Flammable gases produced by TiO₂ nanoparticles under magnetic stirring in water

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Abstract: The friction between nanomaterials and Teflon magnetic stirring rods has recently drawn much attention for its role in dye degradation by magnetic stirring in dark. Presently the friction between TiO₂ nanoparticles and magnetic stirring rods in water has been deliberately enhanced and explored. As much as 1.00 g TiO₂ nanoparticles were dispersed in 50 mL water in 100 mL quartz glass reactor, which got gas-closed with about 50 mL air and a Teflon magnetic stirring rod in it. The suspension in the reactor was magnetically stirred in dark. Flammable gases of 22.00 ppm CO, 2.45 ppm CH₄, and 0.75 ppm H₂ were surprisingly observed after 50 h of magnetic stirring. For reference, only 1.78 ppm CO, 2.17 ppm CH₄, and 0.33 ppm H₂ were obtained after the same time of magnetic stirring without TiO₂ nanoparticles. Four magnetic stirring rods were simultaneously employed to further enhance the stirring, and as much as 30.04 ppm CO, 2.61 ppm CH₄, and 8.98 ppm H₂ were produced after 50 h of magnetic stirring. A mechanism for the catalytic role of TiO₂ nanoparticles in producing the flammable gases is established, in which mechanical energy is absorbed through friction by TiO₂ nanoparticles and converted into chemical energy for the reduction of CO₂ and H₂O. This finding clearly demonstrates a great potential for nanostructured semiconductors to utilize mechanical energy through friction for the production of flammable gases.

Keywords: friction; magnetic stirring; catalysis; CO₂ reduction; TiO₂

1 Introduction

Mechanical energy is abundant in ambient environments and is widely harvested as electricity on large scale through hydroelectric generation, wind power generation, and tidal power generation, etc. In recent years, there has been a growing interest in utilizing mechanical energy as a clean energy for more applications. For instance, piezoelectric nanomaterials, especially those of one- and two-dimensions, undergo considerable deformation under vibrations with piezopotentials generated across them [1], which subsequently induce such redox reactions as degradation of organic pollutants [2–6] and hydrogen production [7–9]. A technology known as piezocatalysis has thus

emerged, which aims to harvest mechanical energy in ambient environments through piezoelectric nanomaterials for chemical reactions and has been extensively investigated [10, 11].

Piezoelectric nanomaterials are mostly driven by ultrasonic vibrations for piezocatalysis. As ultrasonic vibrations are actually not common in ambient environments, piezocatalysis driven by low-frequency motions should also be explored from the viewpoint of energy harvest [12]. For this reason, magnetic stirring has often been adopted to stimulate piezoelectric nanomaterials for piezocatalysis. It has to be admitted that, however, magnetic stirring is much less effective than ultrasonic vibrations for piezocatalysis. Under ultrasonic vibrations, piezoelectric nanomaterials are

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able to produce hydrogen from water, and degrade organic dyes very quickly. While for piezocatalysis driven by magnetic stirring, only very slow dye degradations have been reported for some piezoelectric nanomaterials up to date [13–16].

Very recently, magnetic stirring has been discovered to be able to drive nanomaterials to degrade organic pollutants in a quite unexpected way: For $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$ (BST) nanoparticles under magnetic stirring, the friction between BST and Teflon surface of magnetic stirring rods rather than the deformation of BST nanoparticles has been revealed responsible for the observed degradation of organic dyes [17]. Through friction, it should be possible for some non-piezoelectric materials, such as TiO_2 nanoparticles, to degrade organic dyes under magnetic stirring in dark. These non-piezoelectric materials have been quite neglected in researches on harvesting mechanical energy. More interestingly, as the friction between nanoparticles and Teflon magnetic stirring rods can be dramatically enhanced through increasing contents of nanoparticles and through employing multiple magnetic stirring rods simultaneously, highly accelerated degradation of organic dyes has been observed for BST nanoparticles [17], BiOIO_3 nanoparticles [18], zinc oxide nanorods [19], CdS nanowires [20], and Bi_2WO_6 nanoflowers [21] under magnetic stirring. These results clearly demonstrate that through friction, mechanical energy of low-frequency motions can be effectively converted by some nanomaterials to chemical energy, which has been termed as tribocatalysis [17] and should be highly interesting from the viewpoint of harvesting mechanical energy in ambient environments.

As an important commercial photocatalyst, TiO_2 nanoparticles are well known for their high stability and widely applied in photocatalysis. Presently, we have conducted a study to explore their capability for applications in tribocatalysis. To our great surprise, we have discovered that some flammable gases can be produced by TiO_2 nanoparticles under magnetic stirring in water. As a representative result, 30.04 ppm CO, 2.61 ppm CH_4 , and 8.98 ppm H_2 were produced after 50 h of magnetic stirring when an unusually large amount of 1.00 g TiO_2 nanoparticles were dispersed in 50 mL water and four magnetic stirring rods were simultaneously employed in magnetic stirring. It is

well known that the production of CO, CH_4 , and H_2 from CO_2 and H_2O is of great fundamental and practical importance and has been intensively pursued through various technologies, such as photocatalysis [22, 23]. The finding in this study as well as those previous ones should therefore suggest a great potential for nanostructured semiconductors to harvest mechanical energy through friction for environmental governing and clean energy production.

2 Experimental

Teflon magnetic stirring rods, of cylinder shape and the size of $\phi 8 \text{ mm} \times 25 \text{ mm}$, were commercially purchased and used in magnetic stirring. TiO_2 nanoparticles, a commercial photocatalyst known as Degussa P25, were also purchased and investigated in this study.

In a typical test, 1.00 g TiO_2 nanoparticles and 50 mL de-ionized water were first added into a quartz glass reactor (100 mL in volume). Then a Teflon magnetic stirring rod was placed in the reactor. With about 50 mL air in it, the reactor got gas-closed. The reaction system was kept in dark and the room temperature was kept at 25 °C. A magnetic stirrer was applied to drive the magnetic stirring rod in the reactor to rotate, and the rotating speed of the magnetic stirring rod was kept at 500 rpm. After some designated times of magnetic stirring, the gas inside the reactor was sampled and quantified through a gas chromatograph (GC-2014C, Shimadzu, Japan).

3 Results and discussion

Figure 1 shows a representative scanning electron microscopy (SEM) image taken for as-received TiO_2 nanoparticles. It can be seen that most nanoparticles are of a round shape and are around 30 nm in size. It should be pointed out that no detectable changes in appearance were observed for those nanoparticles after being participated in magnetic stirring tests for dozens of hours in this study. This is reasonable in that TiO_2 nanoparticles are well-known for their high stability. As a matter of fact, TiO_2 nanoparticles are usually magnetically stirred in photocatalytic experiments, in which they are stable in themselves in the course of magnetic stirring and can be used repeatedly.

Fig. 1 SEM micrograph taken for as-received TiO_2 nanoparticles.

Over a certain amount range of TiO_2 nanoparticles, the friction between TiO_2 nanoparticles and stirring rods in magnetic stirring should be enhanced with increasing amount of TiO_2 nanoparticles. So we dispersed a rather large amount of TiO_2 nanoparticles, 1.00 g, in 50 mL water to be magnetically stirred. With such enhanced friction between TiO_2 nanoparticles and stirring rods, as much as 22.00 ppm CO, together with 2.45 ppm CH_4 and 0.75 ppm H_2 , were surprisingly discovered after 50 h of magnetic stirring. Such an amount of CO had been quite unexpected. Obviously CO_2 in the air enclosed in the reactor must have dissolved in water and have been partially reduced to CO through the magnetic stirring.

To reveal the role of TiO_2 nanoparticles in the production of these flammable gases, a reference test had been conducted, in which no TiO_2 nanoparticles were dispersed in water in the reactor and only water was magnetically stirred. 1.78 ppm CO, together with 2.17 ppm CH_4 and 0.33 ppm H_2 were produced after 50 h of magnetic stirring in this reference test. There was only dynamic friction between the Teflon surface of the stirring rod and the reactor bottom in magnetic stirring in this test. Obviously, this friction must have resulted in the production of CO, CH_4 , and H_2 , which is difficult to understand at present and should shed a light to us into the complexity of chemical reactions in friction, or tribochemistry.

On the other hand, there exists a sharp contrast between the gases produced through 50 h of magnetic stirring with and without TiO_2 nanoparticles, as shown

in Fig. 2. With all the other conditions the same, the introduction of TiO_2 nanoparticles increased the production of CO in friction from 1.78 to 22.00 ppm while TiO_2 nanoparticles remained unchanged by themselves after the reaction. By definition, TiO_2 nanoparticles have acted exactly as a tribocatalyst in the production of CO through friction [24]. At the same time, the introduction of TiO_2 nanoparticles increased the production of H_2 by 127%, but increased the production of CH_4 by only 12.9%. So TiO_2 nanoparticles have very different catalytic effects on the production of these three kinds of flammable gases.

As a matter of fact, we had also conducted a special experiment using a home-made glass magnetic stirring rod, which was fabricated through inserting a Teflon magnetic stirring rod into a glass tube ($\phi 15 \text{ mm} \times 30 \text{ mm}$). With other conditions unchanged, 50 ml water dispersed with 1.00 g TiO_2 nanoparticles in the reactor was stirred through the glass magnetic stirring rod. 21.85 ppm CO, 2.11 ppm CH_4 , and 1.63 ppm H_2 were obtained after 50 h of magnetic stirring using this glass magnetic stirring rod. As there was no polymer involved in friction in this experiment, both CO and CH_4 obviously must have resulted from the reduction of CO_2 dissolved in water.

Employing multiple magnetic stirring rods in magnetic stirring has been found effective to accelerate

Fig. 2 Gases produced from water after 50 h of magnetic stirring: in one test, only 50 mL water was stirred using a Teflon magnetic stirring rod; in the other test, 1.00 g TiO_2 nanoparticles were dispersed in 50 mL water and stirred using a Teflon magnetic stirring rod.

dye degradation by magnetic stirring [17–21]. In this study, we have also conducted some tests to employ four magnetic stirring rods simultaneously to stir TiO_2 nanoparticles in water and some results are shown in Fig. 3. For the test of 50 h of magnetic stirring, 30.04 ppm CO , 2.61 ppm CH_4 , and 8.98 ppm H_2 were produced, whose productions of CO and H_2 were increased by 36.7% and by 11 times, respectively, when compared with those obtained for 50 h of magnetic stirring using a single stirring rod, as shown in Fig. 2. So such a simple modification in magnetic stirring effectively increased the production of flammable gases by TiO_2 nanoparticles under magnetic stirring in water. It is worthy to note the increase in the production of H_2 is especially impressive for this modification, which deserves some further investigations for the production of H_2 from water.

Figure 4 shows the stirring time dependence of the gases produced by TiO_2 nanoparticles under magnetic stirring using four magnetic stirring rods in water. The concentrations of CO and H_2 increase steadily with increasing stirring time, while the concentration of CH_4 almost remains unchanged over the stirring time range of 24–110 h. It suggests that CH_4 was mostly produced in the early stage and then the production was stopped, while the productions of CO and H_2 were not stopped and so their concentrations were continuously increased. The competition among the formation of these flammable gases is interesting and should be studied in details in future.

Fig. 3 Gases produced by TiO_2 nanoparticles under magnetic stirring in water after 24, 50, and 110 h of magnetic stirring, separately. Four magnetic stirring rods were simultaneously employed in the magnetic stirring.

Fig. 4 Magnetic stirring time dependence of the gases produced by TiO_2 nanoparticles under magnetic stirring using four magnetic stirring rods in water.

It is well known that a high energy input is required for the transformations from CO_2 and H_2O to CO , CH_4 , and H_2 [25]. It has thus been quite unexpected that these flammable gases can be produced in considerable amounts by TiO_2 nanoparticles under such mild magnetic stirring in water. Obviously, the mechanical energy of magnetic stirring must have been effectively absorbed by TiO_2 nanoparticles through friction and converted into chemical energy for producing the flammable gases. For two materials in dynamic friction, electron–hole pairs can be excited in one material by the mechanical kinetic energy it absorbs from the other material in friction [26]. Exactly based on such excitation of electron–hole pairs in BST, a tribocatalytic mechanism has recently been proposed for the degradation of organic dyes by BST nanoparticles under magnetic stirring [17]. Similarly, for the production of flammable gases by TiO_2 nanoparticles in this study, it is reasonable to assume that electron–hole pairs are excited in TiO_2 by the mechanical energy it absorbed through friction, which can be expressed as:

where e_{CB}^- represents an electron excited to the conduction band (CB), and h_{VB}^+ represents a hole formed in the valence band (VB).

Once electron–hole pairs are excited in TiO_2 , they are able to induce various redox reactions, including the reduction of CO_2 and H_2O , as well as the oxidation

of H_2O , as shown in Fig. 5. As a matter of fact, this process is quite similar to the photocatalytic reduction of CO_2 and H_2O by TiO_2 nanoparticles, except that electron-hole pairs are excited in TiO_2 by light irradiation for photocatalysis [27, 28].

Nowadays there has been a growing concern over CO_2 as a major contributor to global warming. For carbon capture and utilization (CCU), it is of great importance to transform CO_2 into valuable carbon based fuels and materials. For most transformations, however, a high energy input is required [25]. To avoid energy-related pollution, those clean energies, such as sunlight, should be first considered as the energy input for the transformations. Accordingly, there have been a huge number of studies devoted to photocatalytic reduction of CO_2 in the past decades [22, 23]. On the other hand, mechanical energy, as another important clean energy in ambient environments, has been quite neglected for the transformation of CO_2 . The results in this study have clearly demonstrated a convenient way for mechanical energy to be utilized through friction for the reduction of CO_2 and H_2O . Much more attention should be paid to mechanical energy for the establishment of a closed CO_2 cycle and for the production of flammable gases.

Fig. 5 Schematic illustration for the production of CO , CH_4 , and H_2 by TiO_2 nanoparticles under magnetic stirring in water.

4 Conclusions

A catalytic role of TiO_2 nanoparticles in producing flammable gases under magnetic stirring in water has been successfully revealed through a comparison experiment: for 1.00 g TiO_2 nanoparticles dispersed

in 50 mL water, as much as 22.00 ppm CO , together with 2.45 ppm CH_4 and 0.75 ppm H_2 were produced after 50 h of magnetic stirring; while only 1.78 ppm CO , together with 2.17 ppm CH_4 and 0.33 ppm H_2 were obtained after the same time of magnetic stirring without TiO_2 nanoparticles. A catalytic mechanism has been established, in which electron-hole pairs are excited in TiO_2 by mechanical energy absorbed through friction. As much as 30.04 ppm CO , 2.61 ppm CH_4 , and 8.98 ppm H_2 have been produced after 50 h of magnetic stirring using four magnetic stirring rods simultaneously, which should demonstrate a great potential for nanostructured semiconductors to harvest mechanical energy through friction for the production of flammable gases.

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