

- Materials

The materials used were: Nickel (II) chloride and copper (II) acetate [Merck]. Hydrogen peroxide and Nicotinic acid (NA) is purchased from Adwiic and polyvinyl alcohol, PVA; MW 125,000 (Fluka, Germany).

Indigo carmine dye [3,30-dioxo-1,3,10,30-tetrahydro-[2,20]-bi-indolylidene-5,50-disulfonic acid disodium salt] was delivered from the general chemical company limited, Wembley Middlesex, England. M.F. $C_{16}H_8N_2Na_2O_8S_2$, M. Wt. 466.35 g/L. Maximum wavelength is 608 nm; molar absorptivity is $6309 \text{ mol}^{-1} \text{ cm}^{-1}$ and the dye content is 85% [Merck].

- Instruments:

Physical studies

The crystal structure as well as phase purity were examined using x-ray diffraction (XRD) using a Philips diffractometer (type PW 3710). The patterns were run with Ni-filtered copper radiation ($\lambda = 1.5404 \text{ \AA}$ at 30 kV and 10 mA) with a scanning speed of $2\theta = 2.5^\circ \text{ min}^{-1}$.

The Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrometer (RXI FT-IR) system, single beam with a resolution of 2 cm^{-1} . The samples were ground with KBr (1:100) as a tablet and mounted to the sample holder in the cavity of the spectrometer. The measurements were recorded at room temperature in the region. $4000\text{-}400 \text{ cm}^{-1}$.

Thermogravimetric and differential thermal analyses (TGA/DTGA) were carried out using Netzsch-Sta 409 C/CD instrument (Selb, Germany). Sensitivity of TG and DTGA measurements was 0.01 mg and $25 \mu\text{V}$, respectively. In each run 10 mg of uncalcined sample was heated from 298 to 1273 K with heating different rate (283, 293 and 303 K/min) in a current of N_2 flowing at a rate of 30 ml/min .

Diffuse Reflectance Ultraviolet–visible spectroscopy (UV–vis DRS) of the models was carried out at room temperature using UV–vis JASCO spectrophotometer, V-570. The UV-vis spectra were treated with Microsoft Excel software, consisting of calculation of the Kubelka-Monk function, $F(R_\infty)$, which was extracted from the UV-vis DRS absorbance. The edge energy (E_g) for allowed transitions was determined by finding the intercept of the straight line in the low-energy rise of the plot of $[F(R_\infty)h\nu]^2$, for the direct allowed transition, vs $h\nu$, where $h\nu$ is the incident photon energy.

Solution-state NMR spectroscopy has been applied for the determination/analysis of molecular interactions at atomic resolution. The NMR 400 MHz and 600 MHz spectrometers (Bruker), equipped with a cryo-probe, are part of Portuguese NMR Network.

Photocatalytic evaluation

All the experiments were carried out using a horizontal cylinder annular batch reactor. IC was selected, as a model for the photocatalytic degradation experiments due to it is a nonvolatile and common contaminant in the industrial wastewaters. A black light blue florescent bulb (F18W-BLB) was positioned at the axis of the reactor to supply UV illumination. The light intensity after passing through a reaction suspension was 256 nm. The experiments were performed by suspending calculated amount of the catalyst into IC solution (100 ppm, 100 ml). The suspension was vigorously stirred while the photo-reactor open to air during the process. The reaction was carried out isothermally at 25 °C and samples of the reaction mixture were taken at time intervals for a total reaction time 1 h. The heterogeneous portions were immediately centrifuged to separate the catalyst, and the residual dye concentration after illumination was detected by UV–vis spectrophotometer (JASCO V-570unit, serial no. 29635) over the 190–800 nm range. Calibration plots based on Beer–Lamberts law were established relating the absorbance to the concentration. The decolorization was determined at the maximum 608 nm.

Decolorization in air (adsorption)

Decolorization experiments of IC on M/PVA-NA in the absence of ultraviolet irradiation were carried out in a batch mode. A 100 ml volume of the IC dye (100 ppm), previously adjusted to affix pH value with diluted NaOH and HCl solutions, was added to a 250 ml beaker containing different amounts of suspended M/PVA-NA. The suspensions were immediately shaken in an air for 1 h using a magnetic stirrer prior to following up the uptake amounts of the dye by M/PVA-NA that maintained for 1 h adsorption time.

Molecular Modeling Study and Computational Model:

The Quantum chemical computations were performed, using the PM3 semi-empirical Hamiltonian molecular orbital calculation MOPAC16 package, then employing density function theory “DFT” in Gaussian 09W program package with the Becke3-Lee-Yang-parr (B3LYP) level

using 6-311G* basis set as implemented in MOE 2015 package. The optimization Geometry for molecular structures were carried out, for improve knowledge of chemical structures. The global chemical reactivity have computed for molecules as; “S; softness “stability measuring of the molecule, which direct proportional with chemical reactivity”, η ; hardness (reciprocal of softness), μ ; chemical potential, χ ; electronegativity (gaining strength for the electrons), μ^- ; potency of electron donating, μ^+ ; electro accepting power, ω^- ; electron donating capacity, ω^+ ; electron accepting capacity, ω^\pm ; group philicity (measuring of the relative potential powers between electron accepting and electron donating), ω_i ; Electrophilicity index in ground state (determine decreasing energy obtained from maximal movement electrons current between donor and acceptor). The nucleophilicity excess “ ω^\pm ” calculated by $\omega^\pm = \omega^- - \omega^+$. These parameters are represented in ionization potential and electron affinity terms. **I**; ionization potential is a total energy variance, when electron lose (k-1, Mullikan atomic charges) from parent molecule (k) electrons, and **A**; electron affinity is determined the accepting of the electron (k+1) at the same conditions. The $v(r)$ is external potential of an N-electron system. The reactivity index measures the stabilization in energy when the system acquired an additional electronic charge from the environment via charge transfer. So, the $\Delta N_{\max} = \chi/2\eta$ (maximum number of electrons transferred during a chemical reaction) Fukui function $\Delta f(r)$ describes the reactivity of the atomic contribution at the specific atom in a molecule and represents as $\Delta f(r) = (\delta\sigma/\delta\gamma)_N = (\rho(r)/\delta N)_\gamma$.

For nucleophilic radical equation (S.1)

$$\begin{aligned} f_k^+(\vec{r}) &= (\rho(\vec{r})/\delta N)_\gamma^\pm \\ &= [p_{N+1}(\vec{r}) - p_N(\vec{r})] \\ &= [qk(N+1) - qk(N)] \end{aligned}$$

For electrophilic radical equation (S.2)

$$\begin{aligned} f_k^-(\vec{r}) &= (\rho(r)/\delta N)_\gamma^- \\ &= [p_N(\vec{r}) - p_{N-1}(\vec{r})] \\ &= [qk(N) - qk(N-1)] \end{aligned}$$

Band Gap

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} \quad (S.3)$$

Where: R “absolute reflectance for sampled layer”; k “molar-absorption-coefficient” and s “scattering-coefficient”. The thickness (t) for trials is crucial, and represented as:

$$\alpha = \frac{F(R)}{t} = \frac{\text{absorbance}}{t} \quad (\text{S. 4})$$

We used the cell cavity having a thickness equals 0.5 mm for all samples. The optical band gap can be determined according to Eq. 5

$$F(R)hv = A(hv - E_g)^n \quad (\text{S. 5})$$

where $n = 1/2$ and 2 for direct and indirect transitions, respectively, thus giving direct and indirect band gaps. The plots of $(F(R)hv)^2$ versus hv and extrapolation of linear regions of these plots to $(F(R)hv)^2 = 0$ gives the direct band gap values.

Nonlinear optical effects:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad \text{equation} \quad (1)$$

$$\alpha = 1/3 (\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2) \quad \text{equation} \quad (2)$$

$$\alpha_0 = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy}) + (\alpha_{yy} + \alpha_{zz}) + (\alpha_{zz} + \alpha_{xx}) + 6 \alpha_{xx}^2] \quad \text{equation} \quad (3)$$

$$\beta_0 = (\beta_{xx}^2 + \beta_{yy}^2 + \beta_{zz}^2)^{1/2} \quad \text{equation} \quad (4)$$

$$\beta_x = (\beta_{xxx} + \beta_{xyy}^2 + \beta_{xzz}^2) \quad \text{equation} \quad (5)$$

$$\beta_y = (\beta_{yyy} + \beta_{xxy}^2 + \beta_{yzz}^2) \quad \text{equation} \quad (6)$$

$$\beta_z = (\beta_{zzz} + \beta_{xxz}^2 + \beta_{yzz}^2) \quad \text{equation} \quad (7)$$