Photochemical events during photosensitization of colloidal ZnO nanoparticles by riboflavin

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MS received 28 March 2012

Abstract. The photosensitization of colloidal ZnO nanoparticles with riboflavin (RF) was investigated using absorption, fluorescence spectroscopic measurements and time resolved fluorescence measurements. Riboflavin adsorbed strongly on the surface of ZnO nanoparticles. Apparent association constant was obtained from the fluorescence quenching measurements. The free energy change, ΔG_{et} , for electron transfer process has been calculated by applying Rehm Weller equation.

Keywords. ZnO; riboflavin; photosensitization.

1. Introduction

Nanostructured semiconductors have attracted extensive attention due to their unusual electronic and photophysical properties, differing drastically from the properties of bulk (micrometer) crystals of the same chemical composition, thus they are considered as the front runners in the technologically important materials (O'Regan and Gratzel 1991; Alivisatos 1996; Cushing *et al* 2004). Photosensitization process involves the excitation of dye molecules with visible light and subsequent electron injection into a semiconductor and these sensitized materials are widely applicable in photocatalysis, optoelectronic and photovoltaic devices (Kamat and Patrick 1992; Colvin *et al* 1994; Klein *et al* 1997). As a low-cost alternative to conventional silicon-based photovoltaic devices, dye-sensitized solar cells (DSSCs) are becoming a very important topic in the ongoing research activity in recent years (Law *et al* 2005; Nazeeruddin *et al* 2005; Yu and Chen 2009; Zhang *et al* 2009; Yan *et al* 2010). Photosensitized nanomaterials of wide bandgap *n*-type semiconductors (such as TiO₂, SnO₂ and ZnO) are promising systems for efficient solar energy conversion.

Zinc oxide is a versatile technologically important material for developing optical and electronic components with a wide bandgap of 3.4 eV (Nyffenegger *et al* 1998; Li *et al* 2004) and it is believed to be a good alternative photoelectrode material to TiO₂, owing to its similar bandgap, much higher electron mobility (Law *et al* 2005). ZnO is an eco-friendly oxide semiconductor and it is highly stable under ambient conditions towards sunlight, water and air. These merits make ZnO a promising multifunctional material in the future. More effort has been devoted to research for improving the solar-to-electric conversion efficiency of ZnO-based

DSSCs (Keis *et al* 2000; Westermarck *et al* 2002; Kim *et al* 2003; Cid *et al* 2007; Taratula *et al* 2009).

Riboflavin (RF) vitamin B₂ (scheme 1) is one of the most important biological molecules and is very stable during thermal processing, storage and food preparation (Tommaso *et al* 2002). Riboflavin is widely distributed in organisms and plants, usually acting as a photosensitizer in many metabolism processes and/or photosynthetic processes. The isoalloxazine ring of riboflavin is the main chromophore group and provides a large π electronic cloud and emits greenish yellow fluorescence.

Natural pigments have been extensively investigated as sensitizers for the dye sensitized solar cells (Kathiravan *et al* 2009). Based on this, an effort has been made to probe the photophysical property of photoinduced reactions between riboflavin and ZnO by using absorption and fluorescence spectroscopy. Attempts were made to investigate RF binding on semiconductor and use of natural vitamins in dye sensitized solar cells.

2. Materials and methods

2.1 Materials

Zinc acetate dihydrate (98%) was purchased from Aldrich. Lithium hydroxide monohydrate (98%, AG) powder was purchased from Fluka, riboflavin was purchased from Aldrich. Doubly distilled water was used to prepare the solutions throughout all experiments.

2.2 Methods

2.2a Synthesis of ZnO nanoparticles: All chemicals were purchased from commercial sources in analytical grade and used without further purification. Ultrafine nanoparticles

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Scheme 1. Structure of riboflavin.

were synthesized via a hydrothermal method from literature. A ZnO colloidal suspension was prepared following the method described by Anderson (Spanhel and Anderson 1991; Kamat and Patrick 1992). Briefly, an amount of 50 ml ethanol containing 1.10 g of zinc acetate dihydrate was refluxed while stirring at about 80°C for 180 min. After this procedure, a clear precursor solution was obtained followed by gradual cooling to room temperature under a nitrogen atmosphere (to prevent ambient moisture). The precursor was hydrolyzed by adding 0.29 g lithium hydroxide monohydrate powder in an ultrasonic bath at 0°C for 20 min.

2.2b Characterization: The identity of crystalline structure, size and shape of the nanoparticles were observed by X-ray diffraction (XRD). XRD was obtained from a PANalytical X' Pert Pro MPD X-ray diffractometer using Cu K α radiation, $\lambda = 0.154$ nm, with Ni filter. The tube current was 30 mA with a tube voltage of 40 kV. The angular range was $2\theta = 20$ –80°.

2.2c Steady-state measurements: The fluorescence quenching measurements were carried out with JASCO FP-6500 spectrofluorimeter. A 3 ml solution, containing appropriate concentration of riboflavin (1×10^{-6} M), was titrated by successive additions of 30 μ l stock solution of colloidal ZnO nanoparticles (1×10^{-3} M).

Titration were manually done by using micro pipette for the addition of ZnO. The excitation and emission wavelength of riboflavin is 445 and 514 nm, respectively. The slit widths, 5 nm and scan rate, 500 nm/min, for both excitation and emission were maintained constant for all the measurements. Samples were carefully degassed using pure nitrogen gas for 15 min. Quartz cells (4 $\times$ 1 $\times$ 1 cm) with high vacuum Teflon stopcocks were used for degassing. Absorption spectral measurements were recorded using Cary 300 UV–visible spectrophotometer. Fluorescence lifetime measurements were carried out in a picosecond time correlated

single photon counting (TCSPC) spectrometer. The excitation source was the tunable Ti-sapphire laser (TSUNAMI, Spectra Physics, USA). The data analysis was carried out by the software provided by IBH (DAS-6).

3. Results and discussion

3.1 Particle size of colloidal ZnO nanoparticles

Figure 1(A) shows absorption spectrum of as prepared ZnO nanoparticles and emission spectrum at 500 nm (figure 1B) is obtained by employing light of 315 nm wavelength as the excitation source. The particle size of the prepared colloidal ZnO nanoparticles has been determined from the Brus equation

$$\Delta E_g = \frac{\pi^2 \hbar^2}{2\mu R^2} - \frac{1.8e^2}{\epsilon R} + \text{polarization terms}, \quad (1)$$

where $\hbar$ is the Planck's constant, R the radius of the particle, ϵ the relative permittivity of semiconductor and ΔE_g the bandgap shift. The calculated bandgap shift for colloidal ZnO is 0.66 eV (bandgap energy of the colloidal ZnO was measured, $E_g = 3.96$ eV corresponding to $\lambda = 313$ nm, figure 1). μ is the reduced mass of exciton, i.e. reduced effective mass of the electron and hole ($1/\mu = 1/m_e + 1/m_h$) in the semiconductor, e the electron charge and ϵ the dielectric constant of the semiconductor. The value of $\mu = 0.156 m_e$ (m_e is the electron rest mass) is calculated from $m_e = 0.24 m_e$, $m_h = 0.45 m_e$ (Joselevich and Willner 1994). Since the optical dielectric constant of bulk semiconductor is very large ($\epsilon = 170$), coulombic and polarization terms in (1) are neglected. The calculated size of the prepared colloidal ZnO is 2.49 nm.

3.2 X-ray diffraction characteristics

The average crystalline size (t) is calculated by using the Debye–Scherrer equation,

$$t = 0.89\lambda / \beta \cos \theta, \quad (2)$$

Figure 1. Absorption (313 nm) (A) and emission (B) spectra of as prepared ZnO nanoparticles (1×10^{-4} M) (exciting wavelength at 313 nm).

where λ is the X-ray wavelength (0.1540 nm), θ and β are the diffraction angle and full width at half maximum (FWHM), respectively. From XRD diffraction pattern, it was found that the planes (100), (101), (102), (110) fit well with wurtzite structure of ZnO (figure 2). The broadness of XRD peaks reveals the nanocrystalline nature of the ZnO powder, the average nanopowder crystallite size is estimated to be about 9.3 nm.

3.3 Absorption characteristics

UV-Visible spectroscopy is a simple technique to understand the complex formation between riboflavin and ZnO. Riboflavin shows absorbance in 360 nm and 445 nm in water. The absorption spectrum of riboflavin in the presence of different concentrations of colloidal ZnO is shown in figure 3. The absorbance of the riboflavin increases with an increase in the colloidal ZnO concentration. In the presence of colloidal ZnO, the absorption increased without change in wavelengths. Generally the equilibrium for the formation of complex between riboflavin and colloidal ZnO can be

Figure 2. X-ray diffraction (XRD) spectrum of prepared ZnO nanoparticles.

given by (3), where K_{app} represents the apparent association constant:

$$K_{app} = \frac{[\text{Riboflavin} \cdots \text{ZnO}]}{[\text{Riboflavin}] \cdot [\text{ZnO}]} \quad (3)$$

The intensity of the absorption peak at 445 nm changes as a result of formation of the surface complex which can be utilized to obtain K_{app} according to Benesi and Hildebrand (1949) equation,

$$A_{obs} = (1 - \alpha) C_0 \varepsilon_{\text{riboflavin}} l + C_0 \varepsilon_c l, \quad (4)$$

where A_{obs} is the observed absorbance of the solution containing different concentrations of the colloidal ZnO at 445 nm, α the degree of association between riboflavin and ZnO; $\varepsilon_{\text{riboflavin}}$ and ε_c are the molar extinction coefficients at the defined wavelength ($\lambda_{\text{max}} = 445$ nm) for riboflavin and formed complex, respectively in water. Equation (4) can be expressed by (5), where A_0 and A_c are the absorbances of riboflavin and complex at 445 nm, respectively with the concentration of C_0 :

$$A_{obs} = (1 - \alpha) A_0 + \alpha A_c. \quad (5)$$

At relatively high ZnO concentrations, α can be equated to $(K_{app} [\text{ZnO}]) / (1 + K_{app} [\text{ZnO}])$. In this case, (5) can be expressed as (6)

$$1/A_{obs} - A_0 = 1/A_c - A_0 + 1/K_{app} (A_c - A_0) [\text{ZnO}]. \quad (6)$$

Therefore, if the enhancement of absorbance at the wavelength of 445 nm was due to absorption of surface complex, one would expect a linear relationship between $1/(A_{obs} - A_0)$ and the reciprocal concentration of colloidal ZnO with a slope equal to $1/K_{app} (A_c - A_0)$ and an intercept equal to $1/(A_c - A_0)$. The inset in figure 3 shows plot for riboflavin, there is a good linear dependence of $1/(A_{obs} - A_0)$ on

Figure 3. Absorption spectrum of RF (1×10^{-5} M) in presence of colloidal ZnO nanoparticles in concentration range of $0-5 \times 10^{-4}$ M in ethanol. Inset is straight line dependence of $1/A_{obs} - A_0$ on reciprocal concentration of ZnO.

the reciprocal concentration of colloidal ZnO. The value of apparent association constant (K_{app}) determined from this plot is $4.8 \times 10^3 \text{ M}^{-1}$ ($R^2 = 0.9977$).

3.4 Fluorescence quenching studies

The fluorescence spectrum of RF is broad with a maximum around 514 nm. In this case, the interaction of riboflavin with nanoparticles is studied by fluorescence measurement at room temperature. A solution of RF ($1 \times 10^{-6} \text{ M}$) was titrated with various concentrations of ZnO ($0\text{--}5 \times 10^{-4} \text{ M}$). Fluorescence spectra were recorded in the range of 450–650 nm upon excitation at 445 nm. Figure 4 shows effect of increasing concentration of ZnO on the fluorescence emission spectrum of RF. Addition of ZnO to the solution of RF resulted in the quenching of its fluorescence emission. Generally speaking, the fluorescence quenching types often

include static and dynamic quenching. The dynamic quenching, resulting from collisional encounters between the fluorophore and quencher, static quenching is due to the formation of a ground-state complex between the fluorophore and quencher. In both cases, molecular contact is required between the fluorophore and quencher for the fluorescence quenching to occur. In order to obtain a clear insight into the quenching mechanism, the fluorescence quenching data are analysed by the Stern–Volmer equation (Lakowicz 1999).

$$I_0/I = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q], \quad (7)$$

where I_0 and I are the fluorescence intensities of the fluorophore in the absence and presence of quencher, K_{SV} the Stern–Volmer constant, k_q the bimolecular quenching rate constant, τ_0 the excited state lifetime of RF in the absence of quencher and $[Q]$ the quencher concentration. Figure 5 displays the Stern–Volmer plot between I_0/I vs $[Q]$ which

Figure 4. Steady state fluorescence quenching of RF ($1 \times 10^{-6} \text{ M}$; $\lambda_{\text{exi}} = 445 \text{ nm}$; $\lambda_{\text{emi}} = 515 \text{ nm}$) in presence of colloidal ZnO nanoparticles in concentration range $0\text{--}5 \times 10^{-5} \text{ M}$ in ethanol. Inset is linear straight line dependence of $1/(F_0 - F)$ on reciprocal concentration of colloidal ZnO.

Figure 5. Stern–Volmer plot for steady state fluorescence quenching of RF ($1 \times 10^{-6} \text{ M}$) by ZnO ($0\text{--}5 \times 10^{-5} \text{ M}$).

gave a linear plot. For dynamic quenching, the maximum scatter collision quenching constant of various quencher is $2.0 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (Ware 1962). But the rate constant of RF quenching procedure initiated by ZnO is $1.2 \times 10^{11} \text{ mol}^{-1} \text{ s}^{-1}$, which also means that the quenching process is static. Hence the fluorescence quenching results from the formation of complex between semiconductor metal oxide and riboflavin. Therefore, mechanism of fluorescence quenching is a static quenching procedure.

3.5 Apparent association constant

The apparent association constant (K_{app}) can also be obtained from the fluorescence quenching data according to following equation

$$\frac{1}{F_0 - F} = \frac{1}{F_0 - F'} + \frac{1}{K_{\text{app}} (F_0 - F') [\text{ZnO}]}, \quad (8)$$

F_0 is the initial fluorescence intensity of riboflavin, F' the fluorescence intensity of ZnO adsorbed riboflavin and F the observed fluorescence intensity at its maximum. The plot of $1/F_0 - F$ vs $1/[\text{ZnO}]$ for riboflavin is shown in the inset to figure 4. A good linear relationship is obtained between $1/F_0 - F$ and the reciprocal concentration of colloidal ZnO. From the slope, K_{app} has been assessed and the value is $2.19 \times 10^3 \text{ M}^{-1}$.

3.6 Fluorescence lifetime measurements

Fluorescence lifetime measurement is useful for understanding the interaction between donor and acceptor systems. In general, time resolved measurement is the most definitive method for differentiating static and dynamic quenching. Figure 6 shows fluorescence decay curve of RF in the absence and presence of ZnO. While increasing the concentration of ZnO there is no change in the fluorescence lifetime

Figure 6. Fluorescence decay curves for RF ($1 \times 10^{-6} \text{ M}$) in absence and presence of ZnO ($0-5 \times 10^{-5} \text{ M}$).

Figure 7. Overlap spectrum of (A) absorption spectrum of ZnO and (B) emission spectrum of riboflavin.

Scheme 2. Mechanism for quenching reaction.

of riboflavin. This observation shows that quenching follows static mechanism. Static quenching does not decrease the lifetime because only the fluorescent molecules are observed, and the uncomplexed fluorophores have the unquenched lifetime (Lakowicz 2006). Static quenching arises due to the formation of complex between fluorophore and quencher.

3.7 Electron transfer between riboflavin and ZnO nanoparticles

The decrease in fluorescence emission may be attributed to the electron transfer or energy transfer between the riboflavin and colloidal ZnO. The bandgap energy of ZnO semiconductor particle is greater than the singlet excited state energy of the riboflavin and no overlapping of fluorescence emission of riboflavin with colloidal ZnO (figure 7), thus ruling out energy transfer from the singlet excited state of riboflavin to ZnO colloids. Therefore, it was concluded that the fluorescence quenching shown in figure 4 was caused by electron transfer process (scheme 2). The thermodynamic feasibility of the excited singlet state electron transfer reaction was calculated by employing the well known Rehm–Weller expression (Rehm and Weller 1970):

$$\Delta G_{\text{et}} = E_{1/2}^{(\text{ox})} - E_{1/2}^{(\text{red})} - E_s + C, \quad (9)$$

where $E_{1/2}^{(\text{ox})}$ is the oxidation potential of riboflavin (-0.5 V), $E_{1/2}^{(\text{red})}$ the reduction potential of ZnO (i.e. conduction band potential of ZnO (-0.5 V) (Amy *et al* 1995)), E_s the excited singlet state energy of riboflavin (2.7 eV) [it can be obtained from the position of the absorption band i.e. $\lambda = 445$ nm] and C the coulombic term. Since one of the species is neutral and the solvent used is polar in nature, the coulombic term in the above expression is neglected (Lee *et al* 2004). The ΔG_{et} value thus calculated for the electron transfer (ET) processes in the RF–ZnO studied in water is negative (-3.7 eV). Hence, ET process was thermodynamically favourable (Kamat *et al* 1986).

The riboflavin adsorbs on the surface of the semiconductor nanomaterials through $-\text{OH}$ groups, resulting in the transfer of electron from the riboflavin to the conduction band of ZnO (Chen *et al* 1998); this typical reaction would lead

to enhance the pathway of their application towards natural pigment sensitized semiconductors in photovoltaic cells.

4. Conclusions

The interaction between riboflavin and ZnO was studied by steady state measurements. The results presented clearly indicated that the nanoparticles quench the emission intensity of RF through complex formation. The quenching belonged to static fluorescence quenching type and the apparent association constant was calculated from the relevant fluorescence data. This report is expected to provide important insights into the interaction and mechanism of colloidal semiconductor nanoparticles with natural pigments like riboflavin, which may be a useful guideline for further dye sensitized solar cells investigations.

Acknowledgement

(RR) and (EV) thank DST (Ref: SR/S5/NM-16/2007 dt. 03/07/2008) (Government of India) for the project.

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