Generation of optical absorption band in colloidal coffee at extremely alkaline pH

Arindam Kushagra[1] and Akshaya Pandey[2]

[1] Amity Institute of Nanotechnology, Amity University, Kolkata 700135, INDIA
[2] Amity Institute of Biootechnology, Amity University, Kolkata 700135, INDIA

Abstract—Coffee and caffeine have been used as solar absorbers and also to increase the thermal stability and efficiency of perovskite solar cells. In this work, we report the sensing of extremely alkaline pH by colloidal coffee solution aided by generation of an optical absorption band in the near-UV region. This generation of absorption band could be explained by the orientation induced dipole-dipole interactions arising from differing caffeine-solvent interactions with varying pH. Such a generation leads to the lowering of direct as well as indirect bandgaps from 4 eV→2.8 eV& 3.4 eV→2.5 eV, respectively. We also estimate the changes in optical energy storage efficiency, inferring it to be highest for pH 11 having the highest intensity of the generated absorption band ($\lambda_{\mathrm{abs}} \approx 360\,\mathrm{nm}$). With these observations and further deductions, the work reported in this paper would be of immense interest to the researchers working in the field of development of chemical pH sensors and also in the development of novel UV absorbers.

Index Terms—Caffeine, colloidal coffee, optical absorption, pH sensor, solute-solvent interactions, UV absorber

I. INTRODUCTION

Coffee is one of the most consumed beverage around the world [1].Its primary constituent is caffeine, which stimulates the central nervous system [2] and is the world's most widely consumed psychoactive substance that is legally permissible [3]. Recently, coffee and its ingredient caffeine have garnered attention of researchers working in the field of photovoltaics. Colloidal solution of coffee has been shown to be useful as a material for direct solar absorption [4] whereas caffeine has been used to improve the performance and thermal stability of perovskite solar cells [5]. Recently, an alternative way to sense extremely alkaline pH using the shape of hydrophobe-water interfaces was reported [6].

In this paper, we report the sensing of extremely alkaline pH ($11 \leq \mathrm{pH} \leq 13$) aided by generation of an optical absorption peak ($\lambda_{\mathrm{abs}} \approx 360\,\mathrm{nm}$) in the near-UV region when the pH of the colloidal coffee solution was within the stipulated range. However when the pH of the colloidal solution was less than or equal to 10, the aforementioned absorption peak was not found. Henceforth we infer that colloidal coffee has an indirect optical bandgap, which can be further modified to a lower value by the generation of a new absorption band by changing the pH of colloidal coffee. The same phenomenon can be depicted schematically with the aid of an E-k diagram, as shown in Fig. 1.

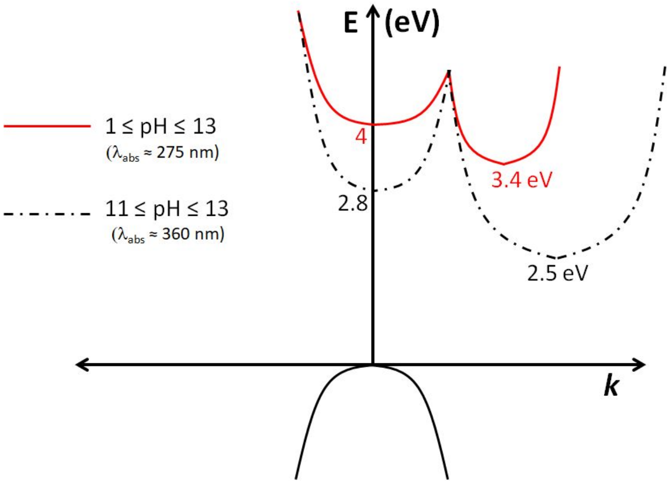

Fig. 1E-*k* diagram of colloidal coffee solution showing the lowering of optical bandgap due to generation of an optical absorption peak ($\lambda_{abs} \approx 360\ nm$) denoted by dashed line.

The coordinates in Fig. 1 lying on the y-axis (i.e. ***k***=0) denote the values of direct bandgap and indirect bandgap is shown for values ***k***≠0 [7]. Details of the same are discussed further in the paper. In continuation to the earlier discussion, since coffee and its ingredient caffeine have now gained attention of researchers working in the field of solar photovoltaics, this work would be of immense interest to the same group especially to those working on the bandgap engineering and further development of novelUV absorbers.

II. MATERIALS AND METHODS

Commercially available instant coffee *Nescafe Classic* was used in this work. Estimated caffeine content in such products is ≈ 26 mg/g of instant coffee [8]. A stock colloidal solution of 1 mg/ml was prepared by mixing instant coffee with Milli-Q water. 0.1 ml of the colloidal coffee was taken from the prepared stock solution and mixed with 2.6 ml of Milli-Q water and 0.3 ml of aqueous solutions

Corresponding author: Arindam Kushagra (email: arindam.kushagra@gmail.com).

of varying pH (pH: 0-14) prepared by serial dilution. For the acidic phase, 35% HCl (Emplura Merck, 1.93401.0521) was taken as stock solution. Normality of the stock HCl solution was calculated to be ≈ 11.33. Since HCl is a monoprotic acid, the molarity would be same as that of normality i.e. ≈ 11.33 M. Suitable dilutions of the same were done to obtain solutions in the range of pH 0 (1 M) till pH 6 (10^{-6} M). Milli-Q water was taken as a neutral standard. For the alkaline phase, 1 M NaOH solution was prepared as stock using NaOH pellets (Himedia, MB095). Serial dilutions of NaOH stock were done to obtain solutions in the range pH 8 (10^{-6} M) till pH 13 (10^{-1} M). Optical absorbance and transmittance measurements were done using U-2910 Hitachi spectrophotometer.

III. RESULTS AND DISCUSSION

Optical absorbance spectra for different pH values of colloidal coffee solution, showing the unique absorption peaks at 360 nm are evident at pH values 11-13 from the following figure, Fig. 2:

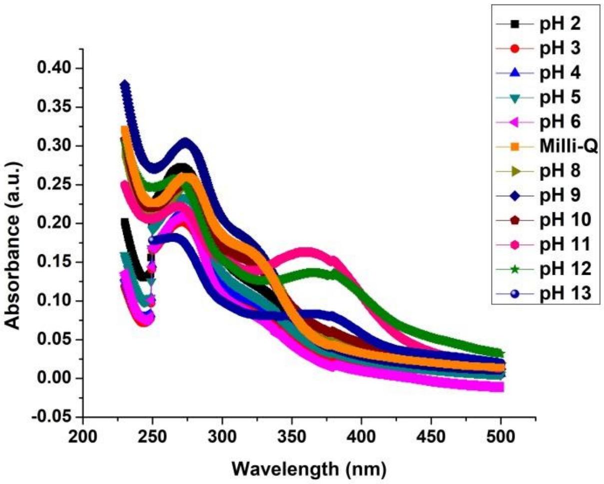

Fig. 2 Optical absorption peaks of colloidal coffee solution at various pH values, ranging from 2-13, showing distinct peaks @ 360 nm for pH values 11-13 only.

Absorption coefficient (α) was calculated using the relationship:$\alpha(T) = -\frac{1}{l} ln\left(\frac{T}{(1-R^2)}\right)$ [9]. Here, l is the path length traversed by light during absorption/transmission measurements (taken to be 1 cm), T is the measured transmittance and R is reflectance. Since the measurements in this work were carried out in liquid phase, reflectance would be negligible i.e. R = 0. Direct and indirect bandgaps were calculated by Tauc plot analysis i.e. by plotting $(\alpha h\nu)^2$& $(\alpha h\nu)^{0.5}$ vs. $h\nu$ (energy of the measured electromagnetic spectrum, in eV), respectively [10]. The calculated direct and indirect bandgaps are shown in following figures 3 & 4:

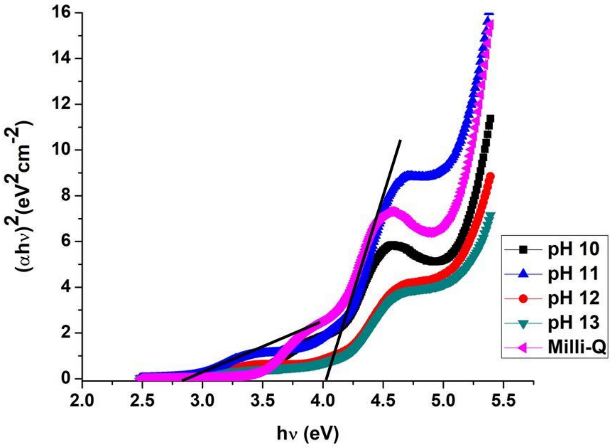

Fig. 3 Calculation of direct bandgaps of colloidal coffee solutions at pH 10, 11, 12, 13 and at neutral pH (represented by Milli-Q water) using Tauc-plot method, showing bandgap ≈ 4 eV for $\lambda_{abs} \approx 275$ nm& bandgap ≈ 2.8 eV for$\lambda_{abs} \approx 360$ nm, respectively.

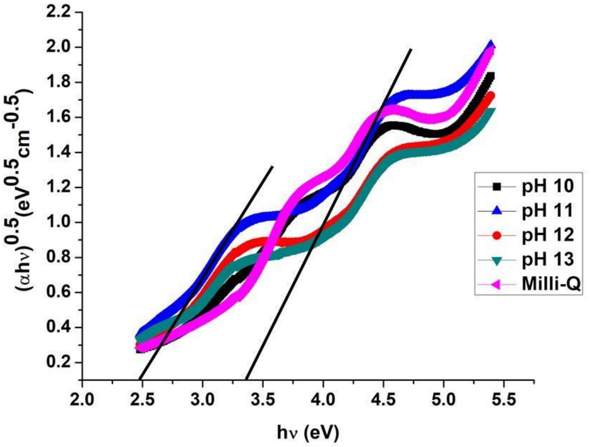

Fig. 4. Calculation of indirect bandgaps of colloidal coffee solutions at pH 10, 11, 12, 13 and at neutral pH (represented by Milli-Q water) using Tauc-plot method, showing bandgap ≈ 3.4 eV for $\lambda_{abs} \approx 275$ nm & bandgap ≈ 2.5 eV for $\lambda_{abs} \approx 360$ nm , respectively.

Generation of the said optical absorption band can be attributed to the solute-solvent interactions in colloidal coffee. These solute-solvent interactions can be described by the following analytical relationships [11], as discussed in the following equations, 1-3.

$$hc\Delta\nu_{ind} = -\frac{2n^2+1}{n^2+2}\left\{\frac{2\mu_g(\mu_g-\mu_e cos\theta)}{a^3}\left[\frac{\epsilon-1}{\epsilon+2}-\frac{n^2-1}{n^2+2}\right] + \frac{(\mu_g-\mu_e)^2}{a^3}\frac{n^2-1}{n^2+2}\right\} \quad (1)$$

where $\Delta\nu_{ind} = \nu_o - \nu_s$ is the change in wavenumber due to induced dipole moments accounting for solute-solvent interactions, ν_o is the wavenumber for isolated molecule in vapor phase (in this case, caffeine) &ν_s is the wavenumber of caffeine molecule in solution.

n&ϵ are solvent refractive index & dielectric constant, respectively. a is the molecular radius of caffeine. μ_g&μ_e are induced dipole moments in the ground & excited states and θ is the angle between μ_g & μ_e vectors. There can be different types of dipole-dipole interactions that might impact the generation of the absorption band, which can be classified into orientation interactions & dispersion force mediated interactions, respectively. As the name suggests, the orientation interactions represent the interactions of dipoles based on their orientations, as given by the relationship shown in equation 2.

$$hc\Delta\nu_{or} = -\frac{hc^2 f}{8\pi m_e \nu_o a^3}\frac{n^2-1}{n^2+2} \tag{2}$$

where$f(\epsilon) = \frac{\epsilon-1}{2\epsilon+1}$&$f(n) = \frac{n^2-1}{2n^2+1}$ and m_e is the mass of an electron. The orientation interaction mediated wavenumber shift is affected by the increasing polarity of the solvent. The dispersion force mediated interactions happen because of the electronic structure deformations of solute and solvent leading to the generation of small temporary dipole moments. Analytically, these interactions can be represented by the relationship shown in equation 3.

$$hc\Delta\nu_{disp} = (\alpha_g - \alpha_e)\frac{3}{2a^3}\frac{II'}{I+I'}\frac{n^2-1}{n^2+2} \tag{3}$$

whereα_g&α_e are polarizabilities of caffeine molecule in ground and excited states after interaction with the solvent medium. *I*&*I'* represent the ionizing potentials in the ground and excited states, respectively. The dispersion force mediated interactions have a mere additive effect that is primarily impacted by the refractive index, *n*, of the solvent. On the basis of discussions made in context of equations 2 & 3, we deduce that the main reason of generation of the optical absorption band at $\lambda_{\text{abs}} \approx 360$ nm is because of the orientation interactions between caffeine and aqueous solvents at pH 11-13. Since these solvents are extremely polar in nature, the electronic structure deformation of the caffeine-base complex formed from the solute-solvent interaction would cause the temporary dipole generation that would eventually lead to the generation of the said optical absorption band.

We also estimated the absorptive optical energy storage efficiency by first normalizing the transmittance values, $T = e^{-\alpha_\lambda l}$ (α_λ: wavelength-dependent absorption coefficient), from 0 to 1. After normalizing, the transmittance values have been subsequently put into the following relationship that yields the energy storage efficiency [4] shown in equation 2:

$$\eta = 1 - \frac{\int_{\lambda_{min}}^{\lambda_{max}} I_\lambda e^{-\alpha_\lambda l} d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_\lambda \, d\lambda} \tag{4}$$

whereI_λ is the wavelength-dependent intensity of incident radiation and we also assume that there is no scattering of light from the colloidal sample. Since the measurements were done using a conventional spectrophotometer in laboratory settings, I_λ can be assumed to be constant, equalling to the intensity of the lamp of spectrophotometer. The integrals given in equation 4 were solved numerically using composite trapezoidal rule [12]. The same is shown in Fig. 5, with an evident increase in optical energy storage efficiency for the generated absorption band at 360 nm in the pH range 11-13.

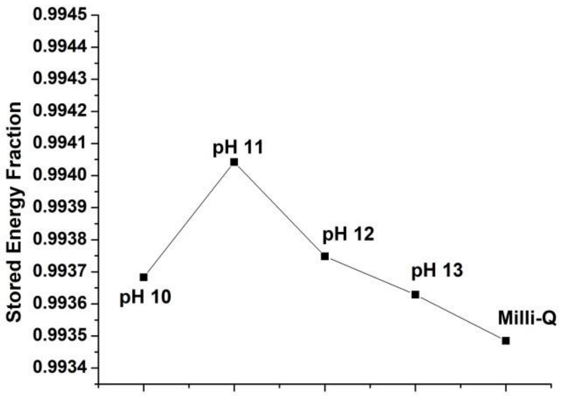

Fig. 5. Optical energy stored for varying pH values is shown. The increase in stored energy can be attributed to the generation of absorption band at ≈ 360 nm, with intensities varying with pH in the order 11 > 12 > 13.

IV. CONCLUSIONS

In this work, we have reported the sensing of extremely alkaline pH with the aid of colloidal coffee solution and also observed the generation of an optical absorption band with an indirect bandgap of ~ 2.5 eV. As discussed earlier in the paper, coffee and its primary ingredient caffeine have found applications as solar absorbers as well as in increasing the stability & efficiency of perovskite solar cells. The results reported in this paper pave way towards the development of novel chemical sensors for extreme alkaline pH based on the spectrophotometric detection. This work could also be potentially used to develop ultraviolet light absorbers with increased capacity in optically absorbed energy storage in the near-UV range of the electromagnetic spectrum, actuated by modulating pH values of the colloidal coffee solution.

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