



A simple mechanical mixing method for preparation of visible-light-sensitive NiO–CaO composite photocatalysts with high photocatalytic activity

Limin Song^a, Shujuan Zhang^{b,*}

^a College of Environment and Chemical Engineering & Tianjin Key Laboratory of Fiber Modification and Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, PR China

^b College of Science, Tianjin University of Science & Technology, Tianjin 300457, PR China

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ABSTRACT

Composite photocatalysts composed of NiO and CaO have been prepared via mechanically mixing of the two powders. The as-synthesized NiO–CaO products were characterized by X-ray diffraction (XRD) and UV–vis spectrometry. The experimental results showed that the absorption wavelength range of the mixed NiO–CaO sample was notably extended towards the visible-light region (400–450 nm). Photocatalytic activity of the NiO–CaO composite was evaluated based on the decomposition of methylene blue under visible-light irradiation. The effects of CaO doping and the duration of heat treatment on the durability of the NiO–CaO products have been investigated in detail. Factors influencing photocatalytic activity and the mechanism of photocatalysis were also addressed.

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1. Introduction

In recent years, the environmental problem of water pollution by organic contaminants has become of increasing concern [1–7]. Among the technologies available for removal of pollutants from water systems, photocatalysis is proving to be promising, especially in terms of the use of solar energy for the removal of organic compounds. In this respect, metal oxide nanomaterials are being explored as photocatalysts that can be driven by visible light for the decomposition or destruction of organic pollutants in water [8–16]. Of these metal oxides, nickel oxide (NiO) has been attracting the most interest, due to the diversity of its potential applications, including use as an optical material, a heterogeneous catalyst, and p-type transparent conducting film, among others [17–19].

Numerous studies have attempted to exploit NiO for the development of visible-light photocatalysts capable of efficiently using solar energy and indoor light [20–23]. The excellent photocatalytic property of NiO depends strongly on its composition and structure. Therefore, in the present paper, we report on the preparation of a composite NiO–CaO photocatalyst formed by a simple mechanical doping of NiO nanoparticles with CaO. At the interface of the NiO and CaO nanoparticles, many micro p–n junction CaO/NiO photocatalysts were formed, which were so effective that the sites

of electron–holes were separated. These NiO–CaO photocatalysts showed high catalytic activity in the oxidative decomposition of an organic molecule under visible-light irradiation.

2. Experimental

2.1. Materials

Commercially available TiO₂ (Degussa Corp., P25, diameter 30 nm) was used as a reference photocatalyst. Other chemicals were all of analytical reagent grade quality and were used without further purification. Deionized water was used throughout this study.

2.2. Catalyst preparation

The NiO–CaO photocatalyst was synthesized by a simple method. Aqueous solutions of Ca(NO₃)₂·4H₂O or Ni(NO₃)₂·6H₂O and NaOH were mixed together in 1:2 molar ratio, with stirring. The mixtures were stirred for 20 min at room temperature. The precipitates that formed were centrifuged, washed with deionized water, and dried at 373 K in air for 3 h. The obtained powder was then calcined at 700 °C for 2–6 h to produce crystalline NiO or CaO. These two materials were then mechanically mixed in different molar ratios under grinding to obtain the NiO–CaO composite photocatalysts.

* Corresponding author. Tel.: +86 22 60600658; fax: +86 22 60600658.

E-mail address: cbnk@yahoo.cn (S. Zhang).

2.3. Catalytic activity evaluation

The photocatalytic activity under visible-light irradiation of the NiO–CaO samples was evaluated by using methyl blue (MB) as the model substrate. 250 mL MB (10 mg/L) aqueous solution and 1.0 g of photocatalyst powder were mixed in a quartz photoreactor. Prior to a photocatalytic reaction, the photocatalyst suspension was sonicated to reach adsorption equilibrium with the photocatalyst in darkness. The above solution was photoirradiated by using a 300 W Xe lamp as light source under continuous stirring. A cut-off filter was used in these experiments ($\lambda > 400$ nm). At a defined time interval, the concentration of MB in the photocatalytic reaction was analyzed by using an UV–vis spectrophotometer at 665 nm.

2.4. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were obtained with a Rigaku D/max 2500 powder diffractometer using Cu K α radiation at a wavelength of 1.5406 Å and recorded from 10° to 80° (2θ). UV–vis absorption spectra were recorded in the range of 300–800 nm on a HP8453 UV–vis spectrometer. The BET surface areas (S_{BET}) were measured by N₂ adsorption at –196 °C using an automatic surface area and pore size analyzer (Autosorb-1-MP 1530VP). S_{BET} measurements were performed using the five-point BET method.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the NiO, CaO, and NiO–CaO samples are shown in Fig. 1. The sharp diffraction lines (around $2\theta = 43.29^\circ$, 37.26° , and 62.89°) of the NiO sample are assigned to the cubic cell of the NiO phase (Fig. 1a). The XRD pattern of NiO is similar to the reference pattern taken from the JCPDS powder diffraction file (Card 89-5881). From the XRD patterns and the corresponding characteristic 2θ values of the diffraction peaks in Fig. 1b, the as-prepared sample was confirmed as cubic-phase CaO (Card 82-1691). Fig. 1c shows the XRD patterns of the NiO–CaO sample obtained by mechanically mixing NiO and CaO calcined at 700 °C. As seen in Fig. 1c, all of the diffraction lines match with the XRD patterns of NiO and CaO. Thus, there were no impurities evident in the phase of NiO and CaO, as seen in Fig. 1c.

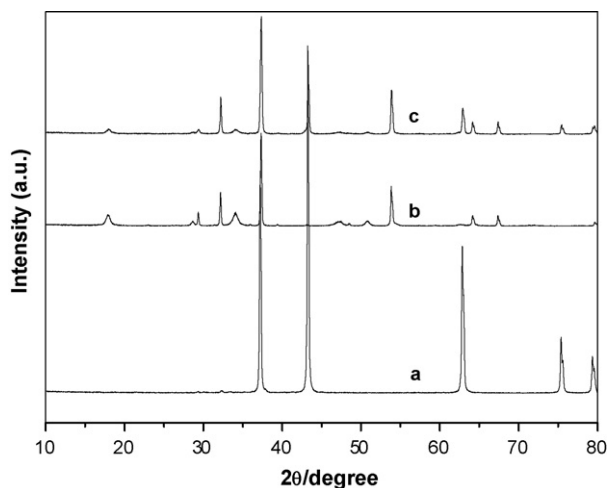


Fig. 1. Powder X-ray diffraction patterns of (a) NiO, (b) CaO calcined at 700 °C, and (c) NiO–CaO obtained by mechanically mixing alone NiO and CaO calcined at 700 °C.

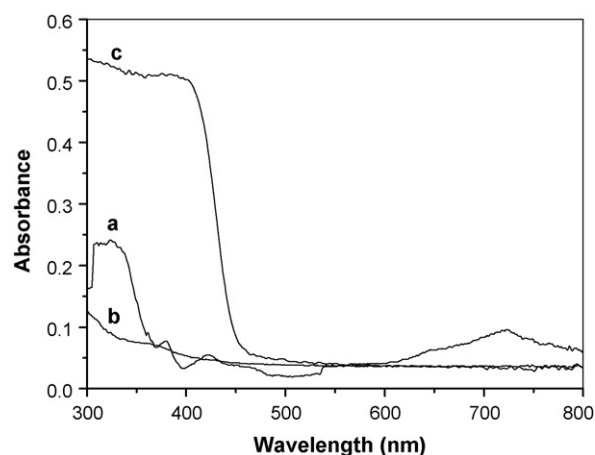


Fig. 2. UV–vis diffuse reflection spectra of the samples. (a) NiO, (b) CaO calcined at 700 °C, and (c) NiO–CaO obtained by mechanically mixing alone NiO and CaO calcined at 700 °C.

Fig. 2 shows the UV–vis absorption spectra of the NiO, CaO, and NiO–CaO samples. The NiO sample had wide absorption bands in the visible range, at 400–500 nm and 650–800 nm (Fig. 2a). In contrast, the as-prepared CaO sample exhibited no obvious optical properties in the visible-light range (Fig. 2b). As seen in Fig. 2c, the absorption wavelength range of the mixed NiO–CaO sample was notably extended towards the visible-light region (400–450 nm), although the absorption band of the NiO sample at 650–800 nm had disappeared. Compared with the NiO and CaO samples, the absorption intensity of the mixture was also greatly increased. In theory, the extended absorption wavelength towards the visible-light region and the increased absorption intensity indicated increased formation of electron–hole pairs on the photocatalyst surface, which could result in the NiO–CaO photocatalyst showing higher photocatalytic activity [17].

3.2. Activity studies

Photocatalytic activity evaluations were investigated by the degradation of methylene blue (MB) in aqueous solution under visible-light irradiation. MB showed a maximum absorption at about 665 nm. The total concentration of MB was determined by the maximum absorption measurement. The specific area of the NiO, CaO, and NiO–CaO samples were 28.13, 40.52 and 35.16 m² g^{–1}, respectively (the mole ratio of Ca/Ni was 1.0).

Fig. 3 shows the decrease in concentration of an aqueous MB solution over a 180 min period in the presence of either NiO, CaO, or NiO–CaO samples. The mechanical mixture of NiO–CaO was 1:1 molar ratio. As a comparison, degradation of MB over P25 and MB photocatalysts under the same condition is also shown in Fig. 3. In the absence of any photocatalyst, only about 10% decomposition of MB molecules was noted (Fig. 3a), which can be accounted for by the natural photodegradation of MB molecules. Under the same reaction conditions, the photodegradation efficiency of the P25, CaO, and NiO samples were about 29.7, 37.8, and 28.8% (Fig. 3b–d), respectively. However, in the presence of the NiO–CaO sample, 96.5% of MB was photocatalytically degraded under visible-light irradiation (Fig. 3e). Fig. 4 shows the effects of CaO content on the photocatalytic activity of the NiO–CaO samples. The samples were heated at 700 °C for 6 h, and the fixed visible-light irradiation time for every experiment was 180 min. It is clear that the photocatalytic activity of the NiO–CaO samples increased strongly with the increase in the amounts of CaO doped into the sample. The activity of pure NiO was the lowest in the absence of CaO, with a photocatalytic efficiency of only 28.8% (Fig. 4a). When the mole

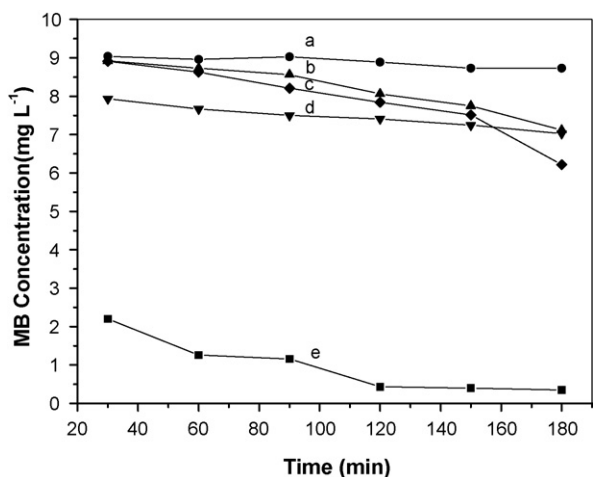


Fig. 3. Concentration of MB as a function of irradiation time under visible-light irradiation (a) MB photolysis, (b) P25, (c) CaO, (d) NiO, and (e) NiO-CaO obtained by mechanically mixing alone NiO and CaO calcined at 700 °C.

ratio of doped CaO was 1.0 (mole ratio of Ca/Ni), the photocatalytic efficiency was 96.5% (Fig. 4f), or about threefold that of pure NiO.

Fig. 5 shows the effects of duration of heat treatment on the effectiveness of the NiO-CaO photocatalysts. The heat treatment temperature was 700 °C, and the molar ratio of CaO and NiO was 1.0. The photocatalytic activity of NiO-CaO gradually increased with the increasing duration of heat treatment from 2 h up to 6 h. For a heat treatment of 6 h, the photocatalytic activity of NiO-CaO reached 96.5% (Fig. 5e). When heated at 700 °C for 2 h, the photocatalytic efficiency of NiO-CaO was only 27.1% (Fig. 5a). The reason may be that the longer time allowed better formation of the NiO and CaO semiconductors. As seen in Fig. 5, the NiO-CaO photocatalyst was highly sensitive to heat treatment time.

To evaluate the reusability of the NiO-CaO photocatalyst, the photocatalyst was tested 5 times in repetition under the same experimental conditions. As seen in Fig. 6, the oxidation of MB in the photocatalytic reaction gradually decreased with the number of reuses of the catalyst. By the fifth test, the photocatalytic efficiency of the NiO-CaO sample had decreased to 81.5%. Therefore, the reusability of the NiO-CaO photocatalyst needs further improvement.

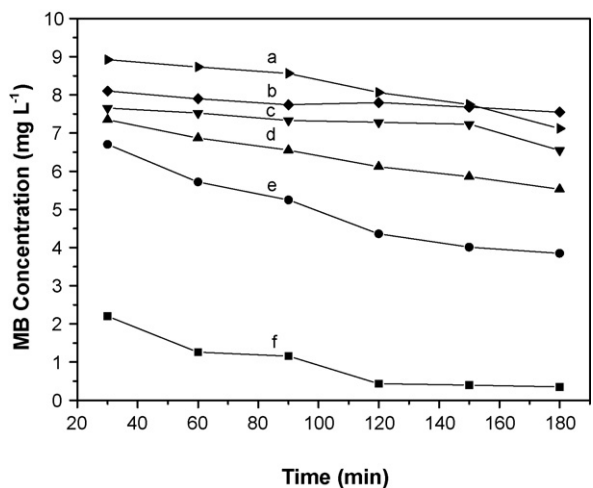


Fig. 4. Effects of amounts of doped-CaO on the photocatalytic degrading of MB under visible-light irradiation for the NiO-CaO samples obtained by mechanically mixing alone NiO and CaO calcined at 700 °C. The molar ratio of CaO/NiO is (a) 0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 0.7, and (f) 1.0.

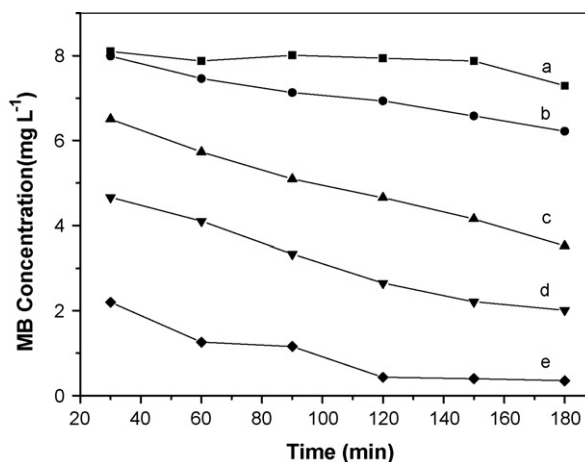


Fig. 5. Effect of heat treatment time on the photocatalytic degrading of MB under visible-light irradiation for the NiO-CaO samples obtained by mechanically mixing alone NiO and CaO calcined at 700 °C. The time is (a) 2, (b) 3, (c) 4, (d) 5, and (e) 6 h.

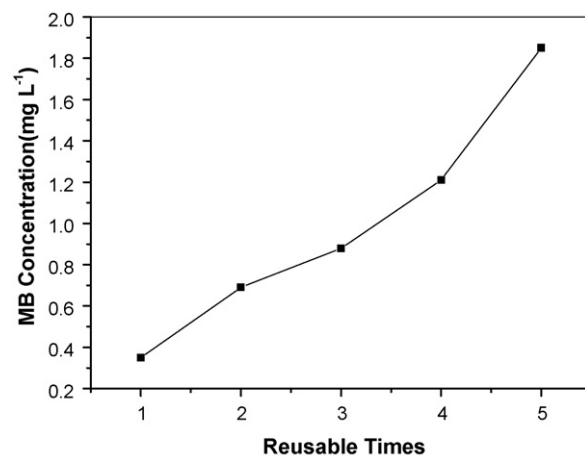


Fig. 6. The reusability of NiO-CaO obtained by mechanically mixing alone NiO and CaO calcined at 700 °C.

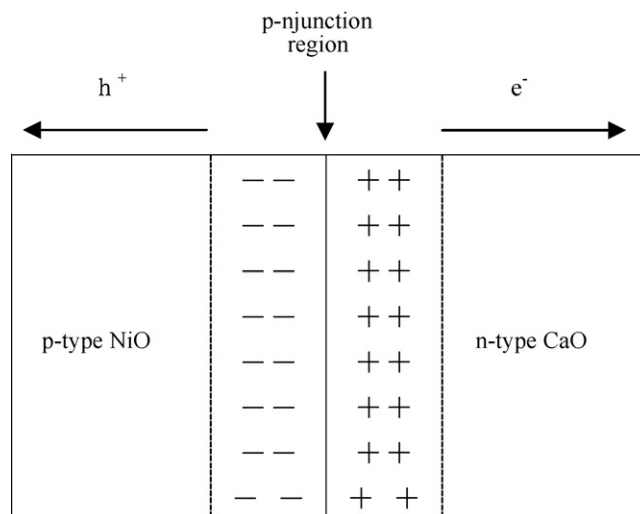


Fig. 7. p-n junction formation model and the schematic diagram of electron-hole separation process.

One possible reason for the higher photocatalytic activity of the NiO–CaO samples is suggested by the data. Fig. 7 depicts the p–n junction formation model and the schematic diagram of electron–hole separation process on the surface of a NiO–CaO sample. Since NiO is a p-type semiconductor and CaO is an n-type semiconductor, many micro p–n junction CaO/NiO photocatalysts will be engendered at the interface of the NiO and CaO nanoparticles when CaO is doped into NiO nanoparticles. At equilibrium, an inner electric field forms that makes the NiO p-type semiconductor regions assume negative charges while the CaO regions have positive charges. Under visible-light irradiation, electron–hole pairs may be generated on the surface of the CaO n-type semiconductor. In response to this inner electric field, the holes flow into the negative field and the electrons move to the positive field. Therefore, the photogenerated electron–hole pairs will be effectively separated by the p–n junction formed in the CaO/NiO. As a result, the CaO/NiO p–n junction photocatalyst shows a high photocatalytic activity [17].

4. Conclusions

In summary, NiO–CaO composite photocatalysts were prepared by a simple mechanical mixing method. The photocatalytic activity of the produced NiO–CaO photocatalysts was higher than that of either pure CaO or NiO. The reasons for the improved photocatalytic activity of the NiO–CaO samples was explored and has been tentatively attributed to an effective separation of photoelectrons and holes generated by the p–n junction formed in the NiO/CaO photocatalyst.

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