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$TiO_2/SrTiO_3$ and $SrTiO_3$ microspheres decorated with Rh, Ru or Pt nanoparticles: Highly UV–vis responsible photoactivity and mechanism

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ABSTRACT

A series of $TiO_2/SrTiO_3$ and $SrTiO_3$ microspheres decorated by Rh, Ru or Pt NPs were prepared by facile hydrothermal method. The as-prepared samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) with energy-dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM), photoluminescence spectrometry (PL), Fourier transform infrared (FT-IR) and Raman spectra and diffuse reflectance spectroscopy (DRS). The formation mechanism of $TiO_2/SrTiO_3$ and $SrTiO_3$ microspheres was proposed and the photocatalytic properties of the samples were characterized using phenol as the pollutant under the UV–vis and light irradiation. The gas chromatography-mass spectrometry was employed to detect organic intermediates to establish degradation pathway of isotopically labeled (1-^{13}C) phenol. The role of the active species in the process of the degradation was evaluated using different types of active species scavengers as well as hydroxyl radical test with coumarin were also carried out. The PL spectra indicate that the formation of $TiO_2/SrTiO_3$ and $SrTiO_3$ decreased the recombination rate of photogenerated carriers. The obtained results revealed that the samples showed an enhanced photocatalytic activity for the degradation of organic pollutant. The $SrTiO_3/Rh_{(0.05)}$ photocatalyst showed a higher photodegradation rate under UV–vis and Vis light (3.6 and 1.2 μmol dm^{-3} min^{-1}, respectively) compared to the unmodified $SrTiO_3$ (0.6 and 0.2 μmol dm^{-3} min^{-1}, respectively). The active species trapping experiments indicated that under UV–vis as well as Vis illumination $O_2^{\cdot-}$ are the main active species in the degradation process. The main by-products detected in phenol oxidation were catechol, hydroquinone, malonic, fumaric and maleic acid. Moreover, GC–MS results indicated the formation of isotopically labeled and unlabeled maleic acid which could be generated by two different pathways: trough decomposition of catechol and hydroquinone at the same time.

1. Introduction

Among the various semiconductors, nanosized TiO_2 has been widely used in photocatalysis due to its high photosensitivity under UV light, low cost, low toxicity, good chemical and thermal stability [1–3]. However, at present, there are two main drawbacks for large-scale applications of traditional photocatalysts such as TiO_2. The first one is undesirable recombination of photogenerated electron–hole pairs with high rate, resulting in their poor photocatalytic activity under visible light irradiation. The second one is very poor absorption ability of the pure TiO_2 semiconductors in the visible region, due to its wide band gap (3.2 eV for anatase and 3.0 eV for rutile), seriously limiting the utilization of sunlight. It has been proved that the fabrication of *p-n* heterostructures by combining *n*-type TiO_2 with *p*-type semiconductors is one of the effective ways to improve the photoelectric conversion efficiency of TiO_2. $SrTiO_3$ is a well-known simple cubic perovskite ($Pm3m$, a = 3.9 Å) and *p*-type semiconductor with an indirect band gap of 3.1–3.2 eV. Although the band gaps of $SrTiO_3$ and TiO_2 are similar, the conduction band edge of $SrTiO_3$ is 200 mV more negative than that of TiO_2, which may make $SrTiO_3$ become a good candidate for coupling TiO_2 and improve its photoelectrochemical performance [4]. Moreover, the proper couple of $SrTiO_3$ and TiO_2 would lead to not only the transfer of electron from the CB of $SrTiO_3$ to that of TiO_2, but also the transfer of holes from the valence band (VB) of TiO_2 to that of $SrTiO_3$, which effectively prevent the recombination of photogenerated electrons and holes in the coupled $SrTiO_3$–TiO_2

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heterostructure and as a result may improve the photocatalytic activity of semiconductors. Literature data showed that the coupled $SrTiO_3/TiO_2$ composite could improve the charge separation and achieve a higher photocatalytic activity [4–12]. Zhang et al. prepared $SrTiO_3/TiO_2$ by forming $SrTiO_3$ on highly ordered TiO_2 nanotube arrays, and indicated that the $SrTiO_3/TiO_2$ nanotube nanojunctions were formed after immersion of the TiO_2 nanotubes into $Sr(OH)_2$ solution [11,12]. Hydroxyl radicals ($^{\cdot}OH$) and superoxide ($^{\cdot}O_2^-$) ions were respectively created by the holes and electrons of $SrTiO_3/TiO_2$ nanotube, resulting in approximately 100% photodegradation of methyl blue within 100 min. Bai et al. synthesized $SrTiO_3/TiO_2$ nanofibers by electrospinning and the hydrothermal method [7]. The heterostructures showed better photocatalytic H_2 production activity than TiO_2 nanofibers because of the fast separation of photoinduced charges. Furthermore, the hierarchical structure, the long fibrous structure, and the larger specific surface area of $SrTiO_3/TiO_2$ nanofiber heterostructures also benefit the photocatalytic activity synergistically. Yan et al. obtained nitrogen-doped $SrTiO_3$ powders by solid phase method, and further combined with TiO_2 by sol–gel method which leads to extend the visible light absorption range of the photocatalyst [9]. Huang et al. prepared novel triple junction $Pt/TiO_{2-x}N_x/SrTiO_3$ photocatalysts for H_2 production under solar light irradiation, fabricated by growing the N-doped TiO_2 on the $SrTiO_3$ support, which was then coated with the Pt metal [8]. Obtained samples improved H_2 production rate, which could be ascribed to the photogenerated charge transfer from $SrTiO_3$ to the N-doped TiO_2 as well as the photogenerated charge separation caused by the Pt metal coating on the outer layer, which formed a Schottky barrier between the metal and the semiconductor. Under solar light irradiation visible light activated the N-doped TiO_2, while UV light excited the $SrTiO_3$. Therefore, photogenerated e^-/h^+ can transfer from $SrTiO_3$ to the N-doped TiO_2. These charges further flowed from the semiconductor to the Pt metal [8]. Dong et al. synthesized porous $SrTiO_3$ spheres by a hydrothermal method [13]. The photocatalytic activity of the porous $SrTiO_3$ spheres was evaluated by the degradation of Rhodamine B (2×10^{-5} mol/l of RhB solution) under UV illumination ($\lambda = 254$ nm). The $SrTiO_3$ samples exhibited enhanced photocatalytic activity and were able to degrade 100% RhB for 20 min of irradiation.

One of the approaches to improve photoactivity is surface modification with monometallic nanoparticles due to acceleration of photoexited electron transfer to the substrate, and ability of visible light absorption either by metal complexes bounded to the semiconductor or by photoexcitation of localized surface plasmon resonance (LSPR) of nanoparticles (NPs) of noble metals attached to the semiconductor [14–18]. Rhodium (Rh) and ruthenium (Ru) photocatalysts, where base material was doped or modified with a small amount of a Rh or Ru species without changing the original crystal structure, have been used to develop visible-light-active TiO_2 or $SrTiO_3$ [19–22]. Kuncewicz et al. obtained TiO_2 particles modified with a small amount (<0.01 mol%) of a rhodium species [16]. Rh–TiO_2 photocatalyst exhibited photocatalytic activity for the oxidative decomposition of acetaldehyde in air under Vis light. Moreover, it was noticed that reaction proceeded *via* a two-photon band-gap excitation mechanism, using a built-in Rh(III)–Rh(IV) redox couple [16]. Kang et al. prepared $SrTiO_3$ powder co-doped with Rh and Ta by spray pyrolysis method and used for increasing the rate of hydrogen evolution [23]. Thorough mixing of the multicomponent spray pyrolysis precursor solution led to obtain highly dispersed Rh ions and porous photocatalyst particles. Kowalska et al. proved that Ru(II) complexes cause enhancement in photocatalytic activity under UV/vis irradiation, due to separation of charge carriers [14].

Taking the abovementioned considerations into account it can be concluded that bare and modified $SrTiO_3/TiO_2$ semiconductor combinations enhance photocatalytic activity through interfacial charge separation in the $SrTiO_3/TiO_2$ heterostructure. Although these successful examples have made significant achievements, most of them just focused on the measuring the photocatalytic activity using organic dyes as a model compound, which according to Ohtani, prevent the feasible determination of photocatalytic activity, especially using spectrophotometric analysis, due to the (1) dye photosensitization of TiO_2, (2) high photoabsorption coefficient of the dyes and (3) complicated mechanism of dye degradation [24]. Thus, in our photocatalytic experiments, we used phenol as a model contaminant instead of organic dyes. In this context, in this paper we have recently obtained $TiO_2/SrTiO_3$ and $SrTiO_3$ microspheres prepared by hydrothermal method and decorated with Pt, Rh and Ru nanoparticles by photodeposition method. Photoactivity of the heterostructure photocatalyst was evaluated under both UV–vis and visible light. For the first time, photocatalytic activity of Pt, Rh and Ru modified $TiO_2/SrTiO_3$ and $SrTiO_3$ was correlated with preparation route, and thus with surface properties. Furthermore, to the best of our knowledge, it was the first time when the mechanism of phenol degradation in the presence of $SrTiO_3$ spheres loaded with Rh NPs under UV and Vis irradiation and with application of labeled carbon ^{13}C isotope (phenol-1-^{13}C) was reported. To provide insight into the oxidative species participating in the degradation mechanism, hydroxyl radical test with coumarin was also studied. Moreover, the role of the active species in the process of the degradation was evaluated using different types of active species scavengers. Based on obtained results, a possible phenol degradation pathway under UV–vis irradiation was proposed. This finding provides an alternative to those who are interested in developing new photocatalysts for heterogeneous photocatalysis. Insights into this new kind photocatalysts will inspire researchers to develop other types of nanomaterials for visible-light-driven organic compound degradation.

2. Experimental

2.1. Chemicals and materials

All reagents used in our experiment are of analytical purity and were used without further purification. Titanium(IV) butoxide (TBT) (97%) and strontium chloride hexahydrate ($SrCl_2{\cdot}6H_2O$, 99%) were purchased from Sigma–Aldrich. Ethanol (99.8%), NaOH and sulfuric acid (98%) (POCH S.A., Poland) were used without further purification. $H_2PtCl_6{\cdot}xH_2O$ (99.9%), K_2PtCl_4 (99.9%), $RuCl_3{\cdot}xH_2O$ (38.0–42.0% Ru basis) and $RhCl_3$ (98%) were used as metal source in the preparation procedure. Coumarin was purchased from Sigma–Aldrich Co. (Germany) and phenol was obtained from POCh S.A. (Poland). *tert*-Butyl alcohol (99.5%), $AgNO_3$ (99%), *p*-benzoquinone (98%) and ammonium oxalate monohydrate (99.5%) from Sigma–Aldrich were used as a scavengers. Ethyl chloroformate (>98% GC), pyridine anhydrous (99.8%), hydroquinone (>99.5%), malonic acid (99%), *p*-benzoquinone (>98%), fumaric acid (>99%), maleic acid (>99%) were purchased from Sigma–Aldrich Co. (Germany) whereas salicylic acid and Na_2SO_4 anhydrous were from Chempur Co. and Stanlab Co. respectively. Isotopically labeled (1-^{13}C) phenol was obtained from Cambridge Isotope Laboratories.

2.2. Preparation of pristine and metal-modified $TiO_2/SrTiO_3$ and $SrTiO_3$ microspheres

In the first step TiO_2 microspheres were obtained according to the procedure described by Zheng et al. and in our previous study [17,25]. $Ti(OBu)_4$ (5.1 g) was mixed with absolute ethanol (75 ml) under vigorous stirring. After that, sulfuric acid (98%, 0.33 ml) and deionized water (0.3 ml) were added. The resulting solution