

## Observation of microwave plasmons in one-dimensional conjugated polymer chain

B. Mondal,<sup>1</sup> D. Majumdar,<sup>1</sup> A. Ghosh,<sup>2</sup> and S. K. Saha<sup>1,a)</sup>

<sup>1</sup>Department of Materials Science, Indian Association For The Cultivation of Science, Jadavpur, Kolkata 700032, India

<sup>2</sup>Department of Solid State Physics, Indian Association For The Cultivation of Science, Jadavpur, Kolkata 700032, India

(Received 26 February 2009; accepted 3 April 2009; published online 6 May 2009)

Observation of extremely low frequency plasmons in highly ordered quasi-one-dimensional (quasi-1D) interrupted metallic polymer chain segments is reported. Rice and Bernascony [Phys. Rev. Lett. **29**, 113 (1972)] predicted giant permittivity in interrupted 1D metal strands because of quantum confinement. We have used this quasi-1D electron system with giant permittivity to realize 1D plasmons in microwave frequency. Polypyrrole nanorods with ordered and aligned chains have been synthesized. These ordered and perfectly conjugated systems interrupted by defects are ideal systems to achieve giant permittivity and as a result, 1D microwave plasmons, which have potential applications in microwave devices, are observed. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3124653]

Surface plasmons are collective oscillations of conduction electrons on a metal surface originated due to interaction with electromagnetic wave.<sup>1</sup> Due to rapid advancement in the fabrication of nanostructures, collective excitation of low dimensional electronic systems such as one-dimensional (1D) plasmon plays an important role to both experimental<sup>2-4</sup> as well as theoretical<sup>5-7</sup> researchers.

Optical properties of these metal/semiconductor nanostructures particularly 1D nanostructures have stimulated intensive research due to its potential applications in biomolecular manipulation,<sup>8</sup> photonic circuits,<sup>9</sup> and molecular detection<sup>10,11</sup> by surface enhanced Raman scattering. Much effort has been paid to explore the optical properties of these nanostructures using numerical approach popularly known as discrete dipole approximation (DDA).<sup>12-16</sup> Using DDA method, plasmon coupling between the particles has been investigated in detail and it is seen that resonant peaks are significantly shifted toward higher wavelength as the interparticle spacing is reduced.<sup>17</sup> Very recently, optical properties of quasi-1D nanostructures synthesized by gold (Au) using porous anodic alumina as template have been explored, and it is seen that due to interparticle coupling longitudinal plasmon peaks shift toward higher wavelength as the length of 1D nanostructures increases.<sup>18</sup>

Unique property of these semiconductor or metal-based 1D plasmons is that they are realized at optical frequency range. Pendry *et al.*<sup>19</sup> proposed periodic structures built by metal wires with dilute electron concentration and enhanced effective mass to observe extremely low frequency plasmons in metallic mesostructures, although later a comment<sup>20</sup> was made regarding the incorporation of both effects in a system of parallel wires by taking the expression for 1D-plasmon. The expression for 1D plasmon frequency is given by<sup>20</sup>

$$\Omega_{1D}^2(q) = (n_{1D}e^2/\epsilon m_{\text{eff}})q_s^2 \ln(1/q_s r), \quad (1)$$

where  $n_{1D}$  is the 1D electron density,  $\epsilon$  is the effective permittivity,  $m_{\text{eff}}$  is the effective mass, and  $q_s$  is the wave vector of the electron. From the above expression it is seen that plasmon frequency of the electronic system comes abruptly down to a lower frequency for the electronic system with giant permittivity.

In 1972, Rice and Bernascony<sup>21</sup> predicted remarkable effect of giant permittivity in interrupted metal strands in the high frequency limit (microwave) as a result of quantum confinement of electronic wave functions [Gor'kov–Eliashberg (GE) effect].<sup>22</sup> In their model, they considered linear chain of metal atoms interrupted by defects as a modified class of dielectric systems, which show giant permittivity as a result of quantum confinement. The expression for dielectric permittivity ( $\epsilon$ ) according to the strand model was calculated as

$$\epsilon = (q_s l_0)^2, \quad (2)$$

where  $q_s$  gives the wave vector of conduction electrons and  $l_0$  is the strand length. Using the value for permittivity given by Eq. (2), the expression for plasmon frequency reduces to

$$\Omega_{1D}^2(q) = (n_{1D}e^2/l_0^2 m_{\text{eff}})\ln(1/qr). \quad (3)$$

The basic physics of GE effect is the localization of states and if number of atoms in the metal strand are very large so that the energy spacing between two levels is small enough to be difficult to observe the effect at the corresponding temperature where thermal energy is higher than the energy spacing between two levels. A couple of years back the present author reported<sup>23</sup> a giant dielectric response ( $\epsilon \sim 10^{10}$ ) in an assembly of ultrafine silver metal particles.

Conjugated polymers are quasi-1D systems and possess wide variation of conductivity from metallic to semiconductor. Polymer chains are quasi-1D metals and its conductivity can be tuned widely just by controlling the disorder and alignment. Therefore, conjugated polymer chains are ideal systems to investigate GE effect of giant permittivity. It is

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: cnsks@iacs.res.in.

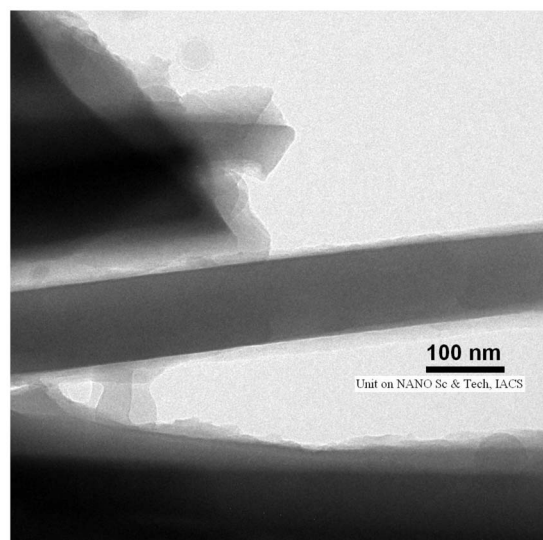


FIG. 1. TEM micrograph of polypyrrole nanorod.

only recently<sup>24</sup> that we have investigated giant permittivity in polypyrrole nanotubes in the frequency range up to 1 MHz.

In all of previous articles related to high dielectric constant, the permittivity was measured up to 1 MHz although Rice and Bernasconi<sup>21</sup> in their article mentioned that GE effect would be observed in the microwave frequency range. In early reports, origin of high dielectric constant was explained by GE effect, and there was no concrete proof as all measurements were carried out up to 1 MHz. Therefore, to achieve GE effect we have to consider two aspects, one the measurement frequency range as in the microwave range and second, the system as interrupted metal strands.

Although, few measurements have already been done on 1D plasmonic system, most of them are realized in UV-visible range. As conjugated polymer chains are real 1D systems (diameter is of few angstroms, length is of several micrometers), it is very interesting and worth to study this system to elucidate 1D plasmonic behavior in real systems. Besides this, from our previous investigation, we have seen that these 1D polymer chains show giant dielectric permittivity, which has strong effect in plasmonic behavior to lowering the frequency range drastically. Therefore, the motivation of this work is to study the excitation of very low frequency plasmons (microwave) in real 1D system with giant dielectric permittivity.

Here, microwave measurements of polypyrrole nanorods synthesized by our own technique reported earlier<sup>25</sup> are carried out over the temperature range 120–300 K.

Figure 1 shows the transmission electron microscopy (TEM) micrograph of a single nanorod. Figure 2 gives the variation of conductance with frequency at temperature 123 K. It is seen that frequency dependent conductivity initially increases with frequency like other amorphous semiconductors but after certain frequency, it increases very rapidly and finally drops down at higher frequencies.

Figure 3(a) shows the variation of capacitance with frequency, from which it is seen that the capacitance, i.e., the permittivity value initially increases slowly with frequency, reaches sharply to a maximum, and then suddenly falls to a negative value. In amorphous semiconductor dielectric permittivity usually decreases with frequency but increase in permittivity value with frequency is very unusual. To explain

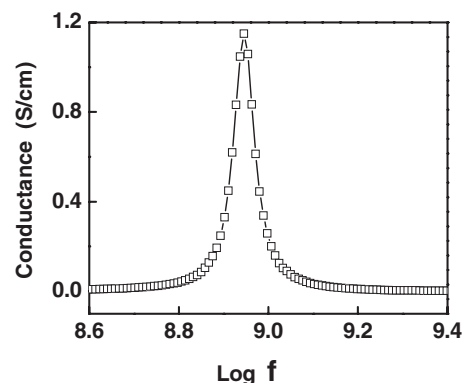


FIG. 2. Conductance data with frequency at temperature 123 K.

our experimental data, we have modeled the polymer chain as an ordered phase while the interconnection of two chains as a disordered phase. The justification behind this assumption is that due to directional growth along the length of the tubes polymer chains are more aligned whereas the interconnected portion of two chains is disordered. Such kind of alternate metal-semiconductor structures have been speculated in our early work<sup>25</sup> to explain single electron tunneling in polypyrrole nanotubes. Evidence of nonlinear current-voltage characteristics shown in Fig. 3(b) gives such kind of alternate metal-semiconductor structure in which charge carriers are delocalized in the metallic segment and localized in the semiconducting segment, respectively.

From the expression for dielectric function given by Eq. (2), it is seen that the value of permittivity of interrupted 1D metallic strand increases with the length of the strand. Near the resonance frequency as metal chain segments are connected together due to switching through the localized segment, permittivity increases due to effective increase in the length ( $l_0$ ) of the chain segment.

Therefore, essentially, we have considered our system as consisting of alternate segments of ordered and disordered (interconnection of two chains) segments. Such kind of localized/delocalized carriers have also been considered by other workers<sup>26</sup> to explain metallic state of conjugated polymers.

The most intriguing result is the observation of extremely sharp loss peaks shown in Fig. 4(a), which do not shift significantly with temperature. The shape of the loss peak is Lorentzian-type with very high peak intensity which cannot be fitted by the formula given by Debye-type relaxation with single relaxation frequency rather the nature of this peak is like resonance type process which shows no shift of peak value with temperature, as shown in Fig. 4(b). In case of relaxation process in amorphous semiconductors,

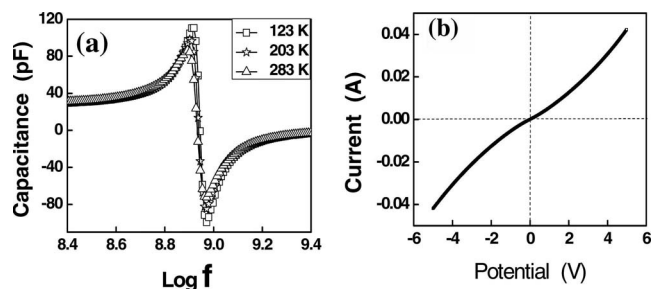


FIG. 3. (a) Variation in capacitance with frequency and (b) nonlinear current-voltage characteristics of polypyrrole nanorods.

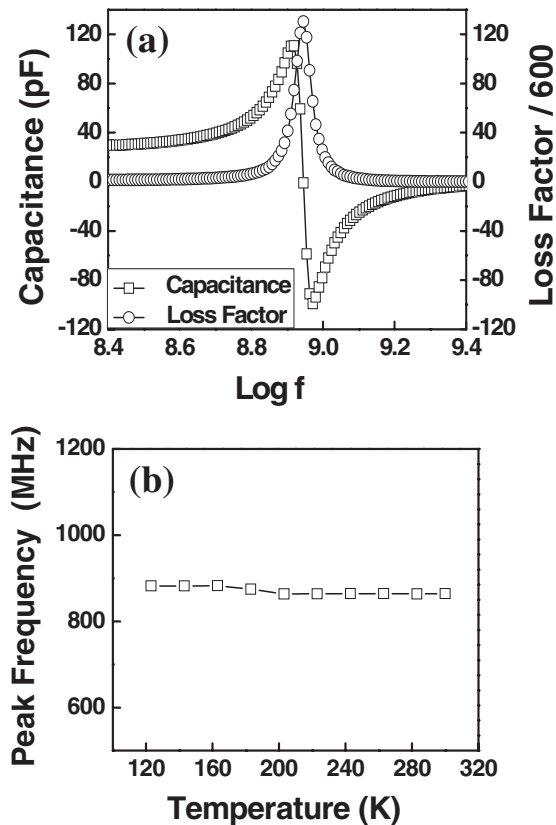


FIG. 4. (a) Variation in capacitance and corresponding loss spectra at temperature 123 K and (b) variation of resonance frequency with temperature.

usually dielectric loss peak shifts with temperature and the permittivity value remains always positive. But, in our case, the loss peak occurs at the transition where permittivity changes from positive (localized state) to a negative (completely delocalized state) value.

This is due to the fact that the carrier defect formed in the disordered segment oscillates with its own natural frequency. The response of this oscillator with applied frequency is very sharp and in the vicinity of the natural frequency, amplitude of vibration suddenly increases to a very high value, which is comparable to or larger than the size of the disordered segment. At the resonance condition, conductivity does not depend only on delocalization of the defect state rather it increases several orders of magnitude due to interconnection of two perfectly conjugated (ordered) segments due to switching through complete delocalization of the defect. This complete delocalization of the carrier wave at the peak frequency is confirmed by the negative dielectric permittivity and as a result, all delocalized charge carriers in the entire chain segment show collective excitations as 1D plasmons. Evidence of very narrow and sharp loss peak indicates that the carrier waves in these quasi-1D polymer chains are weakly interacting system.

Using Eq. (3), and putting the values of  $n_{1D}$  as  $1.66 \times 10^7/\text{m}$ ,  $l_0$  as the thickness of the template, gives the length of the nanorod  $50 \times 10^{-6}$  m,  $m_{\text{eff}}$  as  $10^{-31}$  kg, and  $e$  is the electronic charge as  $1.6 \times 10^{-19}$ ,  $c$  is the value of plasmon frequency has been estimated to  $\sim 1.0 \times 10^9$  Hz, which is exactly equal to the experimentally observed peak frequency.

In this calculation, we have taken  $l_0$  as the length of the nanorod because we have considered all metal chain segments along the entire nanorod are connected through the switching of interconnected portion (disordered segment) at resonance frequency.

Our observation of microwave plasmons in quasi-1D conjugated polymer chains is quite different from others investigated in 1D electron systems. Pendry *et al.*<sup>19</sup> used super lattice of mesostructure and recently 2D metal strip<sup>27</sup> has been used to study microwave plasmon. However, we have used quasi-1D interrupted metal system with giant dielectric permittivity to achieve microwave plasmon, which has potential application as plasmonic device in microwave frequency range.

In conclusion, quasi-1D conjugated polymer chains with giant dielectric permittivity have been used to observe collective excitation as 1D plasmon at microwave frequency.

B.M. and D.M. acknowledge Council of Scientific and Industrial Research for awarding Fellowship. S.K.S. acknowledges support from DST Unit on Nanoscience and Centre for Nanotechnology

<sup>1</sup>W. L. Barnes, A. Dereux, and T. W. Ebbesen, *Nature (London)* **424**, 824 (2003).

<sup>2</sup>T. Demel, D. Heitmann, P. Grambow, and K. Ploog, *Phys. Rev. Lett.* **66**, 2657 (1991).

<sup>3</sup>I. V. Kukushkin, J. H. Smet, S. A. Mikhailov, D. V. Kulakovskii, K. von Klitzing, and W. Wegscheider, *Phys. Rev. Lett.* **90**, 156801 (2003).

<sup>4</sup>T. Nagao, S. Yaginuma, T. Inaoka, and T. Sakurai, *Phys. Rev. Lett.* **97**, 116802 (2006).

<sup>5</sup>S. DasSarma and W. Lai, *Phys. Rev. B* **32**, 1401 (1985).

<sup>6</sup>Q. Li and S. Das Sarma, *Phys. Rev. B* **40**, 5860 (1989).

<sup>7</sup>S. Das Sarma and E. H. Hwang, *Phys. Rev. B* **54**, 1936 (1996).

<sup>8</sup>Y. W. C. Cao, R. C. Jin, and C. A. Mirkin, *Science* **297**, 1536 (2002).

<sup>9</sup>E. Ozbay, *Science* **311**, 189 (2006).

<sup>10</sup>S. Nie and S. R. Emory, *Science* **275**, 1102 (1997).

<sup>11</sup>K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari, and M. S. Feld, *Phys. Rev. Lett.* **78**, 1667 (1997).

<sup>12</sup>B. T. Draine and P. J. Flatau, *J. Opt. Soc. Am. A* **11**, 1491 (1994).

<sup>13</sup>I. Pastoriza-Santos and L. M. Liz-Marzan, *J. Mater. Chem.* **18**, 1724 (2008).

<sup>14</sup>F. J. Garcia de Abajo and A. Howie, *Phys. Rev. Lett.* **80**, 5180 (1998).

<sup>15</sup>R. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, and J. G. Zheng, *Science* **294**, 1901 (2001).

<sup>16</sup>L. J. Sherry, R. Jin, C. A. Mirkin, G. C. Schatz, and R. P. Van Duyne, *Nano Lett.* **6**, 2060 (2006).

<sup>17</sup>K. H. Su, Q. H. Wei, X. Zhang, J. J. Mock, D. R. Smith, and S. Schultz, *Nano Lett.* **3**, 1087 (2003).

<sup>18</sup>S. Kim, K. L. Shuford, H. M. Bok, S. K. Kim, and S. Park, *Nano Lett.* **8**, 800 (2008).

<sup>19</sup>J. B. Pendry, A. J. Holden, W. J. Stewart, and I. Youngs, *Phys. Rev. Lett.* **76**, 4773 (1996).

<sup>20</sup>S. A. Mikhailov, *Phys. Rev. Lett.* **78**, 4135 (1997).

<sup>21</sup>M. J. Rice and J. Bernasconi, *Phys. Rev. Lett.* **29**, 113 (1972).

<sup>22</sup>L. P. Gor'kov and G. M. Eliashberg, *Zh. Eksp. Teor. Fiz.* **48**, 1407 (1965) [*Sov. Phys. JETP* **21**, 940 (1965)].

<sup>23</sup>S. K. Saha, *Phys. Rev. B* **69**, 125416 (2004).

<sup>24</sup>S. K. Saha and D. Chakravorty, *Appl. Phys. Lett.* **89**, 043117 (2006).

<sup>25</sup>S. K. Saha, *Appl. Phys. Lett.* **81**, 3645 (2002).

<sup>26</sup>R. S. Kohlman, A. Zibold, D. B. Tanner, G. G. Ihas, T. Ishiguro, Y. G. Min, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. Lett.* **78**, 3915 (1997).

<sup>27</sup>I. V. Kukushkin, J. H. Smet, V. A. Kovalskii, S. I. Gubarev, K. von Klitzing, and W. Wegscheider, *Phys. Rev. B* **72**, 161317 (2005).