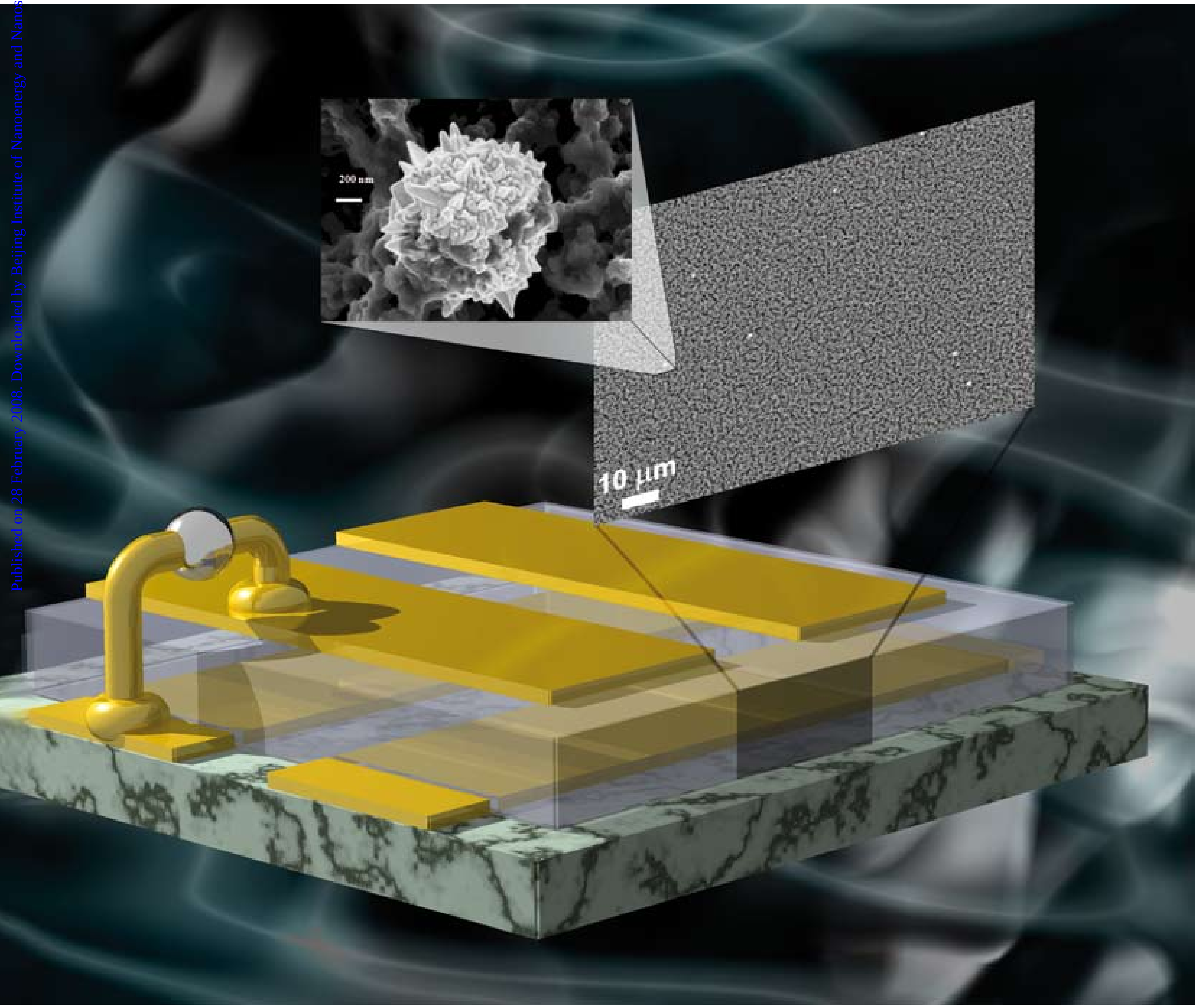
Journal of Materials Chemistry

www.rsc.org/materials
Volume 18 | Number 16 | 28 April 2008 | Pages 1821–1936



ISSN 0959-9428

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Electrochemical fabrication of a nonvolatile memory device based on polyaniline and gold particles

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Received 26th November 2007, Accepted 6th February 2008
First published as an Advance Article on the web 28th February 2008
DOI: 10.1039/b718227a

In this work we describe a simple electrochemical process to fabricate an air stable nonvolatile memory device based on polyaniline (PANI) and gold (Au) particles in one step. The PANI and Au particle composite material was synthesized by cyclic voltammetry on a modified ITO glass in the room temperature ionic liquid (IL), 1-ethyl-3-methyl-imidazolium tosylate [EMIM][Tos] containing 1 M trifluoroacetic acid. The Au particles were synthesized during electropolymerization of aniline and distributed in the PANI matrix. This is the first report of the electrochemical synthesis of such a material in an IL. This material can be used directly as an air stable nonvolatile memory device. Both bistability (switching) and negative differential resistance (NDR) were observed in this single layer device. The composite PANI:Au material was kept in air for 8 weeks and the NDR characteristic was still repeatable. That makes it possible to use these composite materials in printable electronics.

1 Introduction

Conjugated materials with π-conjugated backbones represent a particularly intriguing type of environment for metal nanoparticles.[1,2] Conducting polymers can be combined with variable inorganic nanoparticles of different sizes, giving rise to a novel composite material with interesting physicochemical properties and possibilities for important applications. Polyaniline (PANI) is one of the most studied conducting polymers due to its high stability and interesting electrochemical characteristics.[3,4] By letting aniline monomer react with chlorauric acid ($HAuCl_4$), gold (Au):PANI nanocables and nanotubes were formed by self-assembly.[5] Sawall *et al.* have carried out interfacial polymerization of PANI nanofibers grafted to Au surfaces, and they found that the covalent attachment of the PANI nanofibers to Au leads to improved durability to abrasion and acid/base exposure.[6] The PANI:Au composite has previously been synthesized chemically and it was found that the Au nanoparticles act as nucleation sites for the oxidative formation of PANI, encapsulating the metal in the form of a polymer:metal composite.[7] Sarma *et al.*[8,9] prepared PANI:Au nanoparticle (~100 nm in diameter) composites with conductivity of two orders of magnitude higher than that of PANI. They used hydrogen peroxide to both reduce chloroaurate and simultaneously oxidize aniline monomer to initiate polymerization. Electrochemical formation of Au clusters in PANI has also been reported.[10] It indicated that chloroaurate interacts with PANI and is reduced to the metallic Au preferentially at the nitrogen linkages. Electrochemical methods have proved to be effective in incorporating metal nanoparticles in either pre-deposited polymers or in growing polymer films. The pre-deposited method employed a two-step electrochemical process. Conducting polymers such as PANI are initially deposited on the working electrode and then dipped in a solution containing ionic metal species followed by their chemical reduction yielding metal clusters embedded in the polymer, mainly on the polymer surface. The alternative approach to electrochemically incorporate metal nanoparticles into the polymer matrix is to trap the metal nanoparticles during electropolymerization. This method results in a material where the nanoparticles are embedded in the polymer matrix instead of being confined on the surface.

PANI:Au multilayer films were found to be useful in biological applications.[11] The PANI:Au composite system facilitates the electrical contacting of the redox enzyme with the electrode and therefore improves the bioelectrocatalytic oxidation of glucose by enhancing charge transport through the Au nanoparticles.[12] Combination of Au nanoparticles with PANI also gives new possibilities in organic electronics. Electrical bistability and memory characteristics have recently been reported by using chemically synthesized PANI nanofibers embedded with Au nanoparticles as the polymer memory element.[13] The PANI:Au composite was spin coated in aqueous solutions containing poly(vinylalcohol), which serves as the electrically insulating matrix for the composite. The mechanism for the bistability observed by Yang and co-workers is electric field-induced charge transfer between PANI and the Au particles.[13]

2 Results and discussion

Formation of PANI nanotubules in room temperature ionic liquids by means of electrochemical polymerization has been reported earlier by our group.[14] In the present work, the electrochemical fabrication of PANI:Au composite in ionic liquids will be described and application of the material in an air stable nonvolatile memory device will be discussed. A solution

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containing 6 mM hydrogen tetrachloroaurate (III) trihydrate and 1.0 M trifluoroacetic acid (CF_3COOH) was made in an ionic liquid, 1-ethyl-3-methyl-imidazolium tosylate [EMIM][Tos]. Then 0.2 M aniline was added and mixed homogenously using an ultrasonic oscillator for 2 min. The electrochemical polymerization was then carried out in a three-electrode quartz cuvette cell by cyclic voltammetry. An Ag/AgCl wire was used as the reference electrode and a platinum wire as the counter electrode. The potential was controlled by an Autolab (PGSTAT 20) potentiostat and scanned between −0.3 V and 1.5 V with a scan rate of 50 mV s^{-1} for 50 scans. The modified ITO glass (MITO) with aniline silane (3 cm × 1 cm slide) was used as the working electrode. The modification procedure has been described earlier[15] and MITO electrode was reported to enhance the electropolymerization of PANI.[15,16] As a comparison, pure PANI film without any Au particles was also electropolymerized on MITO by using the same parameters. The morphology of the obtained PANI and PANI:Au composite film were studied by scanning electron microscopy (SEM), which was from Leica Cambridge Instruments. The SEM picture (Fig. 1A) shows that the Au particles with diameters in the range from 500 nm to 800 nm are distributed in the PANI matrix. Inset (1) in Fig. 1A shows the porous PANI structure and (2) shows the shape of the Au particles. It has been shown that Au particles will always be wrapped around by PANI layers.[2,5,17] EDAX analysis (Fig. 2), which is equipped with SEM confirms that the core of the round particle is made of Au. Fig. 1B illustrates the surface morphology of pure PANI film and inset (3) is the picture with an enlarged scale. It shows a similar porous structure as can be seen in (1).

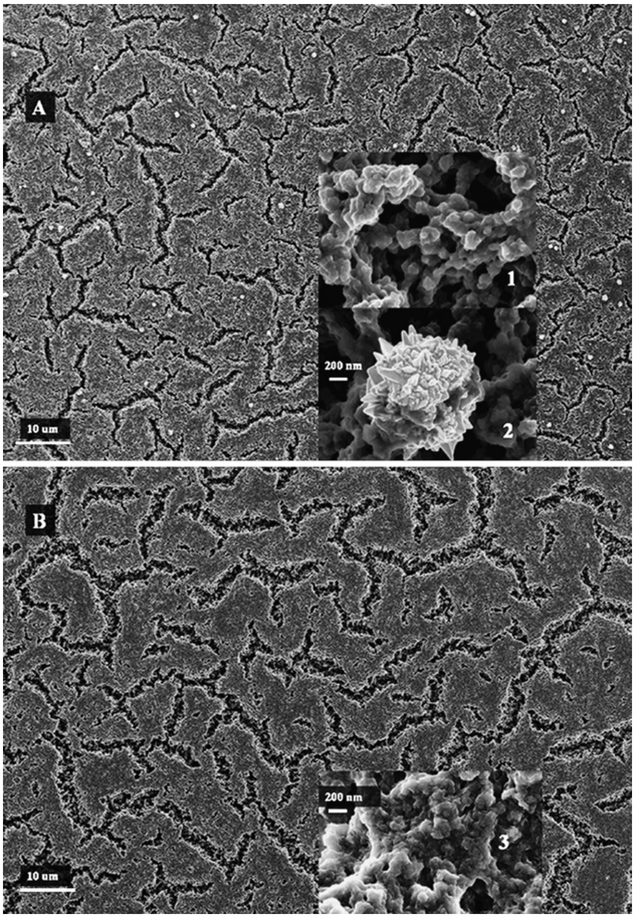


Fig. 1 SEM images of PANI:Au composite material (A). The shinning spot is from the Au particle. Inset (1) porous PANI (2) Au particle from the composite. SEM images of pure PANI film (B). Inset (3) porous PANI with an enlarged scale.

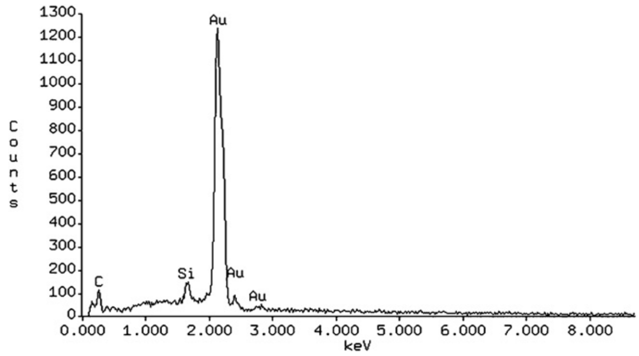


Fig. 2 EDAX for the Au particles in PANI matrix.

The thickness of PANI and PANI:Au composite films are determined by a confocal optical profilometer, µsurf® from NanoFocus AG. The average thickness of the PANI:Au composite film (h_1) is around 3.6 µm and that of the pure PANI film (h_2) is around 2.8 µm as Fig. 3 shows.

The PANI:Au composite film can be directly deposited on the MITO glass by electrochemical methods and thus simplifies the fabrication of the memory device significantly. The structure of the bistable memory device is shown in Scheme 1. A layer of Al with a thickness of 50 nm was evaporated under a vacuum of *ca.* 1×10^{-6} mbar on top of the composite film at a uniform rate of evaporation (1.0–1.2 Å s^{-1}) to avoid Al penetration into the active medium. The thicknesses of the thermally evaporated Al electrode was measured by a thickness monitor TM-100 from MAXTEK, INC. Electrical characterization of the devices was performed by using a Keithley 2400 programmable voltage source meter and a Keithley 617 programmable electrometer or an Agilent 4142B modular DC source/monitor. Positive and negative bias were applied to the bottom ITO and the top Al electrodes, respectively. All electrical experiments were conducted in air.

The current density–voltage (J–V) characteristics of the MITO/PANI/Al and MITO/(PANI:Au)/Al devices are shown in Fig. 4(a) and (b), respectively. The MITO/PANI/Al device was scanned from 0 V to 6 V, 6 V to −6 V and −6 V back to 0 V in steps of 0.1 V s^{-1} as shown in Fig. 4(a). No effect of the voltage is found on the impedance, and it simply acts like a poor insulator. Neither bistability nor NDR has been observed in this PANI-only device, as previously reported.[13]

In Fig. 4(b), the effect of the inclusion of gold particles into the PANI matrix is shown, *i.e.* scanning the MITO/(PANI:Au)/Al device from 0 V to 3 V, 3 V to −3 V and 3 V to 0 V. Below a certain critical threshold voltage (V_{th}), the MITO/(PANI:Au)/Al device is stable and no drastic changes in conductivity are observed. Once the V_{th} is exceeded, the state of the device is changed from a higher impedance state (OFF) to a lower impedance state (ON). In the first scan in Fig. 4(b), the voltage

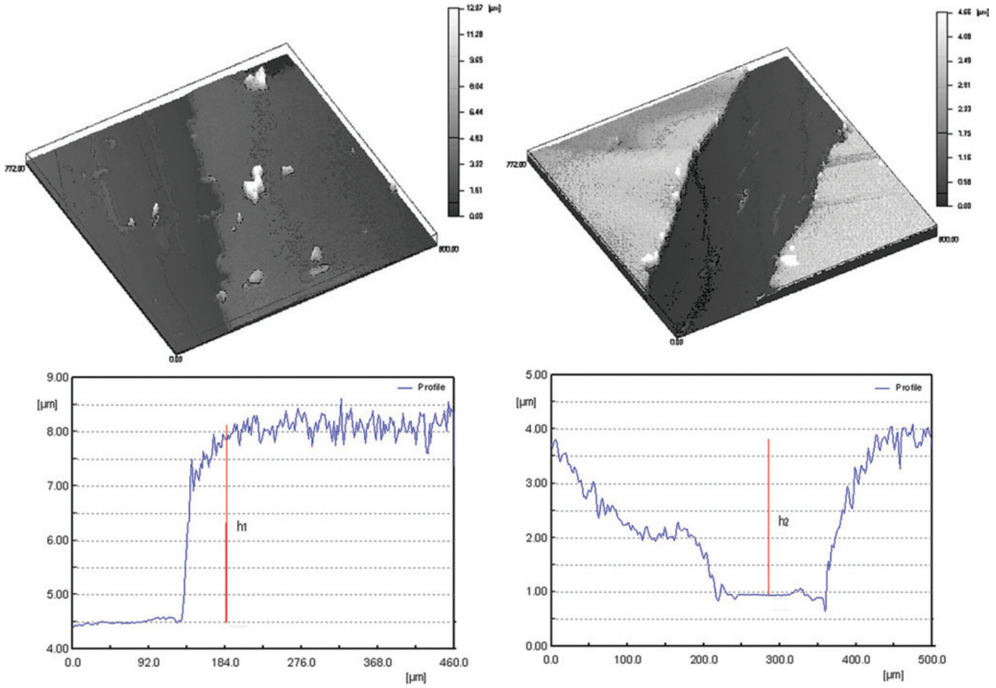
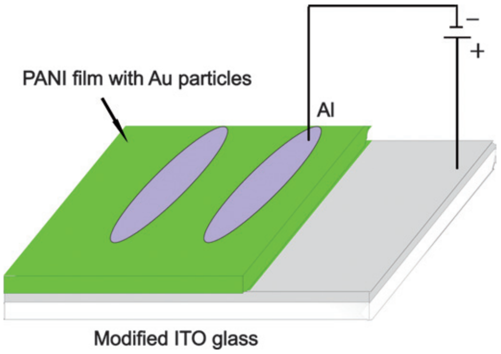


Fig. 3 Thickness determination by confocal optical profilometer for PANI:Au composite film (h_1) and pure PANI (h_2).



Scheme 1 The memory device structure based on PANI and embedded Au particles.

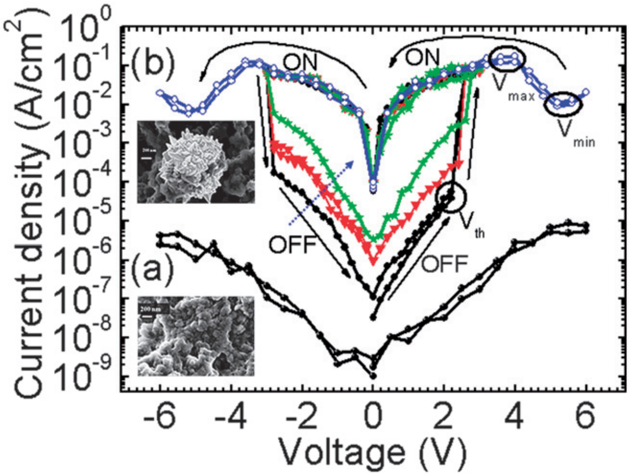


Fig. 4 Current density (J) *vs.* voltage (V) plot of (a) the MITO/PANI/Al device and (b) the MITO/(PANI:Au)/Al device. The arrows represents the pathway of current in different bias scan directions to get into bistability and NDR and the ON state. The threshold voltage ($V_{\rm th}$), maximum voltage ($V_{\rm max}$) and minimum voltage ($V_{\rm min}$) are also shown.

goes from 0 to 3 V. Above $V_{\rm th}$ ($\approx$ 2.2 V), the current increases abruptly, and the device switches to a lower impedance ON state. The ON state is retained during the voltage scan back from 3 V to -3 V. The current in the ON state is several orders of magnitude higher than that in the OFF-state. After application of a $-V_{\rm th}$ (≈ -2.8 V), the impedance switches back to almost the same OFF-state, *i.e.* the device current once again decreased by several orders of magnitude. This reversible transition of device from OFF state to ON state is called bistability.[18] The bistable behaviour of this device was observed when repeating the voltage cycle over again. However, the OFF-state level is gradually increasing leading to a disappearance of the bistability after about 5 times of continuous cycling as indicated by the broken arrow in Fig. 4(b)

After the disappearance of bistability, when the device was further scanned at a higher bias sequence from 0 V to 6 V, 6 V to -6 V and -6 V back to 0 V using a step voltage of 0.1 V s^{-1}, the region of negative differential resistance (NDR)[18] was found between 4 V and 6 V, where current decreases with increasing voltage. There are several unique features noticeable in this state, such as the observation of a local current maximum at $V_{\rm max}$ and a local current minimum at $V_{\rm min}$. This J–V curve is called 'N-shaped' NDR.[18] In addition, the NDR phenomenon was still repeatable after this composite (PANI:Au) material was kept in air for ~2 months whilst the bistable switching disappeared. The NDR is usually attributed to electron hopping between isolated Au particles.[19] The average distance between the Au particles must be much smaller than what is seen on the surface of the PANI:Au composite film in Fig. 1(A), indicative of diffusion of Au particles into the (insulating) PANI materials. This memory device is air stable in contrast to the devices based on C_{60} and polystyrene[18] and the similar PANI:Au composite,[13] which must be operated in a vacuum. The switching and air stable NDR memory properties therefore, might be very useful from the point of view of printable electronic applications

Both films of PANI and PANI:Au composite were characterized by Raman spectroscopy. The excitation wavelength of 780 nm (Renishaw, NIR diode laser) was used for Raman measurements. The spectra are shown in Fig. 5 where (a) is the Raman spectrum of the quartz glass, (b) of the pure IL, [EMIM][Tos], on quartz glass and (c) of the mixture of [EMIM][Tos] and chloroaurate on quartz glass. The spectra (d) and (e) are of freshly made PANI and PANI:Au composite film, respectively. Both films were thoroughly washed with acetone before the Raman measurements. The spectrum (f) is of PANI:Au composite film after 5 cycles in *J*–*V* characteristics when losing the bistability.

The spectra (d), (e) and (f) are characteristic Raman spectra of PANI and confirm that the possible residue of the IL electrolyte does not interfere with the absorption of PANI on MITO. However, there are certain differences between the spectra (d) and (e). The bands at 1553 cm^{-1} and 1466 cm^{-1} are attributed to C–C stretching from the benzenoid unit and C=N streching from the quinoid unit, respectively.[20] The band at 1147 cm^{-1} is assigned to C–H in plane bending of the quinoid rings.[20] A strong Raman band at *ca.* 1323 cm^{-1} can also be seen and is assigned to $C–N^{\bullet+}$ stretching vibrations of the semiquinone radicals and it is inherently associated with the protonation process *via* a polysemiquinone radical formation mechanism.[21] This band is correlated to the conductance of the PANI film, which means that the Au particles enhanced the conducting form of PANI. This is obvious if we compare (e) with (d). The absorption at 1323 cm^{-1} is much less in spectrum (d) (the pure PANI film) than in (e) (the PANI:Au film). In addition, the C=N streching from the quinoid unit has shifted from 1435 cm^{-1} in (d) to 1466 cm^{-1} in (e). Tian *et al.* have also recently found that PANI can still keep its redox activity at neutral pH values when doped with Au nanoparticles.[11,22] As can be seen in Fig. 4(b), the bistability gradually decreases during the *J*–*V* cycling as the dashed arrow shows, indicating formation of more quinoid structures in the PANI film. When the voltage is scanned in the reverse direction, only some of the quinoid forms will be converted to benzenoid forms, resulting in accumulation of quinoid forms in the PANI backbone [see spectra (e) and (f) in Fig. 5]. This is an indication of irreversibility. PANI has three basic states in acidic solutions, leucoemeraldine (fully reduced insulating, LE) form, emeraldine salt (half oxidized conducting, ES) form and pernigraniline (fully oxidized insulating, PN) form.[23] The benzenoid structures will be dominant in the fully reduced LE form while the quinoid structures will be dominant in fully oxidized PN form. When the bistability disappeared, the quinoid absorptions at 1466 cm^{-1} and 1147 cm^{-1} increased [(f) in Fig. 5]. Yang and co-workers. attributed the transition mechanism from the OFF to ON state (bistability) to an electric field-induced charge transfer between PANI and Au particles.[13] The Raman data reported here supports that this assumption is also valid in our device for bistability.

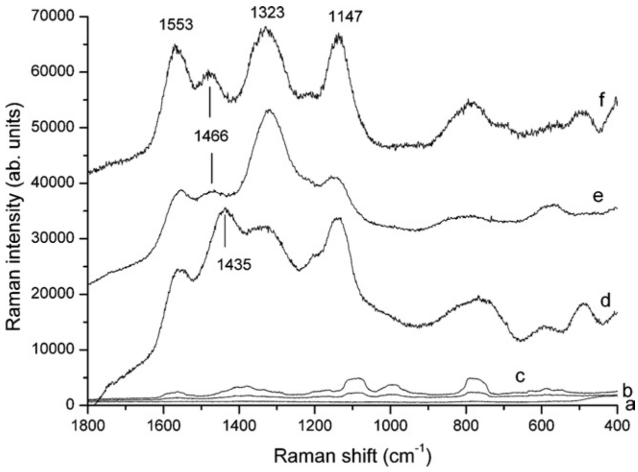


Fig. 5 Raman spectra of (a) the quartz glass, (b) pure IL, [EMIM][Tos], on quartz glass, (c) the mixture of [EMIM][Tos] and chloroaurate on quartz glass, (d) pure PANI film synthesized from [EMIM][Tos] and thoroughly washed with acetone, (e) the freshly synthesized PANI:Au composite film from [EMIM][Tos] and thoroughly washed with acetone, (f) the PANI:Au composite film after losing the bistable property.

3 Conclusions

In conclusion, we have reported an electrochemical fabrication method to produce multi-stable nonvolatile impedance switching PANI:Au composite films where the programming of a continuum of states is possible through the use of applied bias above the critical threshold voltage V_{th}. The PANI:Au composite film can be deposited directly on the MITO glass by electrochemical methods and this simplifies fabrication of the memory device significantly. The impedance states are nonvolatile in nature and can be read and switched several times with minimal degradation in air. Once the mechanism behind the switching effect and existence of multi-stable impedance states is well understood, steps towards optimization and advancement of fabrication can take place to push these devices towards a high-density, low-cost, and reliable data storage application.

4 Experimental

Aniline (>99.5%), was obtained from Fluka. Chlorauric acid (99.9+%) and CF_3COOH (99%) were from Aldrich. [EMIM][Tos] (≥98%) was bought from Solvent Innovation. All chemicals were used as received. The MITO/PANI/Al sample was simultaneously fabricated along with the MITO/(PANI:Au)/Al device. All the parameters for electrochemical fabrication and electronic characterization were kept the same.

5 Acknowledgement

This work is part of the activities of the Åbo Akademi Process Chemistry Centre within the Finnish Centre of Excellence Program (2000–2011) supported by the Academy of Finland. Financial support by the TEKES FinNano Program to

Department of Physics is acknowledged. Mr Ari Laiho is acknowledged for his drawing on the inside cover.

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