полосы поверхностного плазмона Au-НЧ от 520–540 нм до примерно 650 нм в зависимости от концентрации наблюдается в присутствии ионов Hg^{2+}. Предел обнаружения и процентное восстановление составляют 0,001 мг/л и 89–93% соответственно. Чувствительная способность метода успешно применяется к пробам воды реки Иджу. Этот новый метод демонстрирует превосходную чувствительность и селективность для Hg^{2+}, и его можно применять для определения Hg^{2+} в пробах воды.

Key words: gold nanoparticles, mercury, *Chrysophyllum albidum*, sensitivity, surface plasmon resonance.

Ключові слова: наночастинки золота, Меркурій, *Chrysophyllum albidum*, чутливість, резонанс поверхневих плазмонів.

Ключевые слова: наночастицы золота, ртуть, *Chrysophyllum albidum*, чувствительность, резонанс поверхностных плазмонов.

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1. INTRODUCTION

Mercury is a toxic metal that can be released into the environment from natural and anthropogenic sources. Although mercury has numerous industrial and domestic applications in nuclear reactors, as antifungal agents for wood processing, as a solvent for reactive and precious metals, component of batteries, switches, lamps, *etc.*, it is a widespread environmental pollutant, which induces severe alterations in the body tissues and causes a wide range of adverse health effects [1, 2]. All forms of mercury (elemental, organic and inorganic ones) are toxic and their effects include gastrointestinal toxicity, neurotoxicity and nephrotoxicity [1]. Well established techniques used for the detection and quantitation of mercury (II) ions include cold vapour atomic

absorption spectroscopy, inductively coupled plasma-mass spectrometry, x-ray fluorescence, stripping voltammetry, *etc.* [3, 4]. However, high cost, tedious sample preparation process, low sensitivity, *etc.*, are some of the setbacks of these techniques.

Nanoanalytical sensing system is an emerging multidisciplinary field, which combines the inherent characteristics of analytical techniques (*e.g.*, high sensitivity, rapid detection and low cost, *etc.*) with unique electronic, optical, magnetic, mechanical, and catalytic properties of nanomaterials [5, 6]. Metal nanoparticles (MNPs)-based electroanalytical technique shows the enormous potentials for constructing enhanced platforms for chemical sensing and biosensing [7]. MNPs-based colorimetric methods (which utilizes the changes in the Surface Plasmon Resonance (SPR) bands of Au or Ag NPs) are extremely attractive due to their simplicity, high sensitivity, low-cost, easily read out with the naked eye, and allow onsite, real-time qualitative or semiquantitative detection without complicated analytical instruments [8, 9]. MNPs are rapidly emerging as a kind of important colorimetric sensors because their extremely high visible-region extinction coefficients (10^8–10^{10} $M^{-1}{\cdot}cm^{-1}$) are often several orders of magnitude higher than those of organic dyes [7]. Hence, MNPs-based analytical sensing devices exhibit good advantages and potentials for detecting different targets, which have important significance in areas such as environmental pollution, diseases detection, human health and food safety, *etc.*

Tremendous research efforts have been directed towards gold nanoparticles (Au NPs)-based colorimetric assays for DNA, enzyme activity, small molecules, metal ions, carbohydrates, and proteins, *etc.*, using their unique SPR as sensing elements in the last two decades [10–13]. For instance, Mirkin's group pioneered the use of Au NPs-thiolated-DNA conjugates [10, 11], which led to a series of novel colorimetric sensors for the ultrasensitive detection of polynucleotide, DNA, protein, and metal ion, *etc.* In 2014, Zhou and co-workers [14] reported colorimetric sensing of Hg^{2+} ions based on Au NPs and 4-mercaptylphenylboronic acid. Hg^{2+} ions were detected in the presence of other metal ions. Recently, Kiran [15] utilized Au NPs capped with 2-mercaptosuccinic acid for the detection of mercury in water samples.

In this communication, we present a rapid, versatile green synthesis of spherical Au NPs using aqueous extract of *Chrysophyllum albidum* (*C. albidum*) leaves and its excellent colorimetric sensing capacity for Hg^{2+} ions in aqueous media.

2. EXPERIMENTAL

2.1. Chemicals and Plant Extract

Gold (III) chloride trihydrate (99.9%), methanol and $HgCl_2$ were pro-

cured and used as received from Sigma Aldrich, South Africa. Serial concentrations (10.0, 1.0, 0.10, 0.010 and 0.0010 mg/L) of Hg^{2+} were prepared from 1000 mg/L stock solution previously obtained by dissolving 1.354 g of $HgCl_2$ in 1L deionised water. Fresh leaves of *C. albidum* were collected from a local residence in Ibadan, Nigeria. The *C. albidum* leaves were washed with deionised water and air-dried in a fume hood for two weeks. Finely cut leaves were boiled in deionised water (1:10 w/v) for 20 min and extract filtered with a filter paper. The filtrate was cooled to room temperature and refrigerated at 4°C.

2.2. Synthesis and Characterization of Au Nanoparticles

For the green synthesis of Au nanoparticles, our previously established microwave assisted procedure was utilised [16]. 4 mL of 0.1 g/mL aqueous filtrate of the extract was reacted with 4 mL of 1 mM gold (III) chloride trihydrate solution and exposed to microwave irradiation using a DEFY model DMO 35338l microwave at low operating power level 1 for 90 s. The resulting Au NPs was obtained by centrifugation at 4000 rpm for 5 min, purified by resuspending in methanol, and finally centrifuged at 4000 rpm for 2 min. The effect of pH on the synthesis of Au NPs was considered in this study.

2.3. Sensitivity and Selectivity Studies

Aliquots of biosynthesized Au NPs and different concentrations of Hg^{2+} were placed in quartz cuvettes (1 cm path length), and the absorbance recorded to determine the sensing capability of Au NPs. Selectivity of the technique was achieved by analysing aliquots of Au NPs and Hg^{2+} in the presence of 0.1 mg/L concentrations of Cu^{2+}, Fe^{3+}, Mg^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} metal ions under the same conditions. The feasibility of spherical Au NPs for detecting Hg^{2+} in real water samples was explored using river water samples obtained from Iju river, along Sango Otta–Atan road, Ado-Odo/Otta Local Government Area of Ogun State, Nigeria. The river water samples were collected in glass bottles, filtered and spiked with standard solutions containing different concentrations of Hg^{2+} and analysed using standard addition method. Recovery study was carried out in similar manner. All analyses were conducted in triplicates.

2.4. Characterization

A Perkin-Elmer Lambda 20 UV–vis spectrophotometer was used to carry out absorption measurements in the 300–800 nm wavelength range. Fluorescence spectra were recorded at room temperature using

a Perkin-Elmer LS 55 luminescence spectrometer with a Xenon lamp over a range of 300–800 nm. Aliquots of biosynthesized Au NPs were placed in quartz cuvettes (1 cm path length), and the excitation peaks were analyzed and recorded. Samples for transmission electron microscopy (TEM) analysis were prepared by placing an aliquot of the NPs onto an amorphous carbon substrate supported by a copper grid and then allowing the solvent to evaporate at room temperature. The morphology and particle sizes of the samples were observed using a JEOL 1010 TEM at an accelerating voltage of 100 kV. Pictures were captured using a Megaview III camera and imaged using Soft Imaging Systems iTEM software.

3. RESULTS AND DISCUSSION

3.1. Optical Properties

Figure 1 shows the UV–vis absorption and photoluminescence (PL) emission spectra of the aqueous dispersion of the Au NPs. It was observed that the UV–vis spectra of Au NPs exhibited distinct, narrow localized surface plasmon resonance (SPR) band at 530–550 nm with maximum absorbance at 532 nm. The SPR phenomenon is due to the collective oscillation of free conduction electrons induced by an interacting electromagnetic field [17].

Formation of Au NPs was further confirmed by the appearance of a purple colour in the reaction medium (Figure 1, *b*). Rate constant value of $8.89 \cdot 10^{-5}$ s^{-1} was obtained from UV–vis data using Beer–Lambert law and first order rate equation for the bioreduction of Au NPs as shown in Fig. 1, *c*. From Figure 1, *d*, Au NPs showed a strong PL emission peak centred at 453 nm when excited at 300 nm, indicating the nanoparticles are fluorescent. Fourier Transformed Infrared (FTIR) spectroscopic analysis of the aqueous leaves extract, as shown in Fig. 2, revealed the presence of –OH, –COOH stretching at 3400 cm^{-1} and 1630 cm^{-1}, respectively. The broad –OH band can be attributed to hydrogen bonding in the aqueous extract.

From our previous studies, we had established the presence of phytochemicals such as flavonoids, alkaloids, tannins, carbohydrates, saponins, terpenoids, *etc.*, in the aqueous plant extract as being responsible for the bioreduction, capping and stabilization of the nanoparticles [16].

Figure 3 shows the effect of pH variation on the surface plasmon band of Au NPs. At pH 3, no absorption peak was observed in the region corresponding to the SPR band of Au NPs. However, at pH 7, relatively small absorption peak was observed. The peak intensity became more prominent at pH 11 indicating greater concentrations of Au NPs under alkaline conditions. Thus, the most favourable pH for the syn-

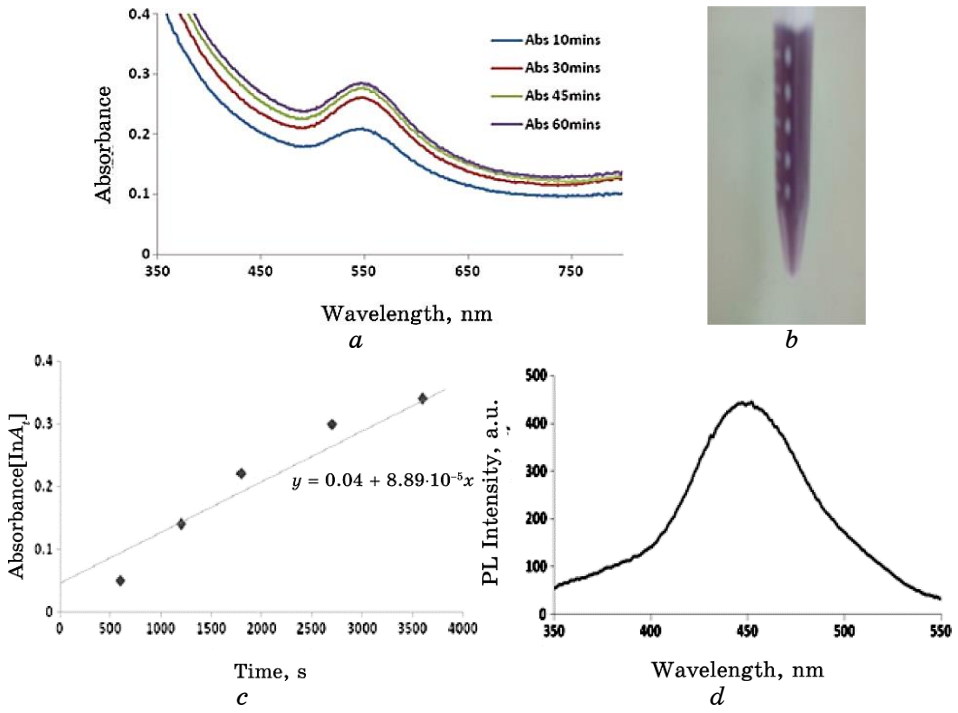


Fig. 1. UV–vis spectra (*a*) and purple colour (*b*) of Au NPs; first-order plot of In (A_t) (A_t: absorbance at time t, t close to infinity) and the reaction time, t (s) of Au NPs (*c*); photoluminescence emission spectra of Au NPs at excitation wavelength of 300 nm (*d*).

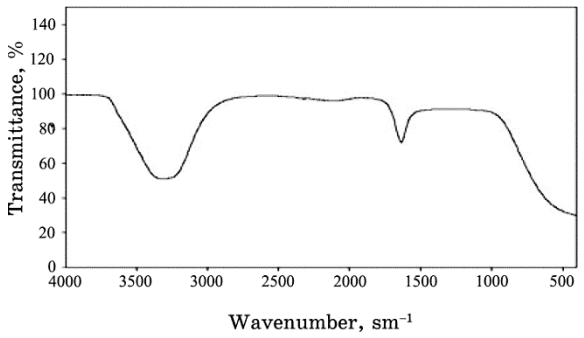


Fig. 2. FTIR spectra of aqueous extract of *C. albidum* leaves.

thesis of Au NPs is pH 11.

TEM images (Fig. 4, *a*) revealed a uniform spherical morphology with particle size range of 14–17 nm. The particle size distribution is shown in Fig. 4, *b*.

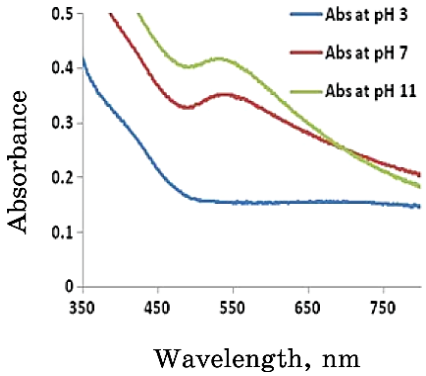
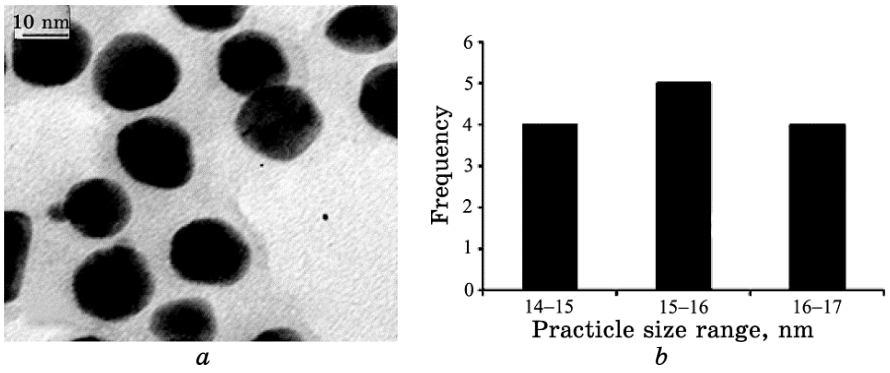


Fig. 3. Effect of pH variation on the surface plasmon resonance band of Au NPs.



a *b*

Fig. 4. TEM (*a*) and particle size distribution (*b*) of Au NPs.

For the sensitivity study, different concentrations of Hg^{2+} in the range of 10.0–0.001 mg/L were investigated.

Figure 5 shows a red shift from the range 520–540 to 650 nm and a corresponding gradual decrease in absorbance intensity as the Hg^{2+} concentration increased from 0.001 to 10.0 mg/L thus revealing that the sensing system is highly sensitive to Hg^{2+} concentration. The detection limit is 0.001 mg/L (1 μg/L) that is much lower than other previously reported values and in the range specified for mercury in drinking water permitted by the United States Environmental Protection Agency and the European Union [14, 18–20]. It is noteworthy that only 5 min of reaction time was required for the detection of Hg^{2+} ions by the spherical green Au NPs. Table shows the comparison of the sensing capacity for Hg^{2+} ions of this method with other studies.

Another major parameter usually employed in the determination of a suitable analytical technique is selectivity. The changes in absorbance intensity in the presence of 0.1 mg/L concentration each of Cu^{2+},

Fe^{3+}, Na^{+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} metal ions under the same reaction conditions was studied as shown in Fig. 6.

A red shift from 520–540 to 650 nm and a remarkable reduction in

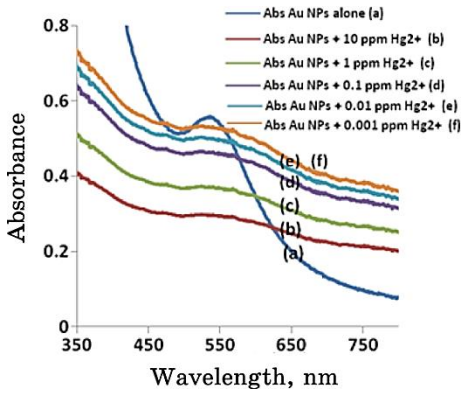


Fig. 5. UV–vis spectra of Au NPs in the presence of different concentrations (10–0.001 ppm) of Hg^{2+} ions.

TABLE. Comparison of different sensing probes for Hg^{2+} detection.

	Detection limit, μg/L	Linear range (nM)	Ref.
Fluorescent Au NPs	2.0	$10–5{\cdot}10^{3}$	[18]
Au@Ag core shell NPs	1.8	10–450	[19]
Green Au NPs	1.0	$5–5{\cdot}10^{4}$	This study

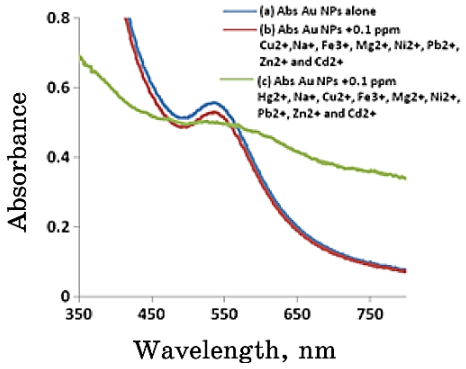


Fig. 6. UV–vis spectra of: *a*) green synthesized Au NPs alone, *b*) in the presence of 0.1 mg/L: Cu^{2+}, Na^{+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} metal ions (without Hg^{2+}), c) in the presence of 0.1 mg/L: Hg^{2+}, Cu^{2+}, Na^{+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} metal ions.

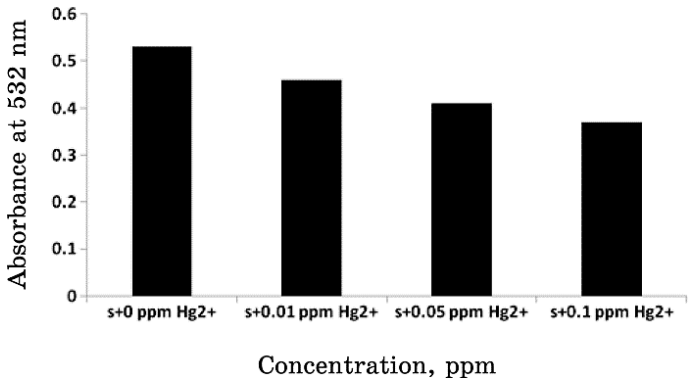


Fig. 7. Plot of absorbance intensity of Au NPs in the presence of river water sample(s) spiked with different concentrations of Hg^{2+}.

absorbance intensity is observed upon addition of Hg^{2+} to the spherical green Au NPs (*c*). However, no significant change in absorbance intensity and wavelength was observed by adding other metal ions alone into the colloidal gold dispersion (*b*). The excellent sensitivity and selectivity of this spectroscopic technique might be attributed to the facile complexation between Hg^{2+} ions and different functional groups such as –OH and –COOH serving as the capping, reducing and stabilization agents in the gold nanoparticles.

The standard addition calibration curve for determining Hg^{2+} in river water was obtained by plotting the values of absorbance versus concentrations of Hg^{2+} spiked with 0.5 mL river water sample (Fig. 7). In this way, both known and unknown interferences in the river water samples were taken care of. Peak absorbance values of 0.53 ± 0.03, 0.46 ± 0.01, 0.41 ± 0.02, 0.37 ± 0.02 were obtained upon spiking with 0 mg/L, 0.01 mg/L, 0.05 mg/L and 0.1 mg/L Hg^{2+} concentrations, respectively. From this result, the analytical sensing capacity of the spherical Au NPs clearly distinguished between the river water sample and that spiked with different Hg^{2+} concentrations despite the interference from minerals and organics present in the river water samples, hence, fulfilling practical Hg^{2+} detection ability in real water samples. Validity of this technique was determined through recovery studies using river water sample previously spiked with different concentrations of standard solutions of Hg^{2+} ions. Percentage recovery range of 89–93% indicates a good quantitative recovery of the analytical method under prevalent conditions.

4. CONCLUSION

In conclusion, we have demonstrated a simple, rapid, reliable, cost-

effective, label-free, selective and highly sensitive colorimetric technique for Hg^{2+} ions determination in the presence of other metal ions with detection limit of 1 μg/L level in aquatic media using spherical green Au NPs. It is believed that the development of this technique would assist in monitoring mercury levels in the environment.

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REFERENCES

1. P. B. Tchounwou, W. K. Ayensu, N. Ninashvilli, and D. Sutton, *Environ. Toxicol.*, **18**: 149 (2003).
2. B. A. Sarkar, *Rev. Environ. Health*, **20**: 39 (2005).
3. H. Wang, B. Kang, T. F. Chancellor, T. P. Lele, Y. Tseng, and F. Ren, *Appl. Phys. Lett.*, **91**: 042114 (2007).
4. H. Li, J. Zhai, J. Tian, Y. Luo, X. Sun, H. Li, J. Zhai, J. Tian, Y. Luo, and X. Sun, *Biosens. Bioelectron.*, **26**: 4656 (2011).
5. S. Guo, S. Dong, S. Guo, and S. Dong, *Trends Anal. Chem.*, **28**: 96 (2009).
6. S. Guo and E. Wang, *Anal. Chim. Acta*, **598**: 181 (2007).
7. S. Guo and E. Wang, *Nano Today*, **6**: 240 (2011).
8. D. Li, S.P. Song, and C. Fan, *Acc. Chem. Res.*, **43**: 631 (2010).
9. G. Q. Wang, Y. Q. Wang, L. X. Chen, and J. Choo, *Biosens. Bioelectron.*, **25**: 1859 (2010).
10. C. A. Mirkin, R. L. Letsinger, R. C. Mucic, and J. J. Storhoff, *Nature*, **382**: 607 (1996).
11. N. L. Rosi and C. A. Mirkin, *Chem. Rev.*, **105**: 1547 (2005).
12. M. Han, A. Lytton-Jean, B. Oh, J. Heo, and C. Mirkin, *Angew. Chem. Int. Ed.*, **45**: 1807 (2006).
13. J. Liu and Y. Lu, *Angew. Chem.*, **118**, No. 1: 96 (2006).
14. Y. Zhou, H. Dong, L. Liu, M. Li, K. Xiao, and M. Xu, *Sensors Actuators B: Chemical*, **196**: 106 (2014).
15. K. Kiran, *Appl. Nanosci.*, **5**: 361 (2015).
16. K. O. Sodeinde, E. O. Dare, A. A. Lasisi, P. Ndungu, and N. Revaprasadu, *J. Bionanoscience*, **10**: 216 (2016).
17. P. Mulvaney, *Langmuir*, **12**, No. 3: 788 (1996).
18. C. Guo and J. Irudayaraj, *J. Anal. Chem.*, **83**: 2883 (2011).
19. S. Guha, S. Roy, and A. Banerjee, *Langmuir*, **27**: 13198 (2011).
20. Y. Gong, X. Zhang, Z. Chen, Y. Yuan, Z. Jin, L. Mei, J. Zhang, W. Tan, G. Shen, and R. Yu, *Analyst*, **137**: 932 (2012).