Talanta 117 (2013) 352–358

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Green synthesis and characterization of novel gold nanocomposites for electrochemical sensing applications

Shivani Tanwar [a,b,*], Ja-an Annie Ho [a], Emanuele Magi [b]

[a] *BioAnalytical and Nanobiomedicinal Laboratory, Department of Biochemical Science and Technology, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan*

[b] *Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, Genoa 16146, Italy*

ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form
3 September 2013
Accepted 6 September 2013
Available online 25 September 2013

Keywords:
Gold nanocomposite
Green synthesis
Electrochemical sensor
Copper
Hydrogen peroxide
Cyclic voltametry

ABSTRACT

Synthesis, characterization and application of Au-PANI-Calix and Au-PANI-Nap nanocomposites, is reported herein. An easy template free green synthesis is proposed and discussed for easy expediency. A variety of analytical techniques were used to characterize the nanocomposites: UV–vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, Dynamic light scattering (DLS), X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) were used to characterize the nanocomposites. Surface morphology was studied by transmission electron microscopy (TEM). The nanocomposites were immobilized on screen-printed electrode and showed electroactivity in neutral pH, making them promising candidates for various analytical applications. A sensitive and selective detection of Cu^{2+} was perceived on the Au-PANI-Calix modified electrode with no interference from ions K^{+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cr^{3+} with a detection limit of 10 nM. The copper detection is facilitated for accessible ligation with 4-sulfocalix[4]arene, so as the Cu (II)-Calix complex formed. The electrode modified with Au-PANI-Nap showed sensing application towards H_2O_2 with a detection limit of 1 μM. The modified electrodes were reproducible and stable for 2 months.

1. Introduction

Conducting polymers have become important because of their unique optical, electrical, and mechanical properties [1]. Polyaniline is an interesting material and has been studied so far since many decades but lacks commercial applicability in its native and undoped state. Conducting polymers are needed to fabricate for controllable conductivity and catalytically properties. Polyaniline (emeraldine salt prepared with different acid dopants) has broad range of electrochemical sensing applications [2–5]. Gold nanoparticles have attracted attention because of their unique electrical and optical properties as well as extensive applications in diverse areas [6–8].

Composite materials exhibit interesting and excellent physical or chemical properties (optical, electrochemical and conductive properties) due to the hybridization of metal nanoparticles and π-conjugated polymers. Gold-polyaniline composite are known for their unique property in which metal provides good stability, high conductivity, optical properties and polymer is responsible for variable and controllable conductivity through doping. Generally when aniline and gold salt $HAuCl_4$ are mixed together, the redox reaction between aniline and $HAuCl_4$ occurs leading to the formation of gold/PANI composites. A detailed literature is known for the synthesis of gold/polyaniline nanocomposite, which involves chemical, electrochemical, one step, and two step synthesis while most of them includes use of external template/additive/stabilizer [9–11]. Mixing of aniline and $HAuCl_4$ in HCl solution lead to the formation of pure PANI nanofibers as the major products while micrometer size gold/PANI core/shell composites were found as by-products [12]. PANI nanorods and gold microspheres apart from each other were prepared using camphorsulfonic acid to the reaction of aniline and $HAuCl_4$ [13]. Deposition of ultra-fine Au nanoparticles on polyaniline nanofibers has been reported for H_2O_2 sensing [14]. Recently, a detailed review on the synthesis of gold/polyaniline nanocomposites has been published [15]. Keeping a look in the literature, the global demand for sensing application in all the analytical fields is increasing, and then the challenge of inviting new and applicable nanocomposite has become a fascinating work for the researchers.

Copper is the third most abundant metal after Fe and Zn, essential element in human body and has multiple functions ranging from bone formation and cellular respiration to connective tissue development [16,17]. However, excess copper accumulation causes severe maladies, such as Alzheimer's, Parkinson's,

---

* Corresponding author at: Department of Chemistry and Industrial Chemistry, University of Genoa, via Dodecaneso 31, Genoa 16146, Italy. Tel.: +39 010 353 6178.
E-mail address: shivani.shivani@edu.unige.it (S. Tanwar).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.09.011

Mankes' and Wilson's and prions diseases [18–20]. Literature revealed many conventional methods for copper determination are available mainly as atomic absorption spectroscopy [21] inductively coupled plasma-mass spectrometry [22], inductively coupled plasma atomic emission spectroscopy [23]; these methods are expensive, time-consuming, and not suitable for in situ monitoring. Electrochemical methods are definitely less expensive and provide high sensitivity and adequate accuracy. Electrochemical detection of copper ions has been reported using polypyrrole nanowire modified with Gly–Gly–His tripeptide [24], electrode modified with carnosine–silica hybrid material [25] and co-poly (cupferron and β-naphthol)/gold nanoparticles modified glassy carbon electrodes [26]. Although an electrochemical method offers the easiest way of detection, measurements in physiological conditions, particularly with real sample, represent a main challenge. Therefore, it becomes desirable to introduce such an electrochemical sensor that gives a simple, sensitive and selective detection of Cu^{2+} at physiological pH.

Hydrogen peroxide (H_2O_2) is a simple and small compound in nature but with great importance in pharmaceutical, clinical, environmental, mining, textile and food manufacturing applications [27]. As mentioned for copper, conventional techniques for hydrogen peroxide determination such as spectrometry [28], fluorescence [29], chemiluminscence [30] are complex, costly and time consuming. In comparison, electrochemistry can offer a simple alternative since H_2O_2 is an electroactive molecule [31]. Literature reports methods for simple, accurate, and fast analytical detection of H_2O_2 using an electrode modified with the redox active enzyme, horseradish peroxidase (HRP) [32,33] however, insufficient stability is the main drawback of enzyme-based sensors, because enzymes denature easily during fabrication, storage or use. Recently, non-enzymatic electrochemical H_2O_2 detection has been reported using CuO nanoflowers sensor [34] and Pd-decorated PEDOT nanospheres [35]. Therefore it is highly desirable to develop an enzyme-free electrochemical sensor for H_2O_2 with high sensitivity and long-term stability.

In our previous published paper we introduced green template free synthesis of nanocomposite [36], the similar approach is further explored in the present work to develop the one step synthesis of new highly electroactive nanocomposites Au-PANI-Calix and Au-PANI-Nap. $HAuCl_4$ as the oxidant was mixed with the aniline monomers and dopant mixture, the reduction of $HAuCl_4$ and the oxidization of PANI occur simultaneously, leading to the formation of nanocomposite, where dopant function was to produce conductive form of polyaniline. The new nanocomposites were synthesized, characterized and applied as electrochemical sensor for Cu^{2+} and H_2O_2. The new nanocomposites contains gold and polyaniline in common with different dopants said naproxen and 4-sulfocalix[4]arene. The nanocomposites were characterized by UV–vis spectroscopy, FTIR, Raman spectroscopy, DLS, XRD, EDX, XPS and TEM. To the best of our knowledge, the nanocomposites presented herein have not been reported elsewhere in the literature.

2. Experimental

2.1. Chemicals and equipment

Chloroauric acid (HAuCl4), 4-sulfocalix[4]arene, aniline, (S)-Naproxen and all other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Deionized water having a resistivity of not less than 18 M cm^{-1} (Milli-Q, Bedford, MA, USA) was used throughout the experiment. UV–Vis and FTIR spectra were recorded using Cary Eclipse (Varian, Palo Alto, CA, USA), Spectrum One B (Perkin-Elmer, Waltham, MA, USA) spectrometers respectively. Surface morphology was characterized using TEM (JEOL, JEM-1400, Tokyo, Japan). Quantitative analyses were performed using XPS (ULVACPHI XPS spectrometer PHI Quantera SXM, Chigasaki, Japan) and EDX (JEOL JSM-7000 F, Tokyo, Japan). HORIBA JOBIN YVON, HR-800 was used to measure Raman spectra. Philips PW1830 X-ray diffractor meter was used to examine the crystalline behavior of the material. Electroanalytical measurements were carried out at ambient temperature with a CHI 660B electrochemical workstation. The integrated three-electrode strip consisting of a carbon working electrode, a silver pseudo-reference electrode and a carbon counter electrode was purchased from Zensor R&D (Taichung, Taiwan). The average diameter and zeta potential of the nanocomposite were measured using a 90Plus DLS nanoparticle size analyzer and zeta potential analyzer (Brookhaven Instruments, NY, USA).

2.2. Synthesis of Au-PANI-Calix and Au-PANI-Nap

The synthetic procedure of new nanocomposites is similar to our previous published article [36]. However in brief the synthetic procedure is summarized herein. To a stirring solution of aniline (2 ml, 1 mM), 4-sulfocalix[4]arene (2 ml, 1 mM), or naproxen (200 ul, 2% aq. suspension) was added at room temperature. Then 2 ml solution of $HAuCl_4$ (1 mM) was added quickly. The reaction solution turned brown after some time and stirring continued for 20 h and then stopped by centrifugation (20,000 RPM, 10 min), washed 2–3 times with H_2O.

3. Results and discussion

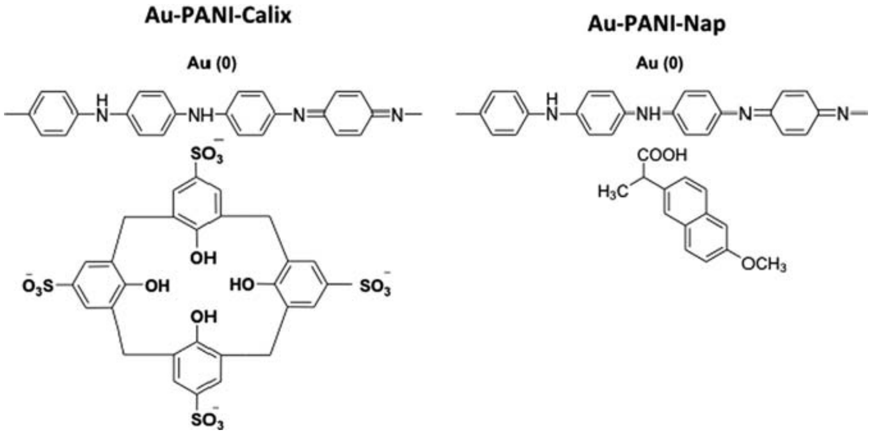
3.1. Synthesis of metal nanocomposite

Au-PANI-Calix and Au-PANI-Nap nanocomposites were synthesized in the present study, using 4-sulfocalix[4]arene/Nap as a dopant anion. Since it involved a template-free synthesis procedure, the nanocomposites products are free from by-products that often arise when conventional initiators, such as ammonium persulfate, are employed. A plausible structure of the nanocomposites is indicated in Scheme 1.

3.2. Spectroscopic characterization

Prior to any other characterization, the absorption spectra of Au-PANI-Calix and Au-PANI-Nap were recorded (Fig. 1). The absorption band at 534 nm and 542 nm correspond to absorption band of Au-PANI-Calix and Au-PANI-Nap nanocomposites respectively, that is markedly different from zerovalent Au absorption band (520 nm).

The FTIR spectral characteristic of Au-PANI-Calix nanocomposite mainly resembles PANI. The characteristic bands of PANI at wavenumbers of 1570 cm^{-1} (assigned to the stretching of the quinoid rings), 1495 cm^{-1} (C=C stretching of benzenoid rings), 1296 cm^{-1} (C–N stretching mode), and 1120 cm^{-1} (N=Q=N, Q representing the quinoid ring) are observed clearly in the FT-IR spectra of the nanocomposites, and are identical to those of the emeraldine salt form of PANI [37]. The peaks at 3460 cm^{-1} and 3257 cm^{-1} corresponding to –NH stretching and hydrogen bonded –OH respectively in both the nanocomposites. In case of Au-PANI-Nap, peaks at 2957 and 2942 cm^{-1} corresponding to asymmetric and symmetric stretching vibrations of $-CH_3$ and bands at 1629, 1607 and 1480 cm^{-1} are assigned to stretching vibrations of aromatic ring. Bands at 1022 and 865 cm^{-1} are assigned to absorption of C–O–C in naproxen, while 1173 cm^{-1} is due to the C–O absorption. The major peaks in the range of 482–1727 cm^{-1}



Scheme 1. Plausible structure of the nanocomposites.

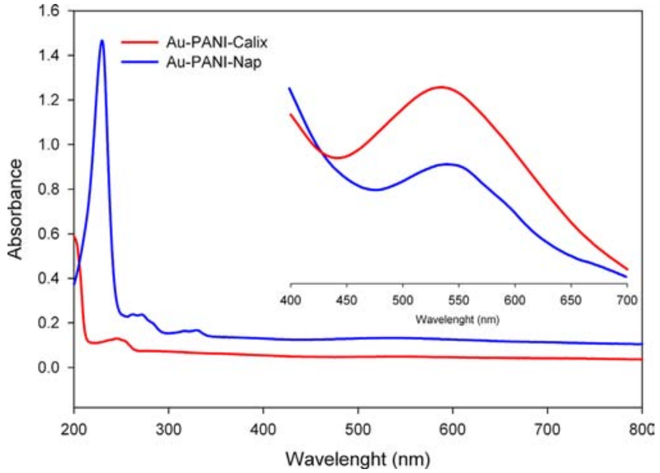


Fig. 1. Absorption spectra of Au-PANI-Calix and Au-PANI-Nap; inset shows the absorption maxima of the nanocomposites (*y*-axis adjusted to get the graphs closer together).

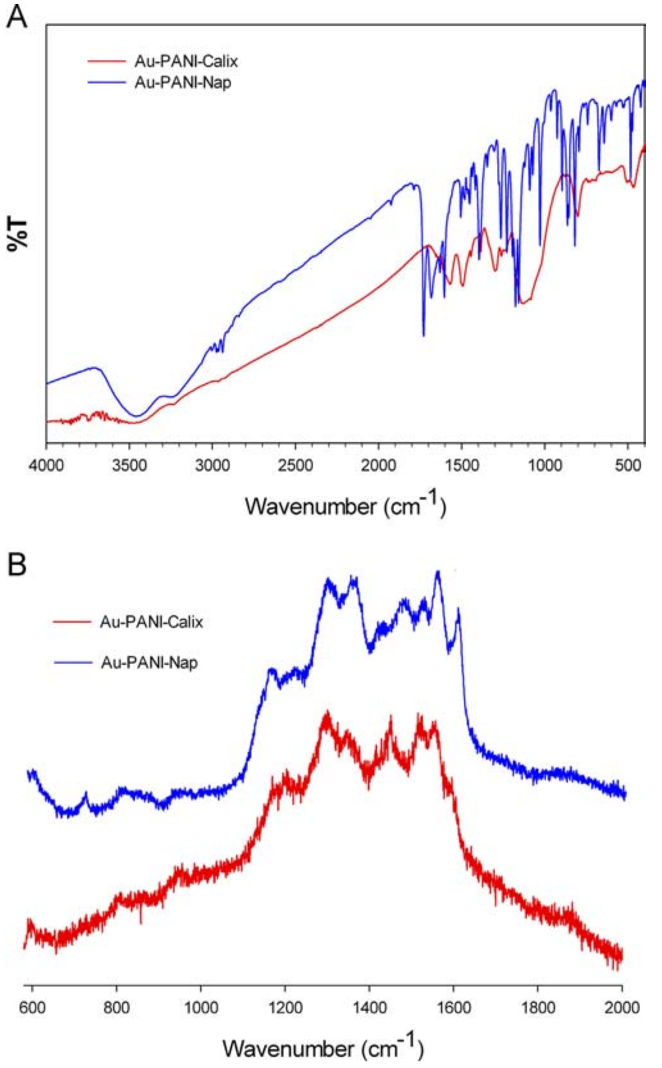


Fig. 2. FT-IR Spectra (A) and Raman Spectra (B) of Au-PANI-Calix and Au-PANI-Nap.

are same as for native naproxen [38], so it clearly shows that the material is fully doped with naproxen (Fig. 2A).

Raman spectra of the nanocomposites were obtained and interpretated as follows. Peaks at 1625, 1596 and 1570 cm^{-1} represent the characteristic bands of semiquinone rings. Band at 1511 cm^{-1} corresponds to the N–H bending deformation band of the protonated amine. Peaks at 1348 and 1252 cm^{-1} are assigned to the C–N stretching modes and 1179 cm^{-1} is corresponding to C–H bending deformation (Fig. 2B).

To further confirm the formation of nanocomposites a powder XRD pattern recorded from a drop-coated film of the sample on a silica substrate. The Bragg reflections (111), (200), (220), and (311) of face-centered cubic (fcc) Au are observed in both the nanocomposites (Fig. 3), similarly to those reported in the literature [39]. Diffraction pattern shows a broad peak centered at $2\theta=23.5^{\circ}$ which is a characteristic peak of PANI [40]. 2θ between 5–35° is assigned to the diffraction peaks of naproxen, according to the literature [41]. XRD analysis supports the presence of doped PANI and Au(0) nanoparticles in the nanocomposites.

To determine the elemental composition as well as the electronic state of metal ion, the XPS quantitative spectroscopic technique was used. Elemental analysis shows the presence of C, N, O, S and Au in nanocomposite as assigned in Fig. 4A. The XPS examination verified that the doublet at 83.5 and 87.2 eV corresponding to 4f5/2 and 4f7/2, respectively, which is due to elemental gold [42]. The splitting of each doublet (3.70 eV) as shown in Fig. 4B, corresponding to the spacing between the 4f5/2 and 4f7/2 levels, is in agreement with the literature value [39], confirming the presence of gold in zerovalent oxidation. Results from XPS together with those from IR and XRD, confirm the doping and successful synthesis of nanocomposites. The elemental compositions of the nanocomposites by EDX and XPS are shown in Table 1, clearly demonstrate the doping of the nanocomposite.

The average diameter and zeta potential of the nanocomposites was determined by DLS. The respective size and zeta potential of the Au-PANI-Nap and Au-PANI-Calix obtained were 34.7 ± 0.04 nm, 40.1 ± 0.02 nm and −28.7 ± 1.7, −23.6 ± 2.6. The morphology of the nanocomposites was examined by TEM (Fig. 5). The nanocomposites look spherical or roughly spherical with average diameter < 50 nm (Au-PANI-Calix) and < 100 nm (Au-PANI-Nap). Examination of the reaction product by TEM images revealed that the PANI formed in the solution nucleates onto the gold particles in both the nanocomposites (magnified image, in the inset of Fig. 5), while some PANI seems to provide surface to the particles.

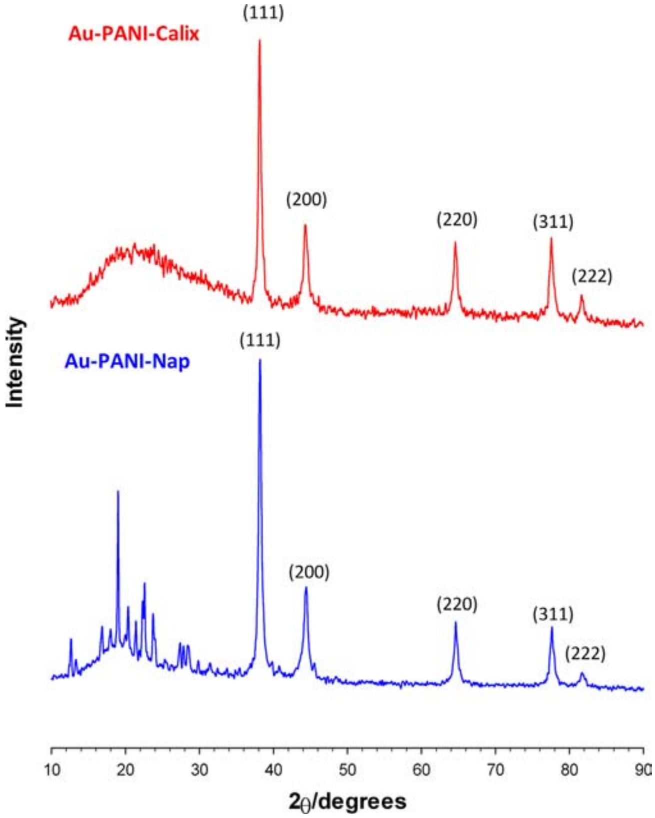


Fig. 3. Powder XRD pattern of Au-PANI-Calix and Au-PANI-Nap.

3.3. Fabrication and electrochemical characterization of modified electrodes

A cast solution of nanocomposite was prepared by ultrasonicating the as-prepared Au-PANI-Nap and Au-PANI-Calix in dimethylformamide (5 mg/ml). 2 μL of this solution was drop coated onto a clean screen-printed electrode with a micro syringe and dried in oven at 37 °C overnight. The as-modified electrode is subsequently washed several times with deionized water to remove the loosely bounded polymer nanocomposite and further used for electrochemical studies. Prior to the electroanalytical application experiments, all the modified electrodes were activated by scanning under the potential window between −0.6 V and 0.4 V in 50 mM phosphate-buffered saline (PBS), pH-7.12 for 20 cycles with a scan rate of 50 mV/s.

The electrochemical properties of the nanocomposite modified electrodes were studied by means of cyclic voltammetry (CV). $Fe(CN)_6^{3-/4-}$ redox couple was selected to compare their characteristics with that of the unmodified electrode. Fig. 6 shows the voltammetric behavior of the two electrodes with PBS and with $Fe(CN)_6^{3-/4-}$ redox couple. The voltammetric behavior of the modified electrodes is noticeably different than the unmodified one (Fig. 6A), the dramatic change in current indicates that modified electrodes has excellent electrochemical properties. As expected, both the modified electrodes show a broad reversible voltammogram, indicating the presence of a large capacitive charging current compared to unmodified electrode as shown in Fig. 6B.

To confirm whether the reaction on modified electrode is reversible or irreversible, a series of cyclic voltammograms (CVs) were then acquired with the modified electrodes varying the scan rate from 50 mV/s to 300 mV/s, in 1 mM $K_3Fe(CN)_6$ with 0.1 M KCl. With both the modified electrodes, the peak current (*Ip*) increases

Table 1
Elemental composition by EDX and XPS.

Element (%)	EDX		XPS	
	Au-PANI-Nap	Au-PANI-Calix	Au-PANI-Nap	Au-PANI-Calix
C	72.37	62.05	69.61	66.52
N	1.73	6.18	6.21	1.70
O	16.69	10.72	22.84	29.12
Au	9.21	20.80	1.33	2.30
S	–	0.26	–	0.36

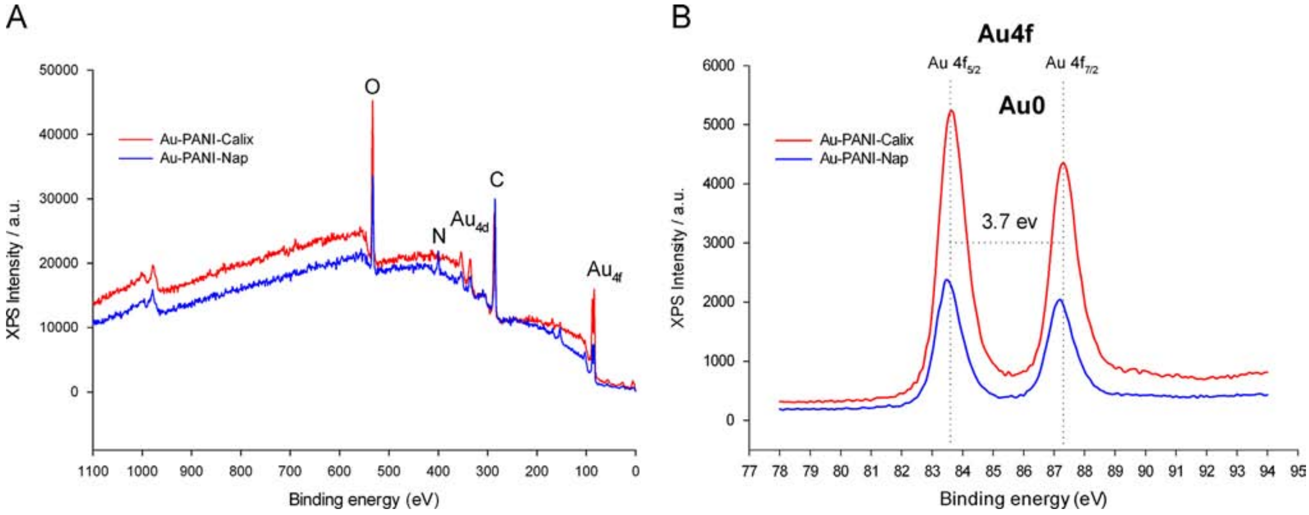


Fig. 4. XPS pattern of Au-PANI-Calix and Au-PANI-Nap.

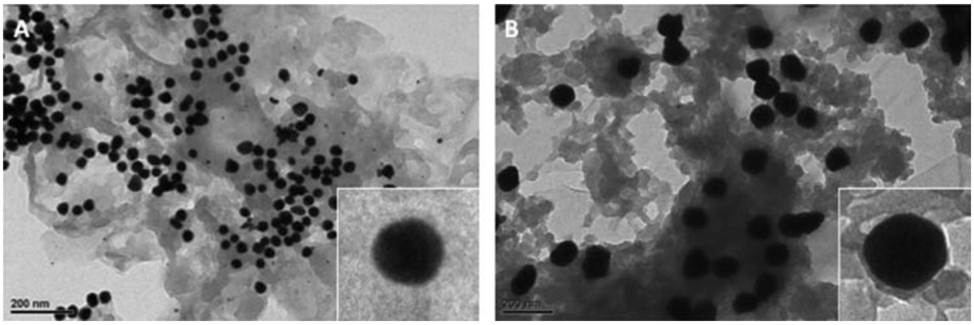


Fig. 5. Transmission electron micrographs of Au-PANI-Calix (A) and Au-PANI-Nap (B); scale bar 200 nm; inset shows the magnified image.

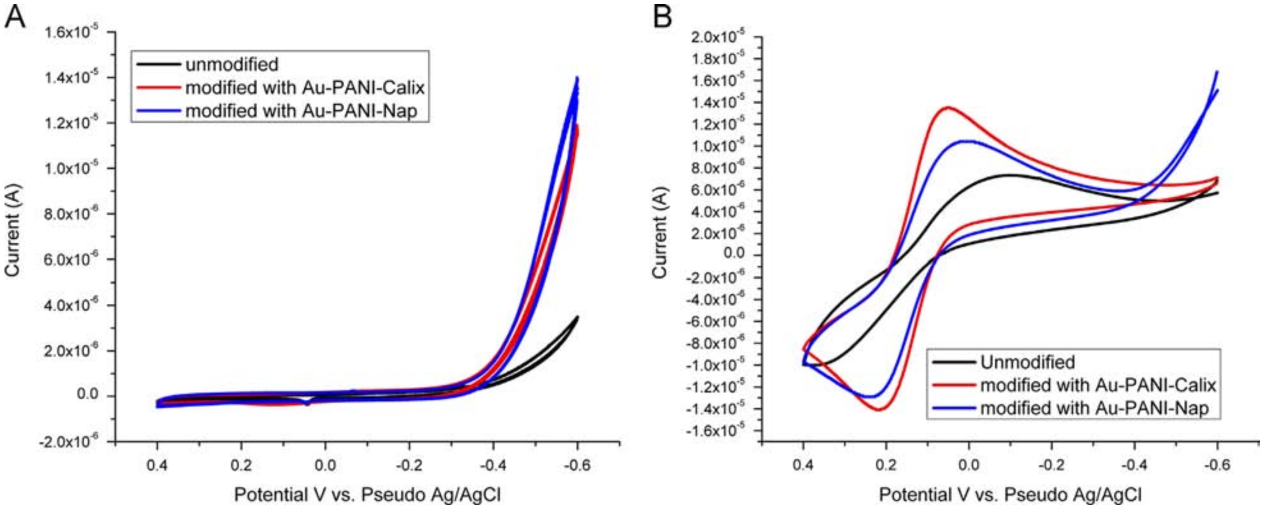


Fig. 6. CV response of unmodified and modified electrode in 50 mM PBS, pH-7.12 (A) and in 0.1 M KCl with 1 mM $K_3Fe(CN)_6$ at unmodified and modified electrode (B). The scan rate was 50 mV/s.

linearly with the increasing of the square root of the potential scan rate ($\nu 1/2$), indicating that the reactions occurring on the modified electrode are nearly reversible; in fact, the Randles' slope would be nonlinear if the redox reactions were either irreversible or quasi-reversible. These results also confirm that the mass transfer phenomenon in the double layer region of the electrodes is a diffusion-controlled process [34].

The reproducibility of both the modified electrodes was checked, it was observed that there was no deterioration in the response of the modified electrodes and they were reproducible and stable for 2 months.

3.4. Copper detection

The CV response of Cu^{2+} in PBS (50 mM, pH-7.12) at the electrodes modified with Au-PANI-Calix, demonstrates the marked change in the performance of cyclic voltametry. In presence of Cu^{2+}, a remarkably broad peak at 0.15 V was observed for modified electrode, indicating that the surface-exposed SO_4^{2-} groups from 4-sulfo-calixarene could effectively capture copper ions (Fig. 7). A square wave voltammogram is recorded showing effect of different concentration of Cu^{2+} (Fig. 7B); the peak current at 0.15 V is proportional to the amount of copper ions complexed at the modified electrode surface; in fact the calibration curve shows a linear response ($R^2=0.995$) in a wide range of Cu^{2+} concentration (1 μm–5 mM). A good sensitivity was achieved on electrode modified with Au-PANI-Calix towards Cu^{2+}; the detection limit calculated against the blank signal was 10 nM (S/N=3), lower than reported in the literature for electrochemical detection of Cu^{2+} by other authors [24,43].

After each experiment, the electrode was washed with EDTA solution followed by water to get the Cu^{2+} free electrode. As selectivity is essential, particularly in case of metal ion sensors, it was investigated by measuring the CV response of Cu^{2+} in presence of common ions (K^+, Ca^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, and Hg^{2+} at 1 mM concentration). The electrode modified with Au-PANI-Calix showed no significant change in current, clearly signifying its selective capture of Cu^{2+} over other ions.

3.5. H_2O_2 detection

The electrode modified with Au-PANI-Nap nanocomposite shows sensing application for H_2O_2 at physiological pH. The electroactive response of Au-PANI-Nap towards H_2O_2 was experimented in N_2-saturated PBS (50 mM, pH-7.12). Upon addition of H_2O_2, the electrode modified with Au-PANI-Nap exhibits significant oxidation and reduction of H_2O_2 (Fig. 8A), which can be attributed to the excellent electrocatalytic property of the nanocomposite. Similar results were reported for oxidation and reduction of H_2O_2 on Co_3O_4 nanowalls electrode [44]. The cathodic and anodic currents increase because of the reduction and oxidation of H_2O_2 and that current change was responsible for the concentration of H_2O_2 indicating the sensing of Au-PANI-Nap modified electrode towards H_2O_2 at physiological pH. The Au-PANI-Nap modified electrode gives a linear response towards H_2O_2 in the concentration range of 5–50 μM ($R^2=0.997$) as depicted in Fig. 8B. The detection limit calculated based on the signal to noise (S/N=3) was 1 μM. Although another non-enzymatic H_2O_2 sensor was already reported in the literature [34], our nanocomposite has

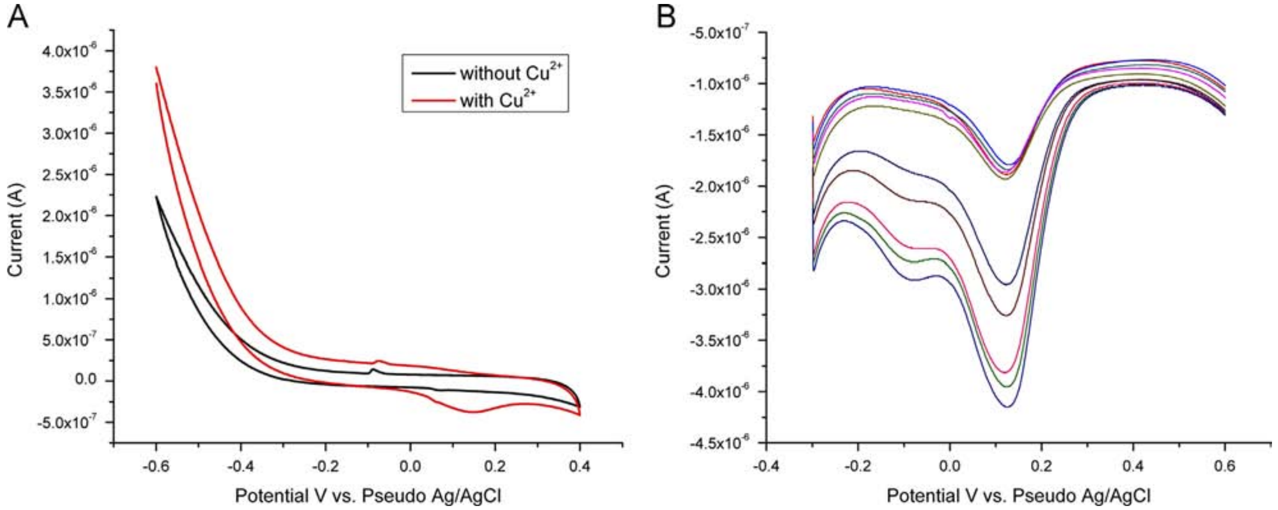


Fig. 7. CV response of electrode modified with Au-PANI-Calix in the absence and presence of Cu^{2+} (1 μM) in PBS (50 mM, pH-7.12) with a scan rate of 50 mV/s (A) and square wave voltammogram recorded on the same electrode using different concentrations of Cu^{2+} (B).

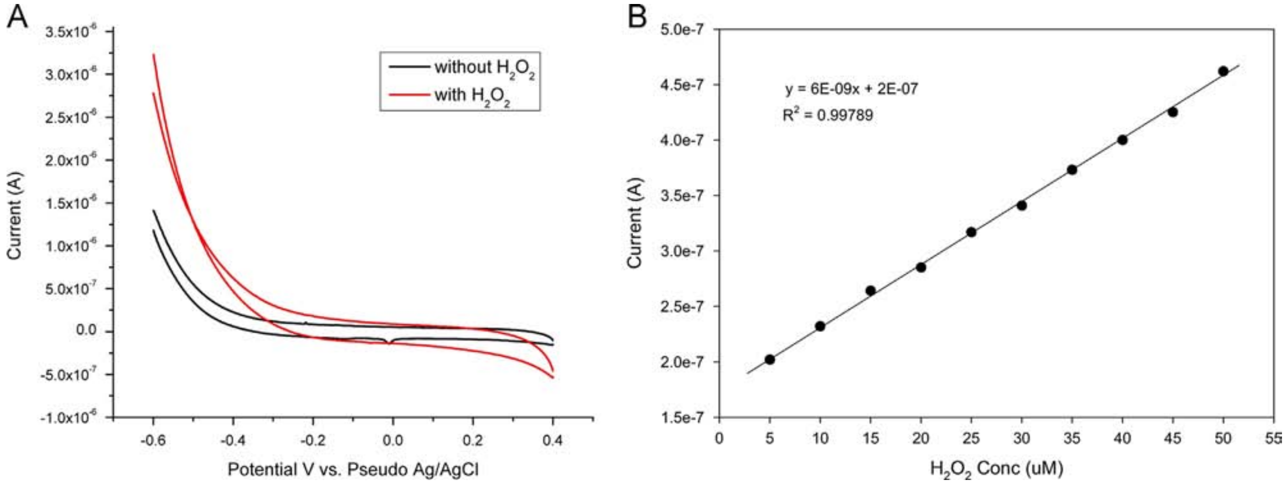


Fig. 8. CV response of electrode modified with Au-PANI-NAP in the absence and presence of H_2O_2 (1 mM) in PBS (50 mM, pH-7.12) with a scan rate of 50 mV/s (A) and calibration curve for the concentration range (5–50 μM) of H_2O_2 (B).

the advantage of sensing at physiological pH, which is particularly important for the detection of H_2O_2 in food and clinical fields.

4. Conclusions

The work presented herein is one-pot synthesis of gold nanocomposites without external additive/stabilizer. A facile green synthetic approach for gold nanocomposite has been successfully developed using PANI as reductant, $HAuCl_4$ as oxidant, 4-sulfocalix[4]arene and Naproxen as dopants. IR, XRD, EDX and XPS analysis confirmed the successful doping of the nanocomposite materials. The electrochemical studies revealed the presence of nano gold that contributes the electrocatalysis nature of nanocomposites. The dopant (4-sulfocalix[4]arene) assumed to capture copper in Au-PANI-Calix. The synthesized nanocomposites Au-PANI-Calix and Au-PANI-Nap showed good catalytical activity and demonstrated to be applicable as sensors for detection of Cu^{2+} (LOD 10 nM) and H_2O_2 (LOD 1 μM), respectively. The synthesized nanocomposites are advantageous because the as-modified electrodes show sensing activity at physiological pH. Electrochemical sensing has the advantage of low sample volume and simple preparation; future studies will be focused on the application of novel nanocomposites to real sample analysis of Cu^{2+} and H_2O_2.

Acknowledgments

We thank National Science Council of Taiwan for financing this project (98J900085 and 99-2811-M-002-137). Regione Liguria is also acknowledged for providing a grant on PO CRO Fondo Sociale Europeo 2007–2013, Asse IV.

References

[1] X.F. Lu, W.J. Zhang, C. Wang, T.C. Wen, Y. Wei, Prog. Polym. Sci. 36 (2011) 671–712.
[2] C.L. Bayer, A.A. Konuk, N.A. Peppas, Biomed. Microdevices 12 (2010) 435–442.
[3] F. Wang, W.B. Wang, B.H. Liu, Z.Y. Wang, Z.P. Zhang, Talanta 79 (2009) 376–382.
[4] M. Elmer-Rico, E. Jelynne, P. Tamayo, Jose Rene L. Micor, World Appl. Sci. J. 2 (2007) 523–526.
[5] S. Virji, R.B. Kaner, B.H. Weiller, Chem. Mater. 17 (2005) 1256–1260.
[6] M.C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293–346.
[7] M.Ca.D.W. Goodman, Acc. Chem. Res. 39 (2006) 739–746.
[8] J.C. Sara, E. Skrabalak, Yugang Sun, Xianmao Lu, Leslie Au, Claire M. Cobley, Younan Xia, OBJOBJOBJOBJOBJOBJAcc. Chem. Res. 41 (2008) 1587–1595.
[9] Y.H. Tang, K.X. Pan, X.J. Wang, C.B. Liu, S.L. Luo, J. Electroanal. Chem. 639 (2010) 123–129.
[10] Z. Wang, J. Yuan, D. Han, L. Niu, A. Ivaska, Nanotechnology 18 (2007) 115610.
[11] Z.Q. Peng, L.M. Guo, Z.H. Zhang, B. Tesche, T. Wilke, D. Ogermann, S.H. Hu, K. Kleinermanns, Langmuir 22 (2006) 10915–10918.
[12] Y. Wang, Z.M. Liu, B.X. Han, Z.Y. Sun, Y. Huang, G.Y. Yang, Langmuir 21 (2005) 833–836.

[13] X.T. Zhang, V. Chechik, D.K. Smith, P.H. Walton, A.K. Duhme-Klair, Macromolecules 41 (2008) 3417–3421.
[14] C.C. Hung, T.C. Wen, Y. Wei, Mater. Chem. Phys. 122 (2010) 392–396.
[15] G. Ćirić-Marjanović, Synth. Met. 170 (2013) 31–56.
[16] R.F.H.Va.A.N. Hulme, J. Am. Chem. Soc. 128 (2006) 11370–11371.
[17] Y.H. Chan, J.X. Chen, Q.S. Liu, S.E. Wark, D.H. Son, J.D. Batteas, Anal. Chem. 82 (2010) 3671–3678.
[18] N. Fatemi, B. Sarkar, Inorg. Chim. Acta 339 (2002) 179–187.
[19] R.A. Lovstad, Biometals 17 (2004) 111–113.
[20] E.L. Que, D.W. Domaille, C.J. Chang, Chem. Rev. 108 (2008) 1517–1549.
[21] G.Y. Yang, W.B. Fen, C. Lei, W.L. Xiao, H.D. Sun, J. Hazard. Mater. 162 (2009) 44–49.
[22] M. Grotti, E. Magi, R. Leardi, J. Anal. At. Spectrom. 18 (2003) 274–281.
[23] M.D. Ioannidou, G.A. Zachariadis, A.N. Anthemidis, J.A. Stratis, Talanta 65 (2005) 92–97.
[24] M. Lin, M. Cho, W.S. Choe, J.B. Yoo, Y. Lee, Biosens. Bioelectron. 26 (2010) 940–945.
[25] S. Sayen, C. Gerardin, L. Rodehuser, A. Walcarius, Electroanalysis 15 (2003) 422–430.
[26] M. Liu, Y.H. Feng, C.H. Zhang, G.F. Wang, B. Fang, Anal. Methods 3 (2011) 1595–1600.
[27] C.G. Tsiafoulis, P.N. Trikalitis, M.I. Prodromidis, Electrochem. Commun. 7 (2005) 1398–1404.
[28] R. Santucci, E. Laurenti, F. Sinibaldi, R.P. Ferrari, Biochim. Biophys. Acta – Protein Struct. Mol. Enzymol. 1596 (2002) 225–233.
[29] Z. Rosenzweig, R. Kopelman, Anal. Chem. 68 (1996) 1408–1413.
[30] L.R. Luo, Z.J. Zhang, Anal. Chim. Acta 580 (2006) 14–17.
[31] J. Wang, Biosens. Bioelectron. 21 (2006) 1887–1892.
[32] C.X. Lei, S.Q. Hu, G.L. Shen, R.Q. Yu, Talanta 59 (2003) 981–988.
[33] Y. Xiao, H.X. Ju, H.Y. Chen, Anal. Chim. Acta 391 (1999) 73–82.
[34] M.J. Song, S.W. Hwang, D. Whang, Talanta 80 (2010) 1648–1652.
[35] F.X. Jiang, R.R. Yue, Y.K. Du, J.K. Xu, P. Yang, Biosens. Bioelectron. 44 (2013) 127–131.
[36] S. Tanwar, M.C. Chuang, K.S. Prasad, J.A.A. Ho, Green Chem. 14 (2012) 799–808.
[37] Q.F. Chang, K. Zhao, X. Chen, M.Q. Li, J.H. Liu, J. Mater. Sci. 43 (2008) 5861–5866.
[38] M. Wei, S.X. Shi, J. Wang, Y. Li, X. Duan, J. Solid State Chem. 177 (2004) 2534–2541.
[39] D.V. Leff, L. Brandt, J.R. Heath, Langmuir 12 (1996) 4723–4730.
[40] M.X. Wan, J.C. Li, J. Polym Sci, Polym. Chem. 36 (1998) 2799–2805.
[41] M. Maghsoodi, O. Taghizadeh, G.R. Martin, A. Nokhodchi, Int. J. Pharm. 351 (2008) 45–54.
[42] H. Tsunoyama, H. Sakurai, N. Ichikuni, Y. Negishi, T. Tsukuda, Langmuir 20 (2004) 11293–11296.
[43] B.S. Flavel, M. Nambiar, J.G. Shapter, Silicon 3 (2011) 163–171.
[44] W.Z. Jia, M. Guo, Z. Zheng, T. Yu, E.G. Rodriguez, Y. Wang, Y. Lei, J. Electroanal. Chem. 625 (2009) 27–32.