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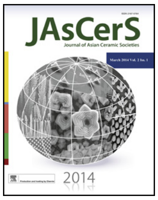

Full Length Article

Hybrid copper doped titania/polythiophene nanorods as efficient visible light-driven photocatalyst for degradation of organic pollutants

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ABSTRACT

The hybrid $Cu–TiO_2$/polythiophene nanorods (HNRs) were prepared by modified sol–gel technique at low temperature through oxidative polymerization of thiophene. The prepared HNRs and $Cu–TiO_2$ nanorods without polymer (CTNRs) were characterized by using XRD, TEM, IR, UV–vis DRS and XPS. IR, XPS and XRD confirm polythiophene (PTh) covered $Cu–TiO_2$ nanorod in hybrid with rutile phase without affecting the crystal form of TiO_2. TEM analysis reveals the shape and morphology of CTNRs and HNRs. TEM images of HNRs show that the metal oxide has nanorods like shape with lengths and diameters of about 35–60 and 15–25 nm respectively. From UV–visible DRS spectra, HNRs exhibit a broad and strong absorption in visible range, indicating that the incorporation of PTh onto the surface of $Cu–TiO_2$ nanorod in hybrid can extend the photo response range of TiO_2. The photocatalytic activity of HNRs shows higher degradation when compared with CTNRs under visible light irradiation by degradation of Rhodamine B (RhB) and Orange G (OG). There is no degradation of PTh was observed under visible light irradiation till five runs which is examined from photocatalytic activity, which indicates stability and reusability of photocatalyst.

1. Introduction

In recent years, vast research has been carried out to explore the novel properties of hybrid nanostructures with conducting polymer/metal oxide semiconductors. This is most advantageous combinations in solar cells, photovoltaic devices [1–7], electrochromic devices, nonlinear optical photo to electrochemical systems [8]. TiO_2 is transition metal oxide with best photocatalytic activity for the degradation of organic contaminants in water and air. In presence of light and oxygen, many of the organic compounds on contact with TiO_2 can be degraded in to CO_2, H_2O and appropriate inorganic ions [9–11]. In the recent past, under visible light, copper doped with TiO_2 shown to have high stability with enhanced photocatalytic degradation [12]. Moreover, copper dopant substitutes Ti in the possible sites that forms new energy states in the host TiO_2 which can alter the particle properties, electronic structure and light absorption properties. These affect their functionality, and hence can be used in different applications like effective CO_2 photo reduction [13], improved gas sensing and enhanced H_2 production [14]. On the other hand, π-conjugated polymers such as polyaniline, polythiophene, polypyrrole and their derivatives can be act as stable photosensitizers combined with wide band gap inorganic semiconductors (e.g., TiO_2, ZnO and CuO) is an emerging area of research for optical, electronic, photoelectric conversion applications and photocatalysis [15–17]. Moreover, they are also efficient electron donors and good hole transporters upon visible light excitation [18]. Among various organic polymers, Polythiophene is sulphur-containing conjugated polymer which exhibits high charge carrier mobility, dissolubility and process ability, longtime stability, strong absorption in visible region and thermally stable under photo irradiation [19]. Beyond that, there is an interesting fact that in the presence of TiO_2, the polythiophene and its derivatives cannot undergo degradation under UV radiation, which is evident from the reported literature [20–22]. Recently, TiO_2/polymer nano hybrid materials and their applications in degradation of various organic pollutants have been studied [23,24]. The reported hybrid materials are having the boundaries

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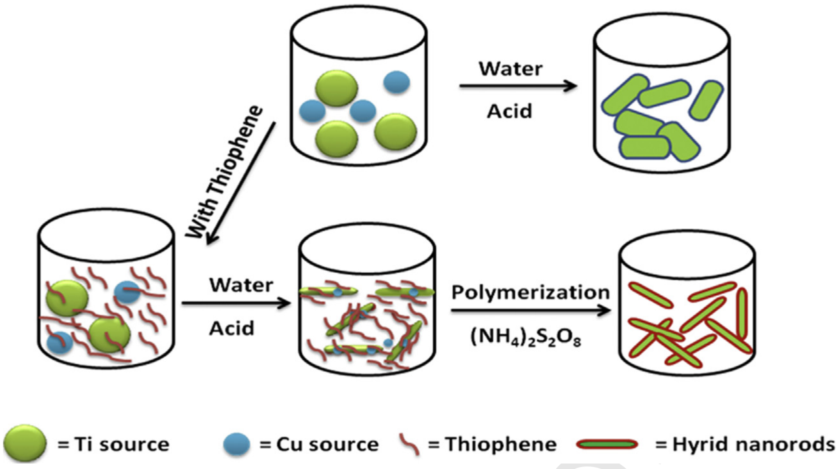

Scheme 1. Schematic illustration for synthesizing hybrid nanorods (HNRs).

in terms of degradation of dyes under visible light, stability and reusability. To overcome these limitations, visible light induced and stable hybrid material is necessary in the area of water purification. In the present work we focused on the preparation of visible light induced, stable and reusable hybrid nanorods at low temperature for degradation of organic pollutants.

The organic pollutants under consideration are Rhodamine B and Orange G dyes, which are widely used as a colorant in textiles and these, are highly water soluble. Because of their disadvantages such as non-biodegradability, toxicity, potential mutagenicity, carcinogenicity and waste water production, and industries serves to be a severe hazard to the surrounding ecosystems and health of living organisms [25]. So the photodegradation of RhB and OG under visible light is potential with regard to the purification of dye effluents.

In the present study, by considering above threats, we have chosen the combination of polythiophene and copper, that acts as photosensitizer and dopant of TiO_2 respectively in hybrid, and it was fabricated by an in-situ oxidative polymerization technique at low temperature and thereby investigation of the photocatalytic activity of HNRs under visible light irradiation is being carried out. The role of polythiophene layer and copper in HNRs and the effects of various factors on the sensitized photoactivity were studied by degradation of organic pollutants Rhodamine B basic red dye of the xanthenes class and azo dye Orange G. The detailed preparation shown in Scheme 1 and characterization methods used for catalyst and evaluation of photocatalysis have been provided in Section 2.

2. Experimental

2.1. Materials

Titanium tetra-*n*-butoxide and copper chloride were used as titanium and copper source for preparing HNRs catalyst respectively. The thiophene monomer (99%), MilliQ-water, ammonium persulphate ($(NH_4)_2S_2O_8$), Hydrochloric acid were used for solution preparation. The colour dyes Rhodamine B and Orange G were used for photodegradation. All the chemicals used for experimentation were of reagent analytical grade and obtained from E-Merck (Germany).

2.2. Catalyst preparation

HNRs was prepared by modified sol–gel process at low temperature. In a typical synthesis, 0.85 g of $CuCl_2$ in a round bottomed flask was previously stirred with 12.5 mL of 2-propanol for 20 min followed by addition of 12.5 mL of titanium tetra-*n*-butoxide. A suitable weight percentage of distilled monomer thiophene 1.0% (Ti/Cu/Thiophene:100/0.75/1.0) was added to the above described solution formed from $CuCl_2$ and titanium tetra-*n*-butoxide. This reaction mixture was subsequently stirred for 20 min to obtain a homogeneous mixture and added 60 mL Milli-Q water to the reaction mixture. The white precipitation occurred immediately which was then peptized with the available concentrated hydrochloric acid at 60 °C for 8 h in a reflux system (water:acid = 2:1). It is important to maintain water and acid ratio for the formation of nanorods. After this, to polymerize the thiophene, 30 mL of aqueous $(NH_4)_2S_2O_8$ solution containing 1.0 mol L^{-1} of HCl was added to the reaction mixture and it was stirred at room temperature for 3 h. The resulting brown coloured solid was separated by centrifugation; it was washed five times with distilled water. Finally, a hybrid material was formed and dried at 40 °C for a week and stored in desiccator for further characterization and the material was stored in dark. Repeated the same experimental conditions and procedure for CTNRs without adding thiophene and $(NH_4)_2S_2O_8$.

2.3. Instrumental techniques

XRD patterns of HNRs, CTNRs catalysts were taken by Panlytical X-ray diffractometer using Cu Kα radiation with 45 kV and 40 mA, at a 0.2 scan rate. Fourier transforms infrared (FT-IR) spectra of nanorods in KBr pellets were recorded on Shimadzu spectrometer from the range 400–4000 cm^{-1}. By using UV–vis diffuse reflectance spectroscopy (UV-DRS) (Scinco Co., Ltd., S-3100) with BaSO4 as a reference, with in the wavelength range of 200–800 nm at room temperature, the band gap energies and absorption edges of the HNRs and CTNRs were calculated. The band gap energies of the synthesized samples were calculated according to equation:

$$\text{Band gap}\,(E) = hc/\lambda \quad (1)$$

where E is the band gap energy (eV), h is Planck's constant, c is the velocity of light (m/s), and λ is the wavelength (nm). The Brunauer–Emmett–Teller (BET) surface area was calculated from the N_2 adsorption–desorption isotherm at 77.3 K using Quanta chrome Nova 2200 E system. XPS measurements were done on a PHI quantum ESCA microprobe system, bu using Al Kα line of a 250W X-ray tube as a radiation source with the energy of 1253.6 eV, Q5 16 mA × 12.5 kV. TEM measurements were done in a JEOL 120 KV instrument with supported by a copper grid. Photoluminescence (PL) spectra was studied at room temperature using fluorescence spectrophotometer (F-7000, Hitachi, Japan) with parameters of excitation wavelength 315 nm, with the scanning speed of

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