

Photo-Induced Tunneling Current in Single-Wall Carbon Nanotubes Investigated by Scanning Tunneling Spectroscopy

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Abstract. The electronic properties of single-wall carbon nanotubes (SWCNT) under light excitation were investigated by scanning tunneling microscopy and spectroscopy (STM/STS), since this technique allows both imaging and probing individual nanotubes. A photo-induced tunneling current (PITC) was observed for semiconducting and metallic SWNT only when the excitation energy exceeds the 1st pairs of van Hove singularity in the density of state. Moreover, the PITC effect occurs at both positive and negative sample bias, increases linearly with the light intensity and is reversible. Further experiments are in progress to elucidate the mechanism of PITC and to ultimately reveal the photoconductivity response of individual SWCNT.

INTRODUCTION

Single-wall carbon nanotubes (SWCNT) constitute a new class of materials owing to their unique one-dimensional geometry and outstanding electronic structure. On the one hand it is well documented that SWCNT exhibit unique electronic transport characteristics ¹ and optical properties ², but on the other hand their synergy is so far unveiled. In this context, it is of great interest to understand the basic photoelectric property of isolated SWCNT and ultimately to explore the photoconductivity of semiconducting SWCNT.

Since our samples inherently contain both semiconducting (s-SWCNT) and metallic (m-SWCNT) nanotubes, and also because they are randomly deposited onto a substrate for characterization, scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are powerful methods for imaging and probing locally the electronic properties of SWCNT under light irradiation. Here we describe and briefly discuss our preliminary results: we stress that using STS under light irradiation at ambient conditions a photo-induced tunneling current (PITC) was observed only when the excitation energy exceeds the 1st pairs of van Hove singularity in the density of state (DOS) of s-SWCNT and of m-SWCNT.

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EXPERIMENTS

SWCNTs investigated in the present study were synthesized by the electric arc discharge method using Ni/Co catalyst (Carbolex). The raw material containing mainly the carbon nanotubes was purified, first by a reflux in HCl (6M), then by a heat treatment at 500⁰C in air, and finally followed by an annealing at 1500⁰C in vacuum. Treated SWCNTs were dispersed in ethanol by ultrasonication for 10 minutes and were spread on a freshly cleaved highly oriented pyrolytic graphite (HOPG) substrate by spin coating method.

Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements were carried out by using SEIKO Instrument (SPI 3800 E) with STM tips made of Pt/Ir, at room temperature under ambient conditions. STM imaging of the sample was done under a typical tunneling current of 0.488 nA and a sample bias of 0.1 volt. STS data (tunneling current versus sample bias, $I_{tc}-V_{sb}$) were collected by sweeping the sample bias from -1 to +1 volt with the feed back loop deactivated to keep the STM tip at a fixed height and position from the sample.

STS data were collected in the absence (dark tunneling current) or presence (photo induced tunneling current) of laser illumination at different energies and intensities. In the present report, the optical excitation source was either a near infra-red He-Ne cw laser ($h\nu=0.82$ eV) or an Ar-ion cw laser ($h\nu=2.36$ eV) fitted with appropriate band pass filters (a wider range of excitation energy would be desirable but unfortunately not available at the present stage). The laser beam coupled through an optical fiber was focused onto the sample surface near the apex of the STM tip. The laser-irradiated area on the sample surface was approximately 1 mm² and the power density was typically about 200 μ W/mm². It is worthwhile to mention that there is no appreciable lateral drift of the STM image under laser illumination.

RESULTS AND DISCUSSIONS

First, we observed a large number of nanotubes (probably bundles of SWCNT according to the resolution of our STM images, not shown here) and we recorded their $I_{tc}-V_{sb}$ curves by STS in dark condition. In addition, their corresponding derivatives (dI_{tc}/dV_{sb} vs V_{sb}) were calculated to reflect to some extent their DOS. Figure 1 shows typical examples of dI_{tc}/dV_{sb} curves and for comparison the theoretically calculated DOS³ of (12,8) semiconducting and (10,10) metallic nanotubes. In the present case, (12,8) semiconducting and (10,10) metallic were deliberately presented because their theoretically calculated DOS accounts for most of the electronic features observed in the dI_{tc}/dV_{sb} curves. Using this procedure the observed nanotubes could be either categorized as semiconducting or metallic SWCNT. Admittedly, detailed characterization of the chiral angle and the diameter of individual SWCNT would be desirable for further discussions.

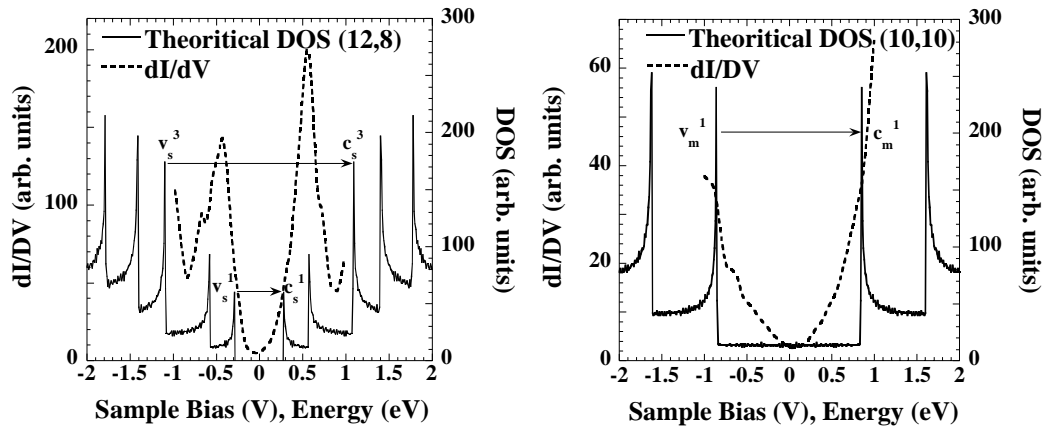


FIGURE 1. Typical examples of dI_{tc}/dV_{sb} curves (numerically calculated from $I_{tc}-V_{sb}$ curves recorded by STS in dark condition as depicted in Fig.2) and for comparison the theoretically calculated DOS of (12,8) semiconducting and (10,10) metallic nanotubes (with $\gamma_0=2.75$).

Next, we recorded the $I_{tc}-V_{sb}$ curves of semiconducting SWCNT under continuous laser irradiation with $h\nu=0.82$ and 2.36 eV (Fig. 2). We have selected those excitation lines because they match the energy of the expected optical transition between the 1st ($v_s^1 \rightarrow c_s^1$ with ~ 0.6 eV gap) and 3rd ($v_s^3 \rightarrow c_s^3$ with ~ 2.2 eV gap) pairs of van Hove singularity in the DOS of (12,8) semiconducting nanotube (see figure 1 for the notation used here). It is very important to stress that we observed in absolute value an increase of the tunneling current for both positive and negative sample bias compared to dark conditions. Moreover, the photo-induced tunneling current (PITC) was observed for both excitation energy and with the same magnitude under similar power density of $\sim 200 \mu W/mm^2$. The observed PITC effect is fully reversible and its kinetic very fast compared to the time scale of our measurements (each scan takes about 30 sec). We notice that dI_{tc}/dV_{sb} vs V_{sb} curves of semiconducting SWCNT recorded under illumination and in dark condition show very similar features. In addition, no photovoltaic effect was observed, because at $V_{sb}=0$ volt no significant increase of the tunneling current was observed.

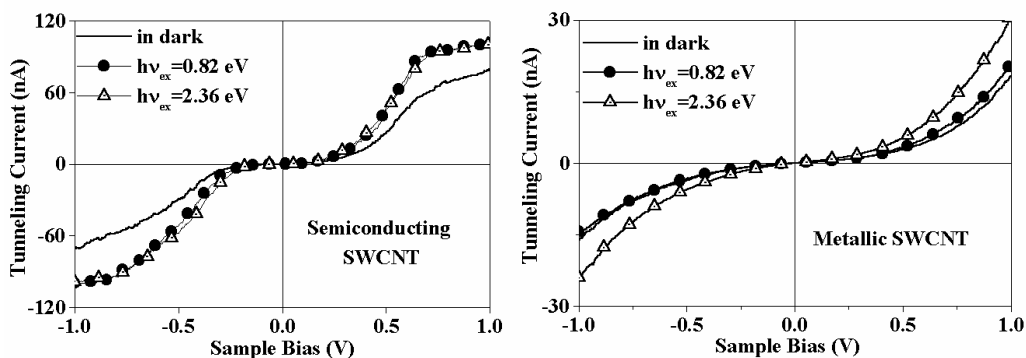


FIGURE 2. $I_{tc}-V_{sb}$ curves for a semiconducting and a metallic SWCNT in dark condition and under cw laser irradiation with $h\nu=0.82$ and 2.36 eV excitation energy (power density $\sim 200 \mu W/mm^2$).

Experiments were also carried out exactly under the same conditions with metallic SWCNT (Fig. 2). With $h\nu=2.36$ eV excitation energy a PICT effect was observed in good agreement with the results mentioned above. In contrast, no significant change in the tunneling current was recorded with $h\nu=0.82$ eV for both positive and negative bias, with power density up to $600 \mu\text{W}/\text{mm}^2$, within our experimental resolution. Here the main difference between the two excitation energy is that $h\nu=2.36$ eV is well above the 1st pair of singularities ($v_m^1 \rightarrow c_m^1$ with ~ 1.8 eV gap) whereas $h\nu=0.82$ eV is below and does not match any allowed optical transition in (10,10) metallic nanotube.

We have also carried out $I_{tc}-V_{sb}$ measurements with different intensities of incident light at constant excitation energy (at $h\nu=2.36$ eV) on both semiconducting and metallic SWCNT. We found that the photo-induced tunneling current at constant sample bias (for example -1 or $+1$ volt) in absolute value increases linearly with the light intensity.

Moreover, we have extended this study to HOPG and multi-wall carbon nanotubes (MWCNT) that bear similarity with SWCNT but with different electronic structure. We did not observe an appreciable change in the tunneling current upon illumination as compare to dark conditions, irrespective of the excitation energy, light intensity and sample bias, within our experimental resolution.

In summary, we strongly believe that the observed PITC effect originate from the unique electronic properties of SWCNT, because it was observed only when the excitation energy matches or exceeds the 1st pairs of van Hove singularity in the DOS of s-SWCNT and m-SWCNT. However, the mechanism of the PITC is open to speculation, bearing in mind the inherent complexity of the tunneling process through the “air” gap between the sample and the STM tip. A tentative interpretation might be that photo-excited electron-hole pairs in either s-SWCNT or m-SWCNT can dissociate and contribute to the tunneling current. But, photo-thermal effect cannot be definitively excluded since we have observed in the case of s-SWCNT (Fig. 2) excited with two different energies ($h\nu=0.82$ and 2.36 eV) and with the same power density ($\sim 200 \mu\text{W}/\text{mm}^2$) that the change in the tunneling current is of the same amplitude. Recently, Chen⁴ has reported that the conductance of individual semiconducting nanotube and SWCNT film in vacuum under ultraviolet irradiation are dominated by molecular photodesorption effects rather than photoconductivity response. In contrast, Fujiwara⁵ claim to have observed photoconductivity in semiconducting nanotubes, from experiments on bulk SWCNT films connected to two electrodes (10 μm gap) under pulse laser irradiation (~ 100 nJ/pulse, 5 ns pulse, 10Hz).

In conclusion, the photoelectric properties of SWCNT are not yet fully understood and further experiments in controlled environment and using 2-probes contacts will be pursued.

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