Application of the soluble salt-assisted route to scalable synthesis of ZnO nanopowder with repeated photocatalytic activity

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Abstract
In this paper, the soluble salt-assisted route has been extended to the low-cost and scalable preparation of ZnO nanostructures via the simple oxidation of Zn–Na\(_2\)SO\(_4\) mixture followed by washing with water. The as-prepared ZnO nanopowders are of nanoscaled size, hexagonal phase, and pure, without being stained by Na\(_2\)SO\(_4\). Their optical band gap is 3.22 eV, exhibiting a red-shift of 0.15 eV in comparison with pure ZnO bulk, and their optical absorbance is strong in the region of 200–400 nm, suggesting their full utilization of most of the UV light in sunlight. The product shows evident photocatalytic activity in degradation of RhB under solar light irradiation, and then its solar light degradation efficiency is close to that under UV irradiation, indicating that there is a possibility of practical application. More importantly, the obtained ZnO nanoparticles, because of the quick precipitation by themselves in solution with no stirring, could be easily recycled without any accessorial means such as high-speed centrifuge. The low-cost and scalable preparation, high photocatalytic activity, and convenient recycling of this ZnO nanomaterial gives it potential in purifying waste water. Hence the interesting results in this study indicate the wide range of the soluble salt-assisted route for the industrial preparation of many other advanced nanomaterials.

Online supplementary data available from stacks.iop.org/Nano/23/065402/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction
Since the first discovery of the photocatalytic splitting of water on a TiO\(_2\) electrode under ultraviolet (UV) light irradiation in 1972 [1], a series of semiconductor-based nanophotocatalysts, and their nontoxicity, high photocatalytic activity and good chemical stability, have been tentatively and extensively explored to resolve photo-activity-related wastewater treatment problems [2]. Among them, TiO\(_2\)– and ZnO-based nanomaterials have received the most ongoing attention in many application fields from photovoltaics and photocatalysis to photo-/electrochromics and sensors. In particular, in view of the excellent contributions to the field of decomposing large organic molecules in waste water under various light irradiation resources, enormous efforts have been devoted to the photochemical degradation of organic pollutants over modifications of TiO\(_2\)-based materials in the last two decades [3, 4]. And Degussa P25, the
only commercially applied TiO$_2$ product, has so far been most extensively used, and become a worldwide reference in laboratories. Meanwhile, the study on ZnO, having a similar band gap to TiO$_2$, has been relatively left behind in comparison with TiO$_2$ as far as its applications for photochemical degradation of organic molecules in purifying waste water are concerned [5]. However, ZnO has some evident advantages in the sense that it absorbs over a larger fraction of the UV spectrum and has lower preparation cost in comparison with TiO$_2$ [6–8].

Practical industrial applications of ZnO nanomaterials would be feasible in the field of photochemical waste water treatment on the premise that they could be prepared economically and on a large scale. Therefore many Zn-containing precursors and preparation methods have been tried for these aims. Vapor growth of ZnO nanostructures is attractive when depositing ZnO-based materials onto different substrates, but it is unfit for scalable preparation of ZnO nanopowder [9]. In contrast, wet chemical routes, because of their simple, less expensive, high yield and scalable processes, are favorably used to fabricate ZnO nanopowder by decomposing Zn-containing salts in liquid phase reactions [10]. However, the decomposition of Zn-containing compounds into ZnO leads not only to increased preparation costs but also to possible contamination of the targeted products from unexpected doping from elements such as C, N and S [8, 11]. Accidental doping into ZnO would disturb the essence of the matrix and make its desired property uncontrollable. Hence, an optimal avenue to obtain pure ZnO nanopowder simply and economically might be the direct oxidation of metallic Zn powder, the cheapest Zn precursor, ZnO nanostructured powders have been harvested conveniently and economically. Moreover, the as-prepared product showed excellent photocatalytic degradation of RhB under solar light irradiation, and repeated reuse without any accessorial means, suggesting potential in purifying waste water.

2. Experimental details

2.1. Preparation and characterization

ZnO nanostructured powder was prepared by the soluble salt-assisted route as shown in figure 1. In detail, 1 g of metallic Zn powder (99.99% in purity and 100–200 mesh in diameter) and 15 g of Na$_2$SO$_4$ powder were added to a stainless steel jar and ball-milled for 24 h with a rotary speed of 150 r min$^{-1}$. The compacted Zn–Na$_2$SO$_4$ mixture was loosened every 2 h by opening the jar. As a result, the diameter of the metal nanoparticles was less than 50 nm (figure S2 available at stacks.iop.org/Nano/23/065402/mmedia). Then the milled mixture was heated in a muffle at 500°C for 3 h. The oxidation mixture was washed with distilled water several times until SO$_4^{2-}$ ions could not be detected in the filtrate. The component of Na$_2$SO$_4$ in the filtrate could be recycled as a dispersant for preparing ZnO material after evaporating the solvent water. Finally, the filtered product was dried in an oven at 90°C for 3 h and 1.198 g of pale white powder was obtained (figure S2 available at stacks.iop.org/Nano/23/065402/mmedia). The yield of ZnO was 96.15%, based on the amount of Zn powder used.

The product was characterized by x-ray diffraction (XRD; Philips X’pert Pro diffractometer), scanning electron microscopy (SEM; JEOL JSM-6300) equipped with x-ray analysis (EDX), transmission electron microscopy (TEM, JEOL-JEM-1005) and high-resolution transmission electron microscopy (HRTEM; JEM-40001X), x-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII),
2.2. Study of photocatalytic activity

The photocatalytic activity of the ZnO samples was evaluated by the photodegradation of rhodamine B (RhB) aqueous solution with an initial concentration of 12 mg l\(^{-1}\). Herein solar light was used as the preferential light source and a 500 W mercury lamp (\(\lambda = 365\) nm) was used sometimes for a consulted UV light source (500 W). The sunlight experiments were carried out between 10.00 am and 14.00 pm during December (winter season) at Shangrao City. Unless otherwise noted, 30 mg of catalyst powder was added into 35 ml of the above RhB solution in a quartz cup, corresponding to a catalyst dosage of 0.86 g l\(^{-1}\). Before solar irradiation, the whole system was placed in the dark for 30 min to ensure an adsorption/desorption equilibrium. At given time intervals, about 2 ml aliquots were sampled and centrifuged. Then the top clear solution was analyzed by recording variations in the absorption in UV–vis spectra of RhB. According to the standard curve between concentration and absorption, the ratio of (1 – \(C/C_0\)) was calculated, denoted as the degradation ratio.

3. Results and discussion

3.1. Structural analysis of the photocatalyst

The off white powder harvested after the calcination and washing was characterized by XRD as shown in figure 2. It is seen that the main diffraction peaks in this XRD pattern, especially the (100), (002) and (101) crystal planes located at 31.85°, 34.50° and 36.35°, respectively, can be indexed as the wurtzite ZnO phase with calculated lattice parameters of \(a = 3.245\) Å and \(c = 5.196\) Å (PDF #792205). Additionally, a trace of metallic Zn was also detected by XRD in the as-prepared product, indicating an incomplete oxidation reaction of Zn particulates in air at 500 °C. Although full oxidation of the Zn NPs in mixture was accomplished when the calcination reaction was conducted at 600 °C (figure S3 available at stacks.iop.org/Nano/23/065402/mmedia), the ZnO product had large-sized particles or short nanowires. The high calcination temperature revealed the difficult oxidation of nanoscale Zn NPs dispersed onto the surface of Na\(_2\)SO\(_4\) powder, though sharply decreased in comparison with the calcination temperature of bulk Zn powder into ZnO product in air [15]. The absent diffraction peaks of the of Na\(_2\)SO\(_4\) dispersant suggested the purity of the product.

3.2. Morphological observations of the photocatalyst

The electron microscopy images in figure 3 show the morphology of the as-synthesized product prepared by oxidation of the ball-milled Zn–Na\(_2\)SO\(_4\) mixture at 500 °C followed by washing. Figure 3(a) exhibits a typical SEM image of the ZnO product, revealing an aggregation of nanoparticles. Figure 3(b) is the corresponding EDX pattern, which indicates the presence of the elements Zn and O. The absence of Na and S signals further demonstrates the high purity of the product, and is consistent with the XRD result. A little of the powder sample was dispersed in ethanol under ultrasonic conditions, and a droplet of the suspension was dripped onto a copper grid coated with ultrathin carbon film. Thus the TEM operation was undertaken and the TEM image is shown in figures 3(c) and (d). It is seen that the ZnO NPs obtained have uniform diameter of a size of ca. 40–50 nm and are monodispersed in ethanol after ultrasonic treatment, while the HRTEM images show distinct particles with well defined crystalline boundaries resulting from highly crystallized material. The spacing of 2.85 Å between adjacent fringes corresponds to the \(d\)-spacing of (100) planes in hexagonal ZnO.

3.3. Component analysis for the photocatalyst by XPS

XPS analysis is a good method usually applied to detect a trace of the samples and find related chemical information. The binding energies of the examined elements are calibrated by using the C\(_1s\) peak (284.6 eV) as a reference. The survey XPS spectrum (figure 4(a)) shows that there are Zn and O peaks, suggesting that the as-synthesized product is pure ZnO. The non-detection of Na and S elements by XPS is in accordance with the results obtained by XRD and EDX. The strong C\(_1s\) peak (figure 4(a)) is due to carbon tape which is usually used in the XPS characterization of powder samples since no carbon-containing substance was introduced in this preparation process. Binding energies around 1021.1 and 1044.0 eV are attributed to Zn 2p\(_{3/2}\) and 2p\(_{1/2}\) electrons, respectively (figure 4(c)). The lone and sharp peak at 1021.1 eV for the Zn 2p\(_{3/2}\) core level is associated with the Zn species in the completely oxidized state [16]. The O\(_{1s}\) core level peak with a shoulder shape was deconvoluted into two sub-peaks (figure 4(d)) with the one at 529.9 eV attributed to the O\(^{2-}\) ions in the wurtzite structure surrounded...
Figure 3. Morphological characterizations of ZnO NPs obtained by oxidation of the ball-milled Zn–Na2SO4 mixture at 500 °C followed by washing, including (a) an SEM image, (b) an EDX curve, (c) a low magnification TEM image and (d) a high-resolution TEM image with the Fourier transform from the framed part in (c) shown in the inset.

by Zn atoms with a full complement of nearest neighbor O2− ions, and the other at 531.5 eV belonging to the adsorbed species containing the C–O bond. After subtraction of the adsorbed oxygen species, the proportion of Zn atoms to O atoms is close to 60:40, revealing an excess of Zn2+ in the product. The O2− deficiency on the surface can capture and trap electrons, and thus help in effective photocatalytic degradation of organic pollutants under light irradiation [17].

3.4. BET surface area for the photocatalyst

The photocatalytic activity of the ZnO NPs is dependent to a large extent on their surface area [18]. Figure 5 shows the corresponding nitrogen adsorption/desorption isotherm and Barrett–Joyner–Halenda pore-size distribution curve for the ZnO NPs calcined at 500 °C. These isotherms belong to type IV with an H3 hysteresis loop, characteristic of
slit-shaped mesoporous structure [19]. Two types of pores can be distinguished in the sample as small mesopores (3.6 nm) and large mesopores (44.6 nm), respectively. The former are from the interstices between ZnO NPs, playing the main role of increasing the BET surface area of the product, while the latter are from the gaps between the inter-aggregated secondary particulates [20]. On the other hand, the surface area of the product can be theoretically expressed by the formula 

$$S_{BET} = \frac{6000}{\rho d}$$  

(where $\rho$ is the density of ZnO with a value of 5.8, $d$ is its average diameter of ca. 40–50 nm as seen in figure 3), since there is no porous hole for the approximately ball-shaped ZnO NPs (figures 3(c) and (d)). The calculated surface area for the prepared product is in the range 20.7–25.8 m² g⁻¹. However the measured value is 18.2 m² g⁻¹ less than the calculated value, also suggesting a little conglomeration of the ZnO NP powder though showing a monodisperse state for the ZnO NPs in ethanol. Therefore the measured BET surface area and pore-size distribution for the product are in perfect accordance.

Herein the calcination temperature of the ball-milled Zn–Na₂SO₄ mixture was reasonably set at 500 °C, because the obtained ZnO product calcined at 600 °C has a large size and a small BET surface area of 8.5 m² g⁻¹ (figures S3 and S4 available at stacks.iop.org/Nano/23/065402/mmedia).

3.5. UV–vis diffuse reflectance spectra of the photocatalysts

UV–vis diffuse reflectance spectra of the ZnO nanomaterials are presented in figure 6. They show similar broad and strong absorptions with a maximum at about 385 nm, which is characteristic of ZnO wide-band semiconductor material. The inset shows a plot of $(\alpha h \gamma)^{2}$ versus the energy of absorbed light, from which the direct allowed band gaps can be estimated to be 3.22 eV for the ZnO nanostuctures calcined at both 500 and 600 °C. Compared with bulk ZnO (3.37 eV), the
absorption edges of ZnO are red-shifted. This phenomenon cannot be explained by quantum size effects, but is ascribed to the occurrence of shallow donor levels introduced by impurity atoms in a previous report [21]. However, in this preparation the final products were not stained by Na₂SO₄, which has been strongly demonstrated by XRD, EDX and XPS results above. Therefore, the simple reaction in this preparation is between metallic Zn and O₂ in air, which leads to the pure ZnO product. There is, however, a known acceptance that red-shift and blue-shift co-occur in a product whose band gap is determined by the quantum effect; on the other hand the increased intra-stress in the particles causes the change of energy band structure, thus the narrowing of the band gap and energy level, which lead to the final red-shift. We have to acknowledge that the factors that caused the red-shifts of the UV–vis absorption bands will have to be further investigated [10]. It is also worth noting that an asymmetric tail was observed toward the higher wavelengths ranging from 400 to 800 nm in the ZnO NP sample calcined at 500 °C, but disappeared in the one calcined at 600 °C. The dragging tail for ZnO NPs calcined at 500 °C is due to residual metallic Zn which was detected by XRD (figure 2). The strong absorption in the UV range reveals the quick response and full utilization of most of the UV light in sunlight for as-synthesized ZnO nanomaterials.

The ZnO sample calcined at 600 °C possesses a rougher surface, leading to multiple ray reflections (as seen in figure 3(a) and figure S2(a) available at stacks.iop.org/Nano/23/065402/mmmedia), and thus has a higher absorbance efficiency than that calcined at 500 °C. However its photocatalytic ability in degradation of organic molecules is inferior to that of the latter, because the practical photodegradation efficiency for the photocatalyst is determined by many factors such as its absorbency, crystallinity, surface area, spatial structure, and so on. On balancing the many issues of as-prepared ZnO samples by this route, the product calcined at 500 °C was selected as the optimal photocatalyst.

3.6. Photocatalytic degradation of RhB over ZnO NPs under solar light and UV irradiation

Figure 7 shows the degradation ratio of RhB over ZnO NPs under solar light irradiation. With the solar irradiation time prolonged from 0 to 4 h, close to a linear increase was observed in the degradation ratio of RhB over the photocatalyst; and up to a solar irradiation time of 4 h the degradation ratio of RhB was almost 100%. Therefore the photocatalytic degradation process of RhB over a surface of ZnO obeys pseudo-first-order kinetics, namely the following equation: \( \ln \left( \frac{C}{C_0} \right) = kt \) [8]. In the absence of photocatalyst, little RhB was degraded though long-time irradiation under solar light, indicating that the self-photosensitized process of RhB could be absolutely neglected. The bright contrasts revealed that ZnO NPs hold high photocatalytic efficiency in the degradation of RhB under solar light irradiation. As is known, powder-like photocatalysts, in particular those with large BET surface area, are usually suspended in aqueous solution, and thus it is difficult for them to recycle themselves unless some accessorional means such as a high-speed centrifuge is provided. The difficulty in recycling would make them unpromising in practical applications though having very high catalytic activity in the degradation of organic pollutants. That is to say, the as-synthesized ZnO NPs powder must have excellent self-recycling ability with no help from any other accessorional means [22]. Figure 8(a) indicates the curve of degradation ratio of RhB versus reuse times of ZnO NPs under solar light irradiation for 4 h. It is noted that ZnO NP powder had good reuse capacity; even though the reuse time number reaches 10, the degradation ratio of RhB is still as high as ca. 68% under 4 h of solar light irradiation. The excellent self-recycling ability of the ZnO NPs is due to their quick self-precipitation in water. Even if the recycle times reached 10, the recovery ratio of ZnO NPs was still high, up to ca. 70%. In contrast, Degussa P25, the most extensively used commercial photocatalyst, had a poor recovery ratio as low as less than 10% after recycling ten times (figure S5 available at stacks.iop.org/Nano/23/065402/mmmedia). Additionally, stable UV irradiation was also used as a substitute for changeable solar light irradiation to examine reuse of the photocatalyst. The curve in figure 8(b) reveals that the ZnO NPs also had evident recycling efficiency under UV irradiation, in good agreement with the results obtained under solar light irradiation (figure 8(a)). The comparisons achieved under solar light and UV irradiation, strongly suggested that the ZnO NPs has good recycling characteristics in the degradation of RhB in aqueous solution, indicating their potential in purifying waste water.

4. Conclusions

In summary, the soluble salt-assisted route has been extended to the scalable preparation of ZnO nanostructures. Due to utilizing the simple reaction between metallic Zn powder and
O₂, the preparation of pure ZnO nanopowder becomes very easy, economical and scalable. Importantly, the product shows evident photocatalytic activity in degradation of RhB under solar light irradiation, and possesses the function of repeated recycling without the help of a high-speed centrifuge. Thus the interesting results in this study indicate the wide range of the soluble salt-assisted route for the industrial preparation of ZnO nanomaterials.

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