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Effect of titanium dioxide on solid state turmeric dye thin film

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In the present work we have studied the semiconducting properties of turmeric dye thin film. The conductivity of herbal material will open a new dimension in material physics. They are nature friendly, biodegradable and also cost-effective. But typical value of the conductivity is very low. Addition of different nano particles (NPs), carbon nano tubes (CNTs) are introduced to enhance its conductivity. In this work we have studied the effect of titanium dioxide (TiO_2) on turmeric dye thin film. Here TiO_2 nano particle is used as a charge transport layer. A thin film of Poly Vinyl Alcohol (PVA) turmeric dye is sandwiched in between two electrodes one of which is a copper (Cu) plate and the other one is Indium Tin Oxide (ITO) coated glass plate. To prepare other device, TiO_2 is coated on ITO glass plate by using a spin coater and PVA turmeric dye is spin coated on Cu plate. TiO_2 and PVA turmeric dye are then sandwiched in between Cu and ITO coated glass plate. We have measured and observed forward and reverse biased I-V characteristic of turmeric dye thin film. Asymmetric nature in I-V relation confirms the diode like characteristics of the device. We have investigated the variation of current with temperature (I-T) to test the semiconducting properties of the device. It is found that the I-T curve is non-linear. Data is fitted to estimate the dissociation energy of the film. It is shown that dissociation energy of PVA turmeric thin film is 0.55 eV and in addition of TiO_2 its value is 0.40 eV. This is due to incorporation of TiO_2 nano particle. It may be used as electronic circuit element.

Keywords: Turmeric dye, TiO_2 nano particle, I-V characteristic, dissociation energy.

Introduction

Recently optical and electronic properties of different herbal dyes are being studied to develop different electronic devices. The herbal dye based devices are nature friendly, biodegradable and also cost-effective. It is possible to fabricate on the large surface on different substrate from its solution by simple processing techniques, such as sol-gel, spin-coating, solvent casting, sublimation, dip coating etc. There are also varieties of dyes to study. Natural dyes like turmeric, *Hibiscus rosasinesis, Sesbania grandiflora* are used as photosensitizers due to its large absorption coefficient in the visible region in dye sensitized solar cell[1–3]. But there is not much report on the semiconducting property of turmeric dye based herbal device. Among all herbal dyes, turmeric dye is easily available and cheapest natural dye. It is nothing but powder form of rhizome of natural plant named *Cucurma longa* L. Now a day few people have shown its anticancer properties. Khalil Ebrahim Jasim, Seamas Cassidy has reported curcumin (Pigment of turmeric) dye sensitized solar cell performance[4]. But diode property and charge transport mechanism in herbal dye is still unknown. The study of dissociation energy, structure of herbal semiconductor is also important because it is directly related to its electrical properties. Chemical composition of turmeric powder is shown in Fig. 1. The chemical formula and the IUPAC name are $C_{21}H_{20}O_8$ and curcumin (hydroxy pigment of turmeric) is (1*E*,6*E*)-1, 7-bis (4--3-methoxyphenyl)-1, 6-heptadiene-3, 5-dione.

Salient features of curcumin atomic structure are two aromatic ring systems containing *o*-methoxy phenolic groups,

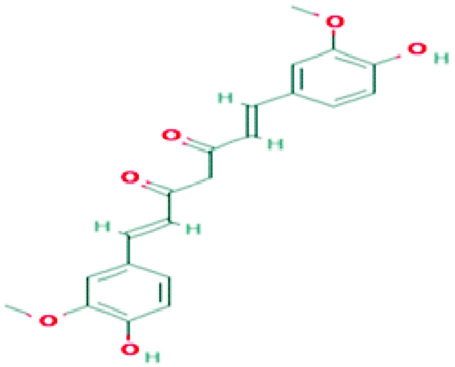


Fig. 1. Diferuloylmethane. The IUPAC name of curcumin is (1*E*,6*E*)-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione.

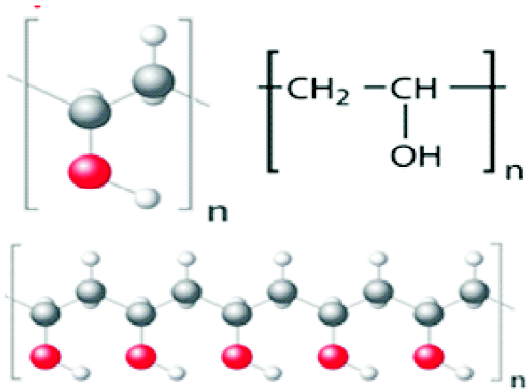


Fig. 2. Structure of PVA.

connected by a seven carbon linker consisting of and α,β-unsaturated β-diketone moiety. Most of the herbal dyes are amorphous and disordered. These bonds create deep electronic levels. Moreover, the surroundings of these dangling bonds are not constant through the device. Molecule is bonded with weak Van der Waals forces and dipole dipole interactions. If the π band of the molecule is filled it is known as the highest occupied molecular orbital (HOMO) and if the π* band is empty it is called the lowest unoccupied molecular orbital (LUMO) like the CB and VB in case of inorganic semiconductors[5–8]. But in case of herbal dye there is no specific band structure so we have measured dissociation energy. Dissociation energy is defined as amount of energy which is required to symmetrically fracture of chemical bond. Charge associated with these bonds contributes the current conduction. We have reported the effect on dye concentration on the electrical characteristic and dissociation energy. In this work we report the effect of TiO_2 on I-V characteristic and dissociation energy of turmeric dye based device.

Experimental

Cell preparation:

We have prepared thin films of turmeric dye with or without using TiO_2. To prepar the cell in 15 ml double distilled water 1 g of Poly Vinyl Alcohol (PVA) is added to form a transparent viscous solution of PVA. Here PVA acts as an inert binder. Atomic structure of PVA is shown in Fig. 2.

Blend of turmeric dye and Poly Vinyl Alcohol (PVA) (wt. ratio 2.0 mg: 5 g) is taken as an active material. A cleaned ITO coated glass plate is taken and a thin layer of this blend is made by spin coating with motor speed of 800 rpm. Acetone solution was used to clean the glass plate and dried under vacuum about 2 h before use. This blend of turmeric dye is sandwiched between ITO coated glass plate and Cu plate. Before and after deposition on Cu electrode the cell was dried under vacuum (10^{-3} mm) for 10 h. This cell is prepared without using the TiO_2 nano particle. For TiO_2 added cell, the TiO_2 is added in the blend of PVA turmeric dye. The similar way TiO_2 NP film was prepared. The cell is dried under vacuum (10^{-3} mm) for 10 h. Film 2 is ready to use. Experimental setup is given in Fig. 3.

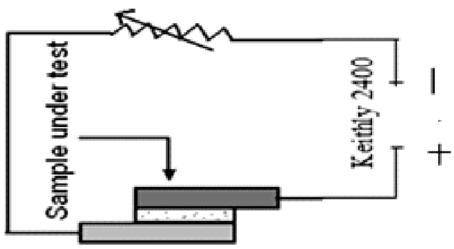


Fig. 3. Circuit diagram of the reverse bias connection of the diode to the Keithley 2400.

Measurement:

The Keithley 2400 source measure unit was used for the I-V measurements. I-T characteristic is performed by using a thermal bath. Experiment is done in the temperature range 306–348 K. The thermal bath is designed in our laboratory which varies temperature from 300 K to 517 K. Temperature measurements were performed by a K-type thermocouple (Cromel Allamel) with an accuracy of ±0.15 K.

Results and discussion

The dependence of electro conductivity of semiconductor on temperature is expressed by Van't Hoff formula

$$\sigma = A\, e^{\frac{-U}{zKT}} \tag{1}$$

where σ is electro conductivity, U is dissociation energy of electron (or hole), K is Boltzmann constant, and T is temperature in absolute scale. According to this formula, between log σ vs 1/KT must hold linear dependence. Determining angular coefficient of straight line we may estimate the value of U. If introduce impurity supplementary levels then should be expected change in constant U.

In this work we have also measured current by varying voltage across the device. ITO coated glass and Cu are connected to positive and negative terminal respectively for forward bias. We have plotted I-V data. I-V curve of both devices are not linear. The current is much for TiO_2 PVA turmeric dye based device shown in Fig. 4.

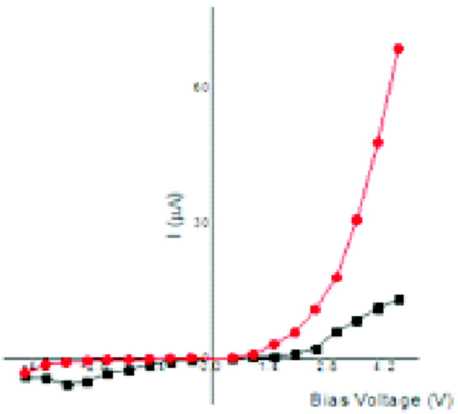


Fig. 4. Forward and reverse bias I-V curve of two turmeric diode and current is higher for TiO_2 added turmeric dye based device than turmeric dye based device without TiO_2.

It may be stated that the I-V of the device may be fitted with thermionic emission (TE) theory. According to the TE theory[9–11] the forward bias I–V characteristics of a diode can be expressed as

$$I = I_0 \left[e^{\frac{qV}{KT}} - 1 \right] \tag{2}$$

where I_0 is the reverse saturation current which is described as,

$$I_0 = AA^* e^{\frac{-qb}{KT}} \tag{3}$$

Here A is contact area, A* is the Richardson constant, T is the absolute temperature and Φ_b is barrier height.

It may be that carriers of turmeric dye are generated through the breaking of covalent bonds which require supply of energy equal to U. So it is possible to evaluate U by studying the temperature variation of the carrier. The variation of carriers can be carried out through a study of temperature variation of reverse saturation current which is the current in the diode under reverse bias condition which is given by[12,13].

$$I = C\, e^{\frac{-U}{zKT}} \tag{4}$$

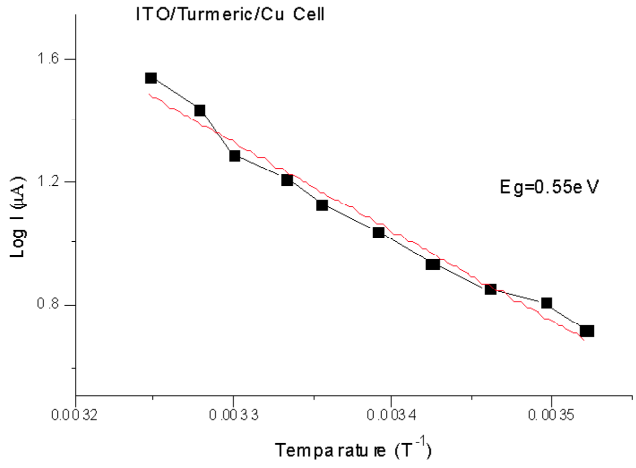
where I is reverse saturation current, C is constant which balances the units of both side, K is Boltzmann constant, U is dissociation energy and T is absolute temperature. It is seen from eq. (4) that the saturation current depends on U/2kT exponentially. Taking logarithms on both sides of eq. (4) we get

$$\ln I = \ln C - \frac{U}{2KT} \tag{5}$$

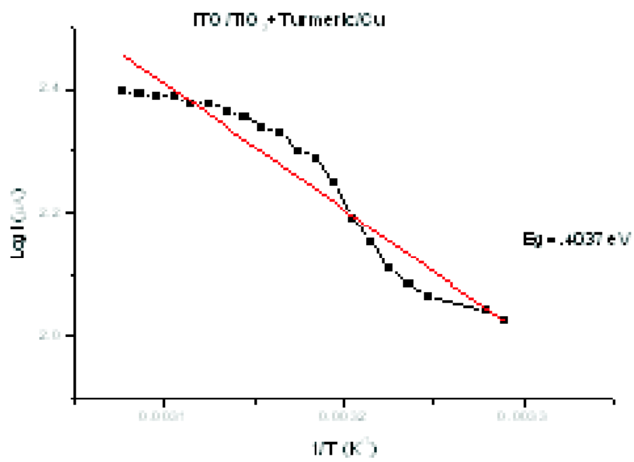
Eq. (5) implies that reverse saturation current I in a semiconductor diode depends only on the junction temperature for particular dissociation energy (U). It varies exponentially with temperature. A plot of ln I vs 1/T gives a straight line with a negative slope of the straight line having a value of U/2k. By determining the slope (m) of the straight line the value of U can be calculated. Thus

$$U = 2mk \tag{6}$$

Keeping fix the reverse bias voltage across the device I-T data is taken using thermal bath. Here we have plotted log I–1/T data which are shown in Fig. 5.



(a)



(b)

Fig. 5. (a) log I–1/T curve of ITO/turmeric/Cu cell and (b) ITO/TiO_2 + turmeric/Cu.

They are following the temperature dependent current equation of the diode eq. (5). Using eq. (6) the exponents can be calculated for different voltage of 2 V, 4 V, 6 V respectively. Slope of curves differ in low temperature region from high temperature. So linear fitting have been done. Though low temperature region is important for calculation of defect potential barrier, we have left this portion due to some limitations in our experimental facility. The concentration of electron is independent of temperature at low temperature. But this portion is beyond our scope in present discussion.

It is shown that dissociation energy are different for two thin films. Values of dissociation energy are 0.55 eV, 0.40 eV for without and with TiO_2 turmeric dye thin film which are shown in Table 1.

Table 1. Values of U (dissociation energy)

Type of films	Values of U (eV)
ITO/PVA turmeric/Cu	0.55
ITO/TiO_2PVA turmeric/Cu	0.40

From our previous work it may be said that structure of ITO/TiO_2 turmeric PVA/Cu is better than Cu/turmeric/Al as electro conductive device. There are various factors which may be responsible for impurity or defects of film formation.

Dissociation energy of TiO_2 added turmeric dye based thin film is low. Actual reason is still unknown. But it can be assumed that TiO_2 layer have more free charge carrier density than PVA turmeric thin film. So addition of TiO_2 with turmeric dye reduces of Gaussian density of states[14,15]. Here we assume turmeric dye is a semiconducting material and its dissociation energy relations with free charge are given by eq. (7).

$$U = qV_{oc} + \left(\frac{\sigma_n^2}{2} + \frac{\sigma_p^2}{2}\right) + KT\ln\left(\frac{N_p N_n}{np}\right) \qquad (7)$$

where U is dissociation energy of the cell, V_{oc} is open circuit voltage, q is the elementary charge, σ_n, σ_p is width of Gaussian density states of acceptor and donor, N_n and N_p is effective conduction band and valance band density states, n is the free electron concentration and p is the hole concentration. It may be said that width of Gaussian density states of acceptor and donor are reduced due to incorporation of TiO_2 with turmeric dye.

Conclusions

In this work we have studied the semiconducting property of PVA turmeric composite thin film. Charge injection mechanism from metal into disordered herbal dye is complicated process. But it is studied that charge conduction is more for TiO_2 PVA turmeric composite thin film than only PVA turmeric composite. Here TiO_2 is used as a charge transport layer. Using the measurement of I-T characteristics of the devices we have shown that current increases with temperature which is also property of semiconductor. The dissociation energy lowers due to incorporation of TiO_2. Variation of dissociation energy with incorporation of dye shows that change in trap level energy states. It may be caused by structural defect or impurity defect. The device may work as the herbal.

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References

1. K. E. Jasim, *et al., Journal of Energy and Power Engineering,* 2017, **11**, 409.
2. S. Shalini, *et al., G. Renewable and Sustainable Energy Reviews*, 2015, **51**, 1306.
3. G. Richhariya, *et al., Renewable and Sustainable Energy Reviews*, 2017, **69**, 705.
4. S. G. Torzo, *et al., Journal of Physics*, 1994, **62**, 66.
5. S. Maity, *et al., Journal of Optoelectronics*, 2013, **15**, 121417,
6. H. li, *et al., Scientific Reports*, 2017, **107**, 40134.
7. A. Halder, *et al., Ionics*, 2008, **14**, 263.
8. A. Halder, *et al., Ionics*, 2008, **14(5)**, 427.
9. S. Maity, *et al., Ionics*, 2008, **14(6)**, 549.
10. A. Halder, *et al., Ionics*, 2009, **151**, 79.
11. S. K. Dey, *et al., Syn. Met*, 2001, **118**, 19.
12. S. K. Dey, *et al., J. Mat. Sci.*, 2003, **381**, 93.
13. M. A. Lampert, *Rep. Prog. Phys.*, 1964, **27**, 329.
14. S. Antohe, *et al., Optoelectronic. Adv. Mater.*, 2003, **5(4)**, 801.
15. S. Antohe, *et al., J. Appl. Phys.*, 2001, **90**, 5928.