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Synthesis and characterization of branched polypyrrole/titanium dioxide photocatalysts

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ABSTRACT

Polymer composites synthesized by fractal growth of polypyrrole in the presence of titanium dioxide nanoparticles were investigated as potential photocatalysts. These branched structures are characterized by high surface area and improved action as photocatalyst in the degradation of rhodamine B. The resulting absorption of photons in the visible region and low rate of electron–hole recombination with adequate generation of radicals for subsequent *N*-deethylation of rhodamine B represent important aspects which corroborate potential application of new composite as efficient photocatalyst.

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1. Introduction

Conducting polymers (CPs) have attracted interest due to their superior electrical and optical properties which contribute to development of promising devices such as microbial fuel cells [1–3], supercapacitors [4–6], strain/stress sensors [7], biosensors and immunosensors [8–9], photocatalysts [10–12] and electroactive actuators [13].

The production of conducting polymer-metal oxide nanocomposites incorporates high conductivity of CPs with intrinsic properties of inorganic semiconductors (high surface area, photostability and low density) [10–12,14].

Particularly, the modification induced by polypyrrole on surface of titanium dioxide improves the action of resulting composite as photocatalyst due to the tunable absorption band of polypyrrole in association with semiconductor response [11].

Yang et al. [15] reported that adequate coupling of PPy and TiO₂ enhances the photocatalytic activity of resulting material under visible light excitation. The disposition of lowest unoccupied molecular orbital (LUMO) above the conduction band of TiO₂ provides the absorption of photons in the visible region followed by rapid charge separation associated with slow recombination [15].

Branched polymeric structures are characterized by high density of internal cavities and available sites for functionalization [16,17], a favorable condition for applications such as drug delivery, tissue targeting (due to the permeability across biological barriers) and enhanced luminescence in lanthanides [18,19].

As reported by Das et al. [17], the production of highly branched conducting polymer (fractal growth of polymeric matrix) depends on combination of surfactant, electric field, monomers concentration and time of reaction. Using these considerations, we have introduced the novelty related with production of new photocatalysts based on nanocomposites of branched polypyrrole and TiO₂.

2. Experimental

Sodium dodecyl sulphate – SDS (Aldrich), cetyl trimethylammonium bromide – CTAB (Aldrich), rhodamine B (Vetec), sodium dodecylbenzenesulfonate – DBSA (Aldrich) and titanium dioxide (anatase particle size in nanopowder of 21 nm, purity of 99.5% and bandgap of 3.2 eV (Aldrich)) were used as received while pyrrole (Aldrich) was distilled before the use.

The morphology of composites was analyzed by scanning electron microscopy (Hitachi TM1000) with an accelerating voltage of 20 kV while overlaid images with EDS of polypyrrole/TiO₂ complex were performed by SEM Vega 3XMH-Tescan.

The structure of composite was characterized by Fourier transform infrared spectrum (KBr method) using an IR Prestige-21 Fourier transform infrared spectrometer Shimadzu.

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XRD diffraction pattern was analyzed by DRX Equinox 1000 – Inel and absorbance by spectrophotometer Hach DR5000. Photoluminescence data were provided by PC1 spectrofluorimeter (ISS). All of experiments were conducted at 25 °C.

Brunauer–Emmett–Teller (BET) surface area measurements were performed by Micromeritics ASAP 2420 surface area analyzer.

Electrical impedance measurements (Nyquist plot) were performed using a Potentiostat/Galvanostat Metrohm Autolab AUT302N in association with a sample holder solartron 12962A.

Results were fitted by equivalent circuit (modified Randles circuit) by association of a bulk resistance in series with a parallel combination of bulk capacitor and Warburg element in series with a charge transfer resistance.

2.1. Synthesis of branched fibers of polypyrrole

64-samples were prepared using all of possible combination of low (↓) and high (↑) values of six parameters viz. DBSA concentration – parameter *a* (↓) 0 mM and (↑) 50 mM; voltage level – parameter *b* – (↓) 4.5 V and (↑) 9.0 V; Time of reaction – parameter *c* (↓) 30 min and (↑) 60 min; pyrrole concentration – parameter *d* (↓) 50 mM and (↑) 250 mM; SDS concentration – parameter *e* (↓) 25 mM and (↑) 125 mM and CTAB concentration – parameter *f* (↓) 12.5 μM and (↑) 300 μM. The complete description of samples (corresponding variation of low and high level of parameters (*a*, *b*, *c*, *d*, *e* and *f*) is shown in the Table 1. The identification of samples is composed by combination of six letters (*a*, *b*, *c*, *d*, *e* and *f*). The presence of specific letter in a sample indicates that corresponding parameter assumes maximum value (e.g., sample *ade* was prepared using maximum concentration of DBSA (*a*), pyrrole (*d*) and SDS (*e*) and minimum in parameters *b*, *c* and *f*).

Surfactants (at relative concentration described in the Table 1) were dispersed in 50 mL of milli-Q water and kept under intense stirring (300 rpm) until complete dispersion of reagents. After this step, pyrrole was introduced in the resulting solution and kept under stirring during additional 2 min. An aliquot of 17 mL of solution was introduced in a reactor in which an aluminum circular cathode (25 mm-diameter) is disposed at 25 mm from anode (metallic wire) at air-liquid interface. Electric field is established between electrodes and electrochemical polymerization takes place during fixed interval of time (according low and high values of parameter *c*). The resulting material is washed with milli-Q water for surfactant elimination and dried at 60 °C during 1 h.

Table 1

Description of samples prepared with possible combination of six parameters (*a* – DBSA concentration, *b* – Voltage level, *c* – Time of reaction, *d* – Pyrrole concentration, *e* – SDS concentration and *f* – CTAB concentration).

Sample name							
Corresponding level (<i>a, b, c, d, e, and f</i>)							
<i>l</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>bc</i>	<i>bd</i>
↓↓↓↓↓	↓↓↓↓↓	↓↓↓↓↓	↓↓↓↓↓	↓↓↓↓↓	↓↓↓↓↓	↓↓↓↓↓	↓↓↓↓↓
<i>be</i>	<i>bf</i>	<i>cd</i>	<i>ce</i>	<i>cf</i>	<i>de</i>	<i>df</i>	<i>ef</i>
↓↑↑↑↑	↓↑↑↑↑	↓↑↑↑↑	↓↑↑↑↑	↓↑↑↑↑	↓↑↑↑↑	↓↑↑↑↑	↓↑↑↑↑
<i>bcd</i>	<i>bce</i>	<i>bcf</i>	<i>bde</i>	<i>bdf</i>	<i>bef</i>	<i>cde</i>	<i>cdf</i>
↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑
<i>cef</i>	<i>def</i>	<i>bcde</i>	<i>bcdf</i>	<i>bcef</i>	<i>bdef</i>	<i>cdef</i>	<i>bcdef</i>
↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑
<i>a</i>	<i>ab</i>	<i>ac</i>	<i>ad</i>	<i>ae</i>	<i>af</i>	<i>abc</i>	<i>abd</i>
↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑
<i>abe</i>	<i>abf</i>	<i>acd</i>	<i>ace</i>	<i>acf</i>	<i>ade</i>	<i>adf</i>	<i>aef</i>
↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑
<i>abcd</i>	<i>abce</i>	<i>abcf</i>	<i>abde</i>	<i>abdf</i>	<i>abef</i>	<i>acde</i>	<i>acdf</i>
↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑
<i>acef</i>	<i>adef</i>	<i>abcde</i>	<i>abcdf</i>	<i>abcef</i>	<i>abdef</i>	<i>acdef</i>	<i>abcdef</i>
↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑	↑↑↑↑↑

2.2. Synthesis of polypyrrole/titanium dioxide branched fibers

Surfactants were dispersed in 17 mL of milli-Q water and maintained under stirring during 30 min. 340 μg of titanium dioxide was introduced in the resulting solution and stirred during additional 30 min for complete dispersion of nanoparticles. 310 μL of pyrrole was added in the solution followed by an additional period of 2 min of stirring. After this step, the solution was transferred to reactor and electrochemical reaction established during 1 h with external DC voltage of 9 V. The resulting material was washed with water for surfactant elimination and dried at 60 °C during 1 h.

2.3. Preparation of pellets

50 mg of resulting polymeric matrix was compressed in a press machine (20 kN) for production of pellets with thickness of 300 μm and 13 mm of diameter.

2.4. Photodegradation measurements

14 mg of resulting PPy/TiO₂ nanocomposite was immersed in 5 mL of aqueous solution of rhodamine B (1 μM) under dark condition. The exposure of resulting solution to white light was established with the use of halogen light (60 W) during standard interval of time of 4 h. Aliquots of solution (3.5 mL) were removed from reactor in fixed interval of 30 min and analyzed in terms of UV–vis absorbance and fluorescence in order to determine the kinetics of photodegradation. Comparison with direct action of neat TiO₂ nanoparticles was provided by similar experiment, in which corresponding concentration of TiO₂ (0.02 g/L) was dispersed in aqueous solution of dye (1 μM of RhB).

2.5. Determination of optical band gap of resulting composites

The band gap of polypyrrole (polypyrrole/TiO₂) was determined from absorption spectra and Tauc relation (Eq. (1)) [20,21]

$$\alpha h\nu = B(h\nu - E_{\text{gap}})^m \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, and $m = 1/2$ for direct band gap material. Ghobadi [22] described a direct method for fitting and determination of band gap using Tauc relation. After substitutions in Eq. (1) (described in Ref. [22]), we can write that

$$\left(\frac{\text{Abs.}}{\lambda}\right)^{1/m} = B\left(\frac{1}{\lambda} - \frac{1}{\lambda_{\text{gap}}}\right) \quad (2)$$

where λ is the wavelength and Abs. the corresponding value of measured absorbance. λ_{gap} can be easily obtained from curve $(\text{Abs.}/\lambda)^{1/m}$ vs. $1/\lambda$ at condition $(\text{Abs.}/\lambda)^{1/m} = 0$. The band gap value is obtained from relation $E_{\text{gap}} = 1239.83/\lambda_{\text{gap}}$.

In order to avoid saturation in the measured absorbance, we have prepared thin films of branched polypyrrole and polypyrrole/TiO₂ under the same experimental conditions than bulk film. Aluminum electrode was substituted by transparent conductive glass slide (ITO) and deposition (under previously described conditions) was established on the surface of electrode during 10 s.

3. Results and discussion

3.1. Optimization of branched polymeric matrix

The structure of synthesized samples and average of grain size are shown in the SEM images of Fig. 1. Sample *bd* (low concentration of three different surfactants, high voltage and high

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