

Charge transfer effect in the polyaniline-gold nanoparticle memory system

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A composite system comprised of polyaniline nanofibers bonded with gold nanoparticles is shown to possess a memory effect via a charge transfer mechanism. The charge transfer occurs between the imine nitrogen in the polyaniline and the gold nanoparticles as confirmed by x-ray photoelectron spectroscopy and Raman spectroscopy. This charge transfer enables a bistable electrical conductivity, allowing the material system to be used as a digital memory device. The charge transfer is further confirmed by the elimination of the conductance switching when the fully reduced form of polyaniline, leucoemeraldine, which possesses no imine nitrogens, is used in place of the emeraldine form. © 2007 American Institute of Physics. [DOI: 10.1063/1.2434167]

Semiconductor technology has enabled radical advances in information processing through the development of high speed, high density, nonvolatile memory devices. Continued advances in memory technology will require the development of nanoscale devices, of which the two terminal device architecture appears especially promising since the overall size of the device is dictated by the size of the electrodes. Bistable molecules,^{1,2} donor-acceptor charge transfer complexes,^{3,4} and nanocomposites constructed by organic molecules and nanoparticles⁵⁻⁷ have all emerged as viable choices for incorporation into this particular memory device architecture. Among the nanocomposites, polyaniline/nanoparticle composites are inexpensive material systems and are easily formed by chemical or electrical reduction of metal ions following the polymerization of aniline. This particular system has recently received much interest due to the nanoparticle size tunability,^{8,9} long term solution stability,¹⁰ and potential uses in chemical sensors,^{11,12} electronic devices,⁶ and also as catalysts. Here we reveal the charge transfer effect in these polyaniline/nanoparticle composites as well as the charge transfer induced conductance switching required for operation of the electronic memory devices. X-ray photoelectron spectroscopy and Raman spectroscopy are employed to characterize the chemical bonds in the materials. Additionally, chemical modifications such as adding a reducing agent to the polyaniline are used in the devices to observe changes in the memory performance.

The synthesis of polyaniline nanofibers with gold nanoparticles attached (PANI-Au) is prepared by the redox reaction of polyaniline with chloroaurate anions.^{6,8} A molar ratio of AuCl₄⁻/PANI of ~1.2 in solution was used to synthesize the PANI-Au nanocomposite (the molar ratio is calculated based on 90.6 g/mol aniline unit and 338.8 g/mol AuCl₄⁻). These solutions result in PANI-Au nanocomposites with a final molar ratio of Au/PANI=0.7, as determined by thermogravimetric analysis (TGA 2050, TA Instruments, Inc.).

The transmission electron microscopy (TEM) images were taken with JEOL JEM-2000FX and JEOL 100CX, with samples prepared by drop casting the PANI-Au solution onto copper grids. X-ray photoelectron spectroscopy (XPS) was used to resolve the binding energies in PANI-Au composites by an Omicron multiprobe with a monochromatic Al K α radiation (1486.6 eV, 300 W) source. The Raman spectra were collected with a Renishaw 1000 Raman system, using a 514 nm laser as the excitation in backscattering mode.

The inset in Fig. 1 shows the hybrid nanocomposite material of polyaniline nanofibers and the surface-attached gold nanoparticles. The polyaniline nanofibers, ~30 nm in diameter, are decorated with nearly spherical gold nanoparticles. The diameter of the nanoparticles ranges from 0.5 to 4 nm with an average diameter of ~1.9 nm [histogram inset in Fig. 1]. Although control of the nanoparticle size is difficult, here we used a low temperature control at 2 °C to slow the reduction process of the nanoparticles. A few large metal crystals are observed and can be attributed to Ostwald ripening especially over periods of several days to weeks; therefore each solution was freshly made and subsequently fabricated into the devices.

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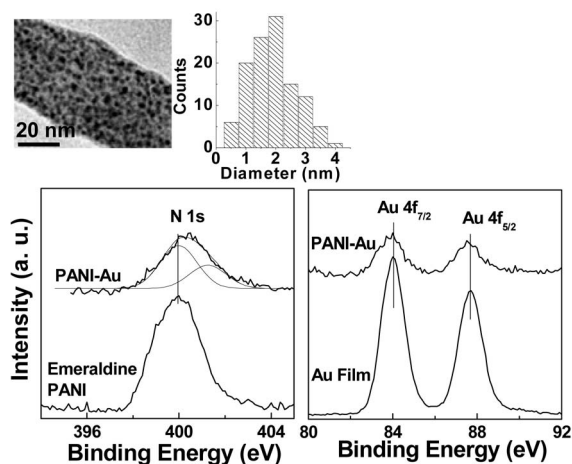


FIG. 1. XPS spectra of polyaniline-Au nanoparticles. The N 1s core level spectra show a higher binding energy component in PANI-Au compared to emeraldine base PANI. The left inset shows a TEM image of gold nanoparticles on a polyaniline nanofiber. The gold particle sizes range between 0.5 and 4 nm (right, inset), with an average particle size of ~ 1.9 nm. The core level spectra of Au 4f exhibit a slight shift to lower binding energy in PANI-Au compared to pure Au film.

Figure 1 shows the XPS spectra of PANI-Au compared to emeraldine PANI and a pure gold film. The core level spectrum of N 1s in PANI-Au [Fig. 1] is found to have a higher binding energy peak centered at 401.2 eV compared to the neutral state N at 400 eV in emeraldine PANI. This high binding energy peak is partially attributed to the positively charged nitrogen. On the other hand, the Au 4f spectrum in the PANI-Au [Fig. 1] shifts 0.1–0.2 eV lower in binding energy compared to pure gold. Similar negative shifts, up to 0.3 eV, for binding energy have been reported for Pt clusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Ref. 13) and gold nanoparticles stabilized by β -cyclodextrin.¹⁴ The chemical interaction between gold and polyaniline suggests a strong bond and a charge transfer process from the positively charged nitrogen to the slightly negatively charged gold nanoparticles. These results are believed to be dependent on the size of the nanoparticles within the system. After the nanoparticles reach a certain size, the binding energy shift is apparently reduced back to bulk values due to the strong metal core signal.¹⁵

To further investigate the charge transfer effect behavior surrounding the nitrogen in the PANI-Au, Raman spectroscopy was employed to observe bond stretching differences on both the amine and imine nitrogens of the bare PANI (with no nanoparticles) and the PANI-Au nanocomposites. Figure 2 shows the Raman spectra of three different materials; dedoped emeraldine PANI, the PANI-Au nanocomposite, and hydrochloric acid (HCl) doped emeraldine PANI (HCl doping concentration of 0.1 mM). The chemical bonds of C–N, protonated C–N⁺, C=N, and protonated C=N⁺ are assigned at 1320, 1340, 1478, and 1495 cm⁻¹ according to literature reports.¹⁶ We found that only the HCl doped PANI showed an obvious C–N⁺ band due to variable protonation and oxidation levels caused by the HCl doping.¹⁷ We took a closer look at the C=N band in these materials. The spectrum shows a broad peak for C=N from HCl doped PANI due to the protonated C=N⁺. A shift to higher wave numbers is observed in the PANI-Au compared to dedoped emeraldine PANI, indicating that the gold nanoparticles bonded to the PANI give a charge transfer property similar to the

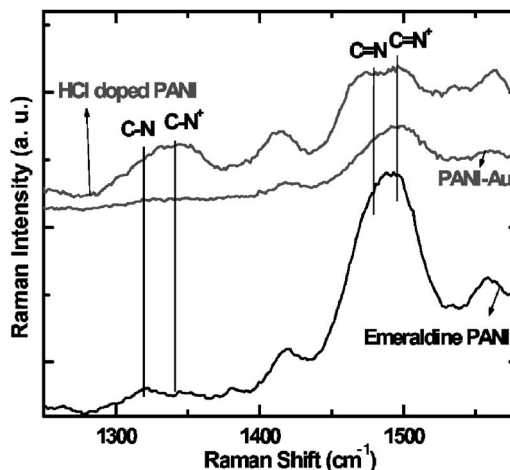


FIG. 2. Raman spectra of PANI-Au, HCl doped PANI, and dedoped emeraldine PANI. The chemical bond stretches of amine nitrogen, C–N and C–N⁺, and imine nitrogen, C=N and C=N⁺, are assigned at 1320, 1340, 1478, and 1495 cm⁻¹, respectively. The regions of C=N and C=N⁺ bands of PANI-Au are shown to have a right shift, suggesting a charge transfer effect for gold nanoparticles bound to PANI.

protonation process by HCl doping. The electron clouds at the conjugate C=N bond can partially transfer to the gold nanoparticles because in this case the PANI is partially positively charged and the gold nanoparticles are partially negatively charged. This charge transfer effect indicates that the PANI and gold nanoparticles act as donor and acceptor, respectively, consistent with the XPS observation.

Two terminal devices were constructed by a composite layer of PANI-Au in polyvinyl alcohol matrix sandwiched between two aluminum metal electrodes.⁶ The thickness of the composite layer is ~ 80 nm verified using a profilometer (Dektak 3030). Current density–voltage (*J*-*V*) characteristics were measured by a semiconductor parameter analyzer (HP 4155B). Since the charge transfer effect is related to the charge donating ability of the conjugated polymer PANI, we further verified the mechanism of a charge transfer effect in these devices by examining materials treated with a reducing agent. The PANI-Au is treated with 0.1 mM hydrazine (N₂H₄) to chemically alter the polyaniline structure, whereby the emeraldine PANI found normally in the nanocomposite is completely converted to the reduced, i.e., nonconjugated, leucoemeraldine form of PANI.¹⁷ Figure 3 shows the *J*-*V* responses of PANI-Au devices with and without hydrazine

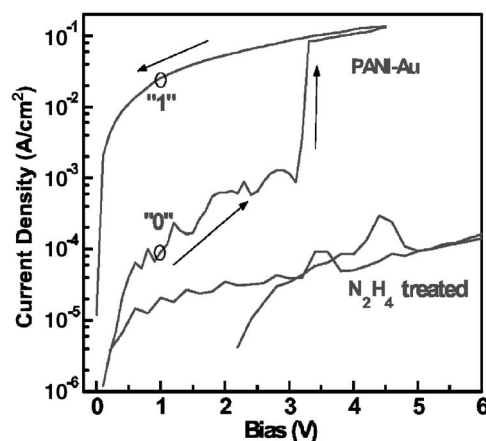


FIG. 3. *J*-*V* characteristics of devices with PANI-Au composites treated with and without a reducing agent (0.1 mM hydrazine).

treatment. Typically, under the influence of an applied bias, we observe conductance switching occurring at ~ 3 V, while sweeping the voltages from 0 to 5 V. Thus, a high conductivity state is stable at a current density of $>10^{-2}$ A/cm², while the initial low conductivity state is only around 10^{-4} A/cm². This electrical bistable behavior is cyclable and can be used to store a virtual “0” or “1,” as represented by the conductivity states, for memory applications. It is obvious that the device fabricated with N₂H₄ treated nanocomposites stays in the low conductivity state and no switching is observed. The conjugated C=N in emeraldine PANI turns to nonconjugated C-N in leucoemeraldine PANI, causing loss of its charge donating ability which enables the charge transfer process. It is therefore believed that charge transfer from the conjugated polymer to the nanoparticles indeed triggers the electrical switching in this type of memory device.

During the voltage ramp-up, as the applied bias voltage reaches the voltage required for turn-on, charge transfer takes place from the PANI to the nanoparticles thus enabling charge tunneling observed by the higher conductivity through the PANI-Au composite. To analyze this mechanism further, previous studies have shown that molecular devices with metal nanoparticle-organic interfaces^{18,19} display a dramatic reduction of the density of states near the Fermi level on the nanoparticles due to strong bond interactions between Au-S or Pd-N, thereby resulting in nonmetallic behavior in these nanoparticles.¹⁸ During the activation of the charge transfer mechanism through the application of an external electric field, charges are redistributed at the interface, which dramatically increases the tunneling probability near the Fermi level, leading to conductance switching in the device.¹⁹ The PANI-Au devices described in this letter exhibit similar behavior, because this interface still exists at each location of the metal nanoparticles on the PANI and could lead to analogous electronic behavior.

Additionally, this tunneling process can be observed from the conduction current in the high conductivity state as a function of temperature as shown in Fig. 4. The *J-V* curves of PANI-Au devices are verified to have repeatable conductance switching from room temperature to 121 K [Fig. 4(a)]. The currents present in the device in the high conductivity state show a slight temperature dependence between 235 and 293 K, and nearly no temperature dependence at temperatures lower than 235 K. The corresponding activation energies in the regions of 293–235 and <235 K are 48.9 ± 3.73 and 3.1 ± 0.82 meV, respectively. Therefore the conduction mechanism in the high conductivity state is nearly a fully tunneling process; however, it is important to note here that the thermal energy close to room temperature may affect the charge conduction.

We report a charge transfer effect in the polyaniline nanofiber/gold nanoparticle nanocomposite memory system. The electric-field-induced charge transfer in this device occurs between the conjugated polyaniline and gold nanoparticle and is responsible for the electrical conductance switching. The realization of the charge transfer effect in this polymer-nanoparticle system could benefit applications of memory devices in the field of organic electronics.

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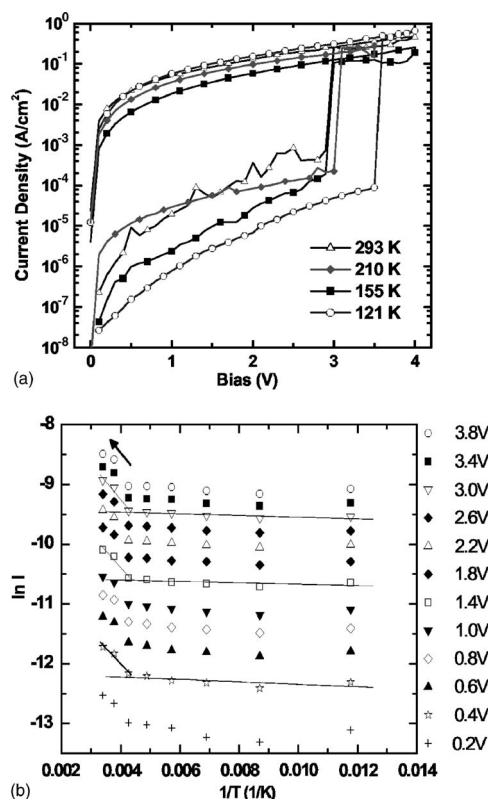


FIG. 4. (a) Temperature dependent *J-V* characteristics of PANI-Au devices. The devices were measured at temperatures from 293 to 121 K. (b) Conduction currents in the high conductivity state as a function of temperature at selected voltages. Activation energy for charge conduction in the high conductivity state is derived from the slope of $\ln(I)$ vs $1/T$.

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