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Indium and cerium co-doped mesoporous TiO_2 nanocomposites with enhanced visible light photocatalytic activity

M. Myilsamy[a], V. Murugesan[b], M. Mahalakshmi[a,*]

[a] Department of Chemistry, SSN College of Engineering, Kalavakkam 603110, Tamil Nadu, India
[b] Department of Chemistry, Anna University, Chennai 600025, Tamil Nadu, India

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ABSTRACT

Indium and cerium co-doped mesoporous TiO_2 nanocomposites with different weight percentage were synthesized by sol–gel route using Pluronic P123 as the structure directing template. The synthesized materials were characterized by X-ray powder diffraction, high resolution transmission electron microscopy, scanning electron microscope with energy dispersive X-ray spectroscopy, N_2 adsorption–desorption studies, X-ray photoelectron spectroscopy, diffuse reflectance UV–vis absorption spectroscopy, Fourier transform infrared spectroscopy, photoluminescence spectroscopy and electron paramagnetic resonance spectroscopy. Indium and cerium co-doped on TiO_2 nanocomposites shifted the light absorption band-edge position to visible region and showed high surface area with large pore diameter. The optimum loading of In_2O_3 and CeO_2 on TiO_2 was 0.2 wt%. Ce^{4+} is good electron scavengers, which easily trapped the exited electrons and transferred the electrons to the adsorbed O_2 molecules to produce $O_2^{-\bullet}$. Hence the electron–hole recombination was efficiently suppressed, which was revealed by the photoluminescence spectroscopy. The large number of structural defects by the substitution of In^{3+} for Ti^{4+} enhanced the surface Brønsted acidity and the adsorption of cationic methylene blue. Consequently, In_2O_3/CeO_2-TiO_2 exhibited promising photocatalytic activity in the degradation of methylene blue under visible light irradiation due to the formation of large number of $O_2^{-\bullet}$ and $^{\bullet}OH$ radicals.

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1. Introduction

Since Fujishima and Honda reported the evolution of oxygen and hydrogen from a TiO_2 electrode under the irradiation of light in 1972 [1], photocatalysis was regarded as one of the most effective and economical ways to remove the organic pollutants from wastewater. In particular, titanium dioxide is a versatile photocatalyst because of special properties like photostability, reusability, inexpensive and relatively low toxic nature [2–4]. However, the anatase phase of TiO_2 semiconductor has a relatively large band gap of 3.2 eV. It can be activated only by UV light with wavelength less than 400 nm, which accounts only about 5% of the solar energy. If TiO_2 absorbs both UV and visible light from the sunlight then the maximum solar energy can be utilized. In the past decade, many attempts have been made to extend the photo response of TiO_2 in the visible region [5–7]. Among these attempts, transition metal ions or nonmetal elements such as V, Co, Fe, C, N, S, and I doped TiO_2 have been the common approach for improving the photocatalytic performance of the catalyst [8,9]. The majority of the metal-ion doped TiO_2 photocatalysts studied were prepared by co-precipitation, incipient wet impregnation or sol–gel method [10]. Transition metal and rare earth metal ions have been attempted as dopants to improve the photocatalytic efficiency of TiO_2 in the visible region. When metal ions were doped into TiO_2, impurity energy levels were formed in the band gap. This tuned the band gap to absorb light at longer wavelength in visible light region. Additionally, the recombination of electron–hole pairs was suppressed by the introduction of other elements. Transition metal ions were either deposited or doped on the TiO_2 surfaces as metallic nanoparticles or the metals were doped as ionic dopants. A common method consists of doping of TiO_2 with transition metal cations, while maintaining a good control of the primary particle size to achieve nanoscale configurations of the catalysts. The doping elements usually used were Cr, Fe, V, Nb, Sb, Sn, P, Si, and Al [11].

In recent years, TiO_2-In_2O_3 composite photocatalysts have been explored by many researchers. In_2O_3, a semiconductor with a direct band gap of 3.6 eV and an indirect band gap of 2.8 eV, had proved to be an efficient sensitizer to extend the absorption spectra of oxide semiconductor photocatalysts from the UV region to the visible region [12]. The electrochemical experiment showed that molecular O_2 was reduced on the In_2O_3 surface at a markedly lower overvoltage than on the TiO_2 surface. Thus mixing TiO_2 with

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* Corresponding author. Tel.: +91 44 27469700; fax: +91 44 27469772.
E-mail address: mahalakshmim@ssn.edu.in (M. Mahalakshmi).

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In_2O_3 is beneficial not only for charge carrier separation but also for accelerating the associated transfer of photogenerated electrons to O_2 and also enhances acidity on the surface of In_2O_3/TiO_2 which increases adsorption [13]. Mu et al. [14] also reported that In_2O_3/TiO_2 nanofibre heteroarchitecture enhanced the photocatalytic activity by supressing e^-/hole recombination**.** Wang et al. [15] reported that the excitation of electrons from valence band of TiO_2 to the surface state energy level was attributed to the surface O–In–Cl species existing on the surface of In doped TiO_2 which was responsive to the visible light activity. The amount of hydroxyl groups on TiO_2 surface increased greatly after doped with indium. The superhydrophilic TiO_2 by In^{3+} doping was also reported by Eshaghi et al. [16]. Gonzaílez et al. [17] reported the synthesis, characterization and photocatalytic properties of In_2O_3-TiO_2 catalysts. The large number of structural defects by substitutional In^{3+} for Ti^{4+} enhanced the acidity and adsorption of pollutants and also H_3O^+ to produce more number of $^\bullet$OH radicals.

As lanthanide metal doping can introduce defect levels within the band gap, it can trap electrons and increase the lifetime of the charge carriers. Among them cerium doped TiO_2 attracts much attention [18,19]. CeO_2 is one of the most reactive rare earth metal oxides with a band gap of 2.92 eV. It has a high optical transparency in the visible region and possesses a high capacity to store oxygen [20,21]. The introduction of CeO_2 into the TiO_2 framework could effectively extend the visible light response of TiO_2. However, CeO_2-TiO_2 catalyst usually has low photocatalytic activity because of its low specific surface area. Hence, many researchers have focused on the preparation of meso structured CeO_2-TiO_2 with a large surface area and controllable pore size to improve its photocatalytic activity. The introduction of CeO_2 resulted in the increase of both the number of oxygen vacancies or defects in the TiO_2 crystal and the ability for the visible light absorption [22]. The electrons trapped in Ce^{4+}/Ce^{3+} sites could easily be transferred to O_2 on the surface of ceria treated TiO_2 catalysts, which prohibited the electron–hole recombination and thus increased the quantum yield of photocatalysis [23]. The important feature of double elements co-doped TiO_2 such as Fe and Ho [24], Sb and Cr [25], Ni and Ta [26], Fe and Eu [27], Zn and Fe [28], N and Ni [29], N and Ce [30] and F and N [31] exhibited apparently higher photocatalytic activity than that of a single doped TiO_2 and some of the elements mentioned above have synergistic effects in the photocatalytic experiments. The well-defined mesoporous structure of TiO_2 is also a promising way to achieve high photocatalytic activity since mesopore channel can facilitate rapid intraparticle molecular transfer [32].

In the present study, different weight percentage of indium and cerium oxides co-doped mesoporous TiO_2 with using triblock copolymer (Pluronic P123) as the structure directing template in ethanol–water solvent mixture was synthesized by sol–gel method. Both indium and cerium dopants shifted the light absorption edge to the visible light region and enhanced the photocatalytic activity by efficiently separating charge carriers (electrons/holes). To the best of our knowledge, there has been no report on indium and cerium oxides co-doped mesoporous TiO_2 as visible light photocatalyst. Hence both indium and cerium were selected for this co-doping work. The spectroscopic characterization of the co-doped TiO_2 photocatalysts and their photocatalytic activities in the degradation of methylene blue under visible light irradiation were also discussed.

2. Experimental

2.1. Materials

All the reagents and chemicals were of analytical grade and used without further purification. Titanium (IV) isopropoxide (Aldrich), cerium (III) nitrate hexahydrate (Aldrich) and indium (III) chloride (Aldrich) were used as the precursors for Ti, Ce and In respectively. Triblock copolymer, [poly (ethylene glycol)-block-poly (propylene glycol)-blockpoly(ethylene glycol)] (Pluronic P123, molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$; Aldrich) was used as the structure directing template. Absolute ethanol (Merck) and triple distilled water were used for the preparation of catalysts. Methylene blue (Fisher scientific) dye was used as the model pollutant for the degradation study.

2.2. Synthesis of mesoporous TiO_2 and In_2O_3/CeO_2-TiO_2

Mesoporous TiO_2 materials were synthesized by sol–gel method using soft template mechanism with Pluronic P123 as the structure directing agent [33]. The gel composition of the synthesis was 1 $Ti(OiPr)_4$:18H_2O with absolute ethanol as co-solute. The optimum ethanol/water ratio of 50:1 was maintained for this synthesis. Triblock copolymer, Pluronic P123 (1 g) was added to absolute ethanol (30 mL). After stirring for 4 h, a clear solution was obtained. Titanium (IV) isopropoxide (3 mL) was added to the above clear solution and stirred for 2 h at room temperature. Then water (18 mL) was added to the mixture and the stirring was continued for 24 h at room temperature. The pH of the mixture was maintained at 3.0 using 0.2 M HCl. Subsequently, the resulting mixture was kept in dark overnight for nucleation. The synthesis was carried out in a closed reagent bottle. The precipitated product was centrifuged in order to remove the template present in the solution of ethanol–water mixture. The solid product was dried and ground to get fine powder. This material was calcined at 400 °C for 5 h under N_2 atmosphere to remove the occluded template. The synthesized mesoporous TiO_2 material was designated as meso TiO_2. The different wt% of In and Ce doped TiO_2 materials were synthesized in the same route by adding stoichiometric amount of cerium (III) nitrate hexahydrate and indium (III) chloride as the cerium and indium sources respectively by dissolving in 18 mL of water during the synthesis. The amount of $InCl_3$ and $Ce(NO_3)_3{\cdot}6H_2O$ for 0.2 wt% In_2O_3/CeO_2-TiO_2 were 0.0101 g and 0.0103 g respectively for 3 mL of $Ti(OiPr)_4$. Mesoporous In and Ce doped TiO_2 materials were prepared by the molar ratio of In_2O_3 and CeO_2 to TiO_2 as 0.05:0.05:99.9 for 0.05 wt% In_2O_3/CeO_2-TiO_2, 0.1:0.1:99.8 for 0.1 wt% In_2O_3/CeO_2-TiO_2, 0.2:0.2:99.6 for 0.2 wt% In_2O_3/CeO_2-TiO_2, 0.3:0.3:99.4 for 0.3 wt% In_2O_3/CeO_2-TiO_2 and 1:1:98 for 1 wt% In_2O_3/CeO_2-TiO_2. In addition, 0.2 wt% In_2O_3-TiO_2 and 0.2 wt% CeO_2-TiO_2 were also synthesized by the molar ratio of In_2O_3 to TiO_2 as 0.2:99.8 for 0.2 wt% In_2O_3-TiO_2 and CeO_2 to TiO_2 as 0.2:99.8 for 0.2 wt% CeO_2-TiO_2 to compare the photocatalytic activities with the mixed metal oxides.

2.3. Catalyst characterization

The X-ray diffraction (XRD) patterns of mesoporous TiO_2 were recorded on Bruker D2 Phaser desktop X-ray diffractometer using Cu Kα radiation ($\lambda = 1.542$ Å) as the X-ray source. The average crystallite size (D) was determined from the broadening of the diffraction peak using the Scherrer formula $D = K\lambda/\beta \cos\theta$ where D is the average particle size in (nm), K is the Scherrer constant (0.89), λ is the wavelength of X-ray source, β is the full width at half-maximum and θ is the Bragg's angle. Transmission electron microscopic (TEM) images were recorded using an electron microscope (TECHNAI G^2 305-twin D 905) operated at an accelerating voltage of 200 keV. Scanning electron microscopic (SEM) pictures were recorded using a scanning electron microscope with energy dispersive X-ray spectrometer (SEM-EDX, Hitachi S 3400 N). The N_2 adsorption–desorption isotherms were measured using Micromeritics ASAP 2020 sorption analyzer. Prior to analysis, the samples were degassed for 3 h at 300 °C under vacuum (10^{-5} mbar) in the degas port of the adsorption analyzer. The specific

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