Electric field enhanced photoluminescence of CdTe quantum dots encapsulated in poly (N-isopropylacrylamide) nano-spheres

Brett W. Garner, Tong Cai, and Zhibing Hu, Arup Neogi[*]

[1]*Department of Physics, University of North Texas, 210 Avenue A, Denton, TX 76205, USA*
[*]*Corresponding author: arup@unt.edu*

Abstract: Photoluminescence from CdTe quantum dots encapsulated within hydrogel nanospheres can be controlled by the application an external dc electric field. Dynamic light scattering measurement of hydrogel placed under an electric field shows the collapse of the hydrogel sphere from 312 to 180nm due to volume phase transition. Distances between quantum dots placed within the hydrogel sphere can be controlled by the applied field. A 50% enhancement in the PL intensity is observed under the influence of a dc field less than 5 V/cm. A red-shift in the peak PL intensity and emission from larger sized dots indicate energy transfer between the quantum dots. The collapse of gels is reversible and therefore has potential application in non-volatile memory devices.

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OCIS codes: (160.2100) Materials: Electro-optical Materials; (160.4236) Materials: Nanomaterials; (160.5470) Materials: Polymers; (250.5590) Optoelectronics: Quantum-well, -wire and -dot devices; (250.5230) Optoelectronics: Photoluminescence.

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1. Introduction

A hydrogel polymer is material with the ability to absorb significant amounts of water and retain its structural integrity. N-isopropylacrylamide, NIPA, is one such hydrogel, first investigated by Tanka in 1973, and described as being 'half-liquidlike' and 'half-solid like' [1]. NIPA hydrogels have become of great interest to the biomedical community because it is water based, its compatibility with biological systems. It is used for applications such as controlled drug delivery [2], artificial muscles, cell adhesion mediators [3], precipitation of proteins [4], and chromatography [5]. These 'smart' polymers respond to external physical environmental stimuli such as temperature [6], pH [7], electric field [8], magnetic field [9], and organic solvents [10]. Further, NIPA hydrogels have applications as sensors, shape memory, tunable optics [11], and molecular imaging [12].

The functionality and versatility of hydrogel is derived from its ability to change shape and respond to many different stimuli. Hydrogels comprise randomly cross-linked polymer chains with water filling interstitial spaces of a formed network [13]. Using the molecular weight and the relation between the interpenetration function and expansion coefficients, it has been shown that the NIPA polymer molecules act as flexible coils [14]. One form of the hydrogel is poly(N-isopropylacramide) or PNIPAM, which is formed as nanospheres was first introduced in 1986 by Pelton and Chibante with diameters of approximately 1μm [15].

PNIPAM hydrogel has been shown to exhibit strong temperature dependence. When the temperature is below a lower critical solution temperature (LCST) the polymer chains are hydrophilic and swollen but above the critical temperature the polymer chains become hydrophobic, decreasing in length, expelling water from the network, as shown in Fig. 1. The temperature induced phase change of PNIPAM nanospheres measured by dynamic light scattering measurement has been observed to be at ~ 34 ^{o}C for the polymer chains considered in the present paper. This temperature dependence of the phase change is well document and described in terms of diameter and temperature [16]. This volume phase transition and resultant shrinkage of the nanoparticle leads to an enhancement in the refractive index of the polymeric medium [25]. This enhancement in the refractive index can lead to the modification in the optical properties such as light scattering, trapping or waveguiding which can make the hydrogels potentially useful for optoelectronic application.

Since PNIPA hydrogel contains ions, when an electric field, of sufficient strength to overcome hydrohylic forces is applied, the gel will undergo a discontinuous volumetric phase change. The first electric field, sensitive gel was reported by Hamlen in 1965, where a PVA gel fiber sharnk under an applied voltage of 5 V [17]. Gel shrinking and swelling behavior has been

shown to be responsive to both ac and dc excitations [18,19]. The degree of collapse is dependent upon the field intensity, the concentration of polyions in the gel and the size of the gel particles [20]. The collapse is based upon the change in osmotic pressure due to ion concentration differences between the inside and outside of the gel. Although most electrolyte gels are rather slow to respond to an applied field, some have been shown to respond within miliseconds [21]. The electric field depenence of PNIPAM hydrogel spheres has not been explored.
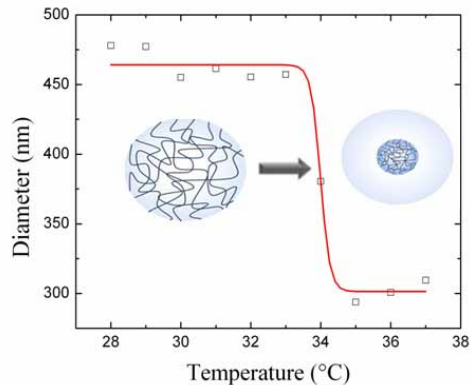

Fig. 1. Change in size of PNIPAM nanoparticles due to temperature induced phase change. Inset shows a PNIPAM sphere below LCST (left) and the sphere above LCST (Right).

PNIPAM gels also do not have fluorescence and cannot be used as tags or markers for biological applications. To make the hydrogels fluorescent, surface passivated CdTe quantum dots (QD) which are ~ 2-3 nm in size can be encapsulated within the PNIPAM micosphers. II-VI QDs are generally insulating and due to large quantum confined potential, the bandgap or photo-emission cannot be manipulated directly without the application of a large electric field (in the order of kV/cm). An external electric field applied to the PNIPAM nanosphere gels encapsulating the QDs can be instead used to manipulate the interdot distance or surface potential of the quantum dot. This field applied to the hydrogel spheres can modify the optical as well as the chemical properties of the medium and thereby the emission properties of the CdTe QDs. The interdot distance which depends on the length of the cross-linkers binding the polymers chains to the QD can be changed by external stimulus [22,23]. As the distances between the QD are varied, the degree of resonant energy transfer between dots can be adjusted. This paper shows an electric field dependent collapse of the PNIPAM nanospheres and employs the electric field dependence as a means to adjust the photoluminescence process of the QDs in a hybrid material.

2. Material Synthesis

The preparation of PNIPAM and the quantum dots, included multi-step process consisting of (1) PNIPAM particle synthesis; (2) CdTe nanocrystal preparation; and (3) encapsulation of nanocrystals in PNIPAM micro-spheres [24]. PNIPAM hydrogel was synthesized by mixing NIPA monomer, N(3-aminopropyl) methylacrylamide chloride monomer, methylene bisacrylamide and N,N-Cysteine-bisacrylamide in deionized water. CdTe nanocrystals were synthesized from sodium hydrogen telluride (NaHTe). $Cd(ClO_4)_2..6H_2O$ with a proper pH adjustment. The diameter of the 1uantum dot were approximately 2 nm emitting in the green. The CdTe nanocrystals were then encapsulated by the PNIPAM spheres using a centrifuge.

N-isopropylacrylamide(NIPA), N(3-aminopropyl) methylacrylamide chloride and N,N-Cysteine-bis-acrylamide was commercial acquired from Polysciences, Inc. sodium

borohydride, thioglycolic acid, tellurium, $Cd(ClO_4)_2.6H_2O$, potassium persulfate and *N,N'*-Methylenebisacrylamide 99% was acquired from Aldrich. Water for sample preparation was distilled and deionized to a resistance of 18.2 MΩ by a MILLIPORE system, and filtered through a 0.22μm filter to remove particulate matter.

For synthesizing PNIPAM particles, 1g NIPA monomer, 0.08g N(3-aminopropyl) methylacrylamide chloride monomer, 1mg methylene bisacrylamide and 0.12g N,N-Cysteine-bis-acrylamide were mixed in 98 ml deionized water. The solution was heated to 70°C with nitrogen bubbling for about 40 minutes, and 0.02g potassium persulfate dissolved in 2 ml deionized water was added to initiate the reaction. The reaction was carried out at 70°C for 4 hrs. CdTe Nanocrystals were synthesized for conjugating with the PNIPAM particles. A molar ratio of 2:1 was used to react with tellurium in water to prepare sodium hydrogen telluride (NaHTe). and thioglycolic acid were dissolved in of water followed by adjustment to pH 9.0. Then, the fresh solution of NaHTe was added and vigorously stirred. Finally, the precursors are converted to CdTe nanocrystals by refluxing the reaction mixture at 100 °C under open-air conditions with condenser attached.
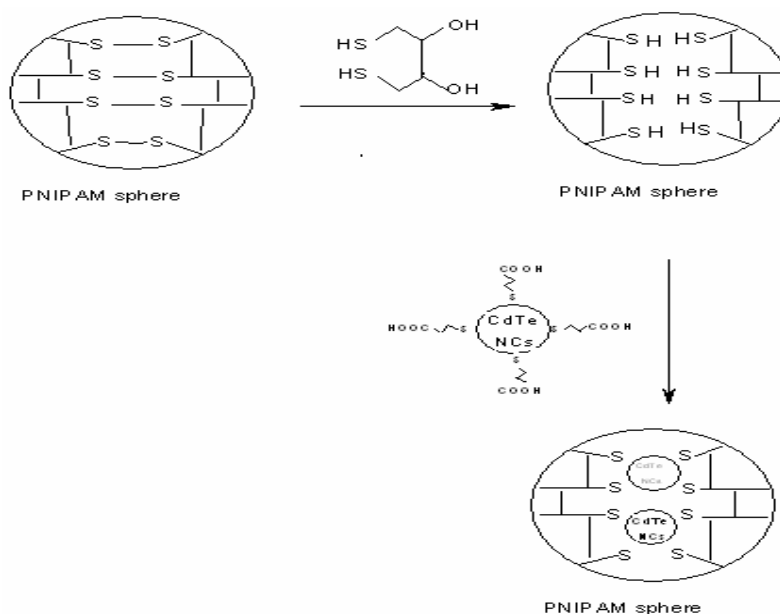

Fig. 2. Schematic for encapsulation of CdTe NCs in PNIPAM microspheres.

Encapsulation of NCs in PNIPAM: The PNIPAM microgels were mixed with 1,4 – dithio-DL- threitol to break S-S bond. The broken S-S bond microgels were dialysis for 7 days before encapsulating the NCs. At room temperature, the dispersion of PNIPAM spheres was mixed with an aqueous solution of CdTe NCs at pH 7 under stirring for 24 h. The mixed solutions were centrifuged at 3000-10000 rpm for 1 hour at 25 C. By decanting the supernatant, followed by repeating the cycle of redispersion with water and centrifugation, the unloaded NCs were removed and PNIPAM spheres loaded with CdTe NCs were obtained, denoted as CdTe-PNIPAM. The schematic is shown in Fig. 2.

3. Dynamic Light Scattering

The hydrodynamic radius of the hydrogel nanospheres was found using dynamic light scattering (DLS). The DLS was performed using a commercially available laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV 500 digital time correlator. A HeNe laser with a power output of 22 mW at 632.8 nm was used. The incident

laser light is vertically polarized with respect to the scattering plane and regulated with a beam attenuator. Light scattered from the medium was gathered and guided, with a ~40μm diameter fiber, to the detector, an active quenched avalanche photodiode.

The relation of interest in dynamic light scattering is the fluctuation of the scattered intensity with time t. The intensity-intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode can be expressed by[1,16]

$$G^{(2)}(t,q) = \langle I(t,q)I(q,0) \rangle = A[1 + \beta |g^{(1)}(t,q)|^2] \qquad (1)$$

where t is the delay time, A is measured baseline, and β is the coherence factor. For a polydispersed sample, $|g^{(1)}(t,q)|$ is the first-order electric field time correlation function $E(t,q)$ and is related to the line-width distribution $G(\Gamma)$ by

$$g^{(1)}(t,q) = \langle E(t,q)E^*(0,q) \rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t}d\Gamma \qquad (2)$$

$G(\Gamma)$ can be calculated from the Laplace inversion of $g^{(1)}(t,q)$. $g^{(1)}(t,q)$ was analyzed by a cumulant analysis to get the average line width $<\Gamma>$ and the relative distribution width $\mu_2/<\Gamma>.^2$ The extrapolation of Γ/q^2 to $q \rightarrow 0$ led to the translational diffusion coefficient (D). This corresponding analysis of this function yields the diffusion coefficient D, which can be translated into the hydrodynamic radius R_h by the Stokes-Einstein relation:

$$R_b = k_B T/6\pi\eta D \qquad (3)$$

where k_B, η, and T are the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively.

The electric field stimulus applied to the PNIPAM hydrogel particles was provided by two parallel electrodes sized to fit inside a test tube and spaced 1 cm apart. The sample height was adjusted such that the incident laser light scattered off the medium disposed between the two electrodes. The electrodes were constructed of copper or platinum with stiff wire leads soldered onto the outward side of the electrode. The concentration of the sample was on the order of 10^{-6} gm/ml, and must be low to accurately determine the hydrodynamic diameters of the spheres.

Data in the experiment was taken every 5 minutes over a sampling interval of 1 minute. The data was collected more rapidly than the thermal experiment because the electric field reaches equilibrium quickly and electrolysis of the solvent (water) can cause anomalous readings due to gas bubbles. Figure 3(a) shows the DLTS measurement for the hydrogel measurement at various dc electric fields. The hydrodynamic radius distribution {f(R_h)} of PNIPAM nanoparticles estimated from light scattering measurement at 36 °C is shown to decrease above a critical value of the dc field. The radial size distribution is also found to increase at higher electric field.

In Fig 3(b), the resulting graph of the hydrogel undergoing an electric field induced, collapse is shown. The hydrogel undergoes a discontinuous phase change at a field strength of approximately 2.1 V cm^{-1}, where the initial diameter of the PNIPAM particles being at 312 nm and collapsed to a size of 180 nm. This collapse is similar to temperature induced collapses shown in Fig. 1. The inset in Fig. 3(b) shows that at higher electric field strength, the scattering efficiency of shorter wavelength light from the PNIPAM particles is more. According to linear light scattering theory, despite the decrease in the overall scattering efficiency of light (at all wavelengths) for smaller particles, the scattering efficiency is inversely proportional to the fourth-power of the wavelength. Thus the shorter wavelength light is scattered more compared to the longer wavelength light resulting in a blue color from the reduced hydrogel nanospheres. The scattered light turns bluer after the application of electric field. In the insets, the picture shows a photonic hydrogel consisting of an array of

hydrogel nanoparticles. These particles self-assemble into a crystal structure and are covalently bonded to stabilize the structure. The color is from light diffraction from the array of these nanoparticles. In the absence of an electric field, the particles are in a swollen state. The interparticle distance is large so the hydrogel diffracts light with longer wavelength. At higher voltage, the particles shrink so that the interparticle distance reduced. As a result, the shorter wavelength (blue) light was diffracted. The change in the scattering properties corroborates the shrinkage of the PNIPAM nanoparticles.

This collapse of the hydrogel nanospheres is a reversible phenomenon provided that the applied electric field is below the break-down voltage. The break-down voltage is the voltage at which the quantum dots encapsulated with the hydrogel nanospheres interact with the electrodes and is about ~ 6 volts in these measurements. The reactivity of the inorganic dots also depends on the ionization potential of the electrodes. Platinum electrodes are observed to be the most stable due to its least reactivity with the CdTe quantum dots in the presence of the electric field. If the applied external field is below the breakdown voltage the hydrogel regain their original size on removal of the external dc field.
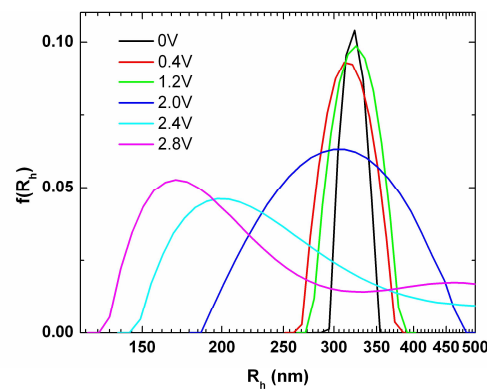

Fig. 3. (a). Effect of size distributions inferred from dynamic light scattering of PNIPAM microgels at various electric field. The temperature is held constant at 24.5 $^{\circ}$C.
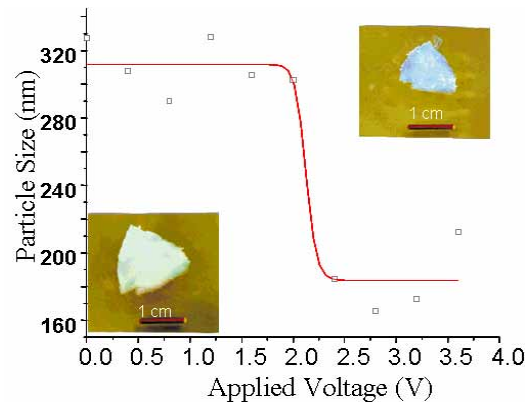

Fig. 1. (b). The DLS measured diameter of dilute colloidal PNIPAM hydrogel particles in water at 36 C. The inset shows the light scattering from concentrated hydrogels sample at 0 V (bottom-left) and at 3 V (top-right).

4. Photoluminescence emission from Quantum Dots in hydrogel nanospheres

The PNIPAM-QD material were placed in quartz glass cuvettes and placed in a sample heater. The temperature of the sample was maintained at a constant temperature with a TE heater attached to a temperature controller. Two parallel electrodes made of aluminum were placed in the cuvette sample holder to provide the applied electric field. Several different materials for the electrodes were tried such as Pt and Cu but Al was found to be the least reactive to the CdTe QDs. The QDs was excited with a 404 nm laser diode source at 45° angle to the sample and the signal was collected using a spectrometer. The concentration of the PNIPAM hydrogel particles embedded with the quantum dots necessary for the photoluminescence measurement is significantly higher than the DLS measurement.
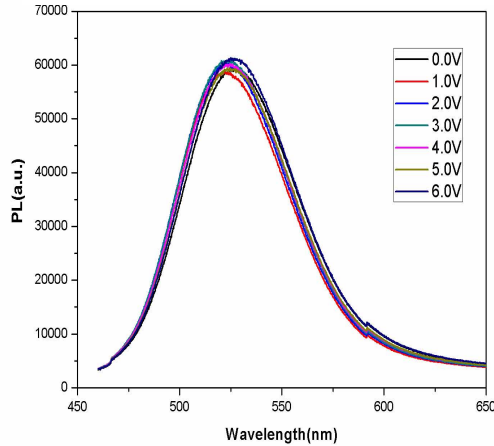

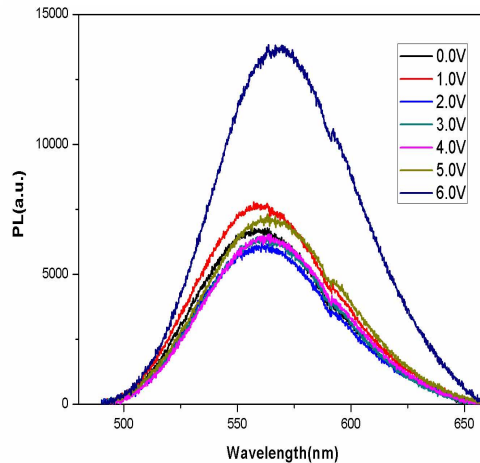Fig. 4. (a). PL of PNIPAM-QDs for varying electric field at T = 25 °C.

Fig. 4(b) PL of the PNIPAM-QDs for varying electric field at T = 36 °C at T = 36 °C.

Figure 4 show the luminescence measured below (25 °C) and above (36 °C) the LCST or the phase transition temperature of PNIPAM for various applied electric field. The data was measured at every 3 minutes in intervals of 0.2 V/cm from 0.0-7.0 volts/cm. At room temperature, when the gel nanospheres are in a liquid-liquid phase [16], the PL intensity is unaffected by the applied DC electric field (Fig. 4(a)). However, above the LCST temperature significant enhancement was found for the PNIPAM-QD material, when an electric field was applied to the sample. There are two predominant features in Fig. 4(b), which occur when the electric field reaches the threshold of 5.6V/cm. The first feature is the enhancement of PL. Second, the peak intensity shifts broadens with a tail toward the longer wavelength side of the spectrum. Figure 5 depicts the same data as a function of electric field and indicates the jump is around 5.6 V/cm.

5. Discussion

The DLS experiment shows a collapse of PNIPAM hydrogel sphere when a certain threshold electric field intensity of 2.1 V/cm is attained, while the threshold electric field for the PNIPAM-QD sample occurred at 5.6 V/cm. There are three factors which contribute to the difference. The required magnitude of the electric field necessary to induce a collapse is strongly dependent upon the concentration of the PNIPAM in the sample or the amount of dielectric material that is disposed between the electrodes. The DLS measurement requires a dilute sample with a low concentration of PNIPAM nanospheres dispersed in water, to achieve accurate measures of particle size (~ 10^{-6} gm/ml). Conversely the PL experiment

requires a high concentration ($> 10^{-3}$ gm/ml). A second factor contributing to the difference is the shape and electrode configuration. In the DLS experiment two round parallel plates were used to induce the electric field while in the PL experiment two parallel wires were used. Lastly, the PL enhancement was seen above LCST ($> 34 \,^{o}$C), where the hydrogel has already undergone a temperature induced collapse. Above 34 ^{o}C the distance amongst adjacent dots is reduced to less than 10 nm due to the shrinkage of the hydrogel thereby increasing the probability of energy transport within the gel network.

The PL enhancement occurs when scattering in the medium increases due to a change in the dimensions of the nano-spheres. The collapse of the hydrogels increases the density of the medium and the resultant size of the nanoparticles ($\sim$ 200 nm which is roughly half the size of the excitation wavelength at 405 nm)- enhances the scattering of the laser excitation incident on the medium. Above the LCST (34 C), an increase in the refractive index and reduced gel dimension leads to a re-excitation process due to increase in the scattering probability of UV photons. The scattered incident laser beam traverses within the samples and has a larger absorption cross-section. Thus as the scattering of the incident GaN laser diode at 405 nm is enhanced above LCST, the PL emission is significantly stronger than the scattering cross-section and excitation is in water or any other colloidal solution.

This result in an increase in the excitation probability of the number of quantum dots likewise because the scattered pump light is incident on a greater number of quantum dots compared to that in the solution phase of the PNIPAM gel at room temperature or in case of a single pass excitation of identical concentration of CdTe solution. The PL enhancement due to the electric field is only observed above LCST and not below LCST as the distances between the network polymer chains at 25 ^{0}C are much greater which require a higher field magnitude to induce a collapse.

However, when a sufficiently high electric field is applied, the encapsulated QDs and the hydrogel disassociate, causing a break down of the hybrid material destroying the enhancement mechanism. The PL enhancement is observed above LCST because the polymer chains are in close proximity to one another and the electrostatic attraction/repulsion between chains requires a smaller electric field to induce a change in geometrical features. The ion exchange is also likely to contribute to PL enhancement process.

An increase in the full width at half-maximum of the PL spectrum above LCST is due to excitation of larger dots in the colloidal hydrogel system. Larger dots in the ensemble usually have lower radiative recombination rate in the absence of the electric field. The emission from larger dots in the ensemble increases due to enhanced scattering of the UV light as the gel collapses. Zeta potential measurements reveals the presence of negative surface charges on the quantum dots. The larger QDs emit only when the applied electric field reduces the surface charge on the dots due to the migration of ions through the hydrogel nanospherical shells. Above LCST, an 8-10% increase in the refractive index at visible wavelengths [25] is also likely to trap PL emission from the relatively smaller QDs. In the presence of the applied field the smaller dots thus acts as an excitation source for the larger dots and the energy is also transferred non-radiatively to dots in close proximity. The energy transfer requires the donor and acceptor pair dots to have overlapping absorption and emission energy levels. As the energy is transferred from smaller or bluer dots to larger or red emitting quantum dots the emitted peak wavelength shifts and broadens toward the red. In conclusion, the PNIPAM hydrogel nanospheres can be modified by a relatively small dc electric field to increase the emission from the CdTe quantum dots.
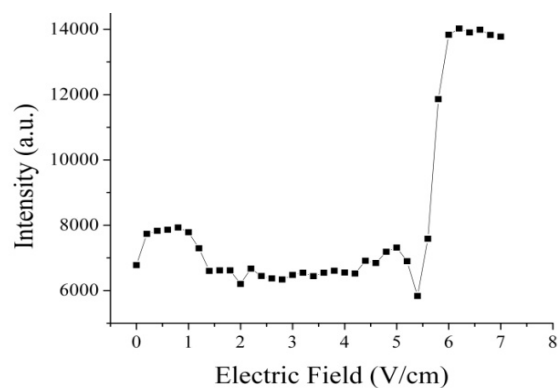
Fig. 5. A plot of the integrated intensity against the electric field applied to the sample.

Acknowledgments