Sonochemical Hydrogen Production Efficiently Catalyzed by Au/TiO_2

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Au/TiO_2 was used as a highly efficient sonocatalyst to produce H_2 from water or aqueous solutions. Au/TiO_2 significantly increased the yields of $H^{\bullet}$ and $^{\bullet}OH$ radicals in the sonolysis of water. Product analysis and isotope evidence indicated that hydrogen molecules derived from methanol/water solutions were formed by three pathways: (1) recombination of two $H^{\bullet}$ atoms from the cleavage of water molecules, (2) H-abstraction from methanol by $H^{\bullet}$ generated by water cleavage, and (3) thermal reforming of methanol. The relative importance of each pathway was assessed by carefully analyzing the hydrogen-isotope composition of the evolved hydrogen gas using a modified gas chromatograph. The source of hydrogen in the H_2 evolved from methanol/water solutions during sonolysis was also addressed. Data showed that, although the addition of methanol in the presence of Au/TiO_2 resulted in a 12-fold increase in the rate of H_2 evolution, nearly half of the hydrogen atoms were nevertheless derived from water molecules. Control studies of H_2 formation in the presence of bare TiO_2 and in the absence of a catalyst were also performed. In both cases, the compositions of evolved hydrogen gas were similar to that of the Au/TiO_2 system, although hydrogen evolution was much slower. These findings reveal that Au nanoparticles on the TiO_2 surface effectively catalyze water cleavage and methanol reforming.

1. Introduction

The catalytic properties of gold nanostructured materials have attracted much attention since the pioneering work by Haruta et al.[1] Au-nanoparticle-loaded TiO_2 (Au/TiO_2) exhibits remarkable catalytic activity and selectivity toward a variety of reactions, such as low-temperature CO oxidation, partial oxidations of hydrocarbons, selective oxidations of alcohols, and hydrogenation.[1−4] More recently, it has also been reported that Au/TiO_2 could be used to realize visible-light-to-energy conversion[5] and could potentially be used in solar cells[6,7] and the photochemical elimination of organic contaminants.[8] In addition to the above approaches, we recently reported the first example of sonocatalysis by Au/TiO_2.[9] Specifically, when supported on TiO_2, 2-nm-diameter gold nanoparticles (NPs) exhibit high catalytic activity for the sonocatalytic degradation of organic dye pollutants.

Application of ultrasound in chemistry has been extensively studied, and commercial instruments for industrial purposes are readily available. Recently, more efficient catalysis has been realized through combination of ultrasonication with NPs.[10−15] Examples include the sonodegradation of organic pollutants catalyzed by TiO_2 NPs,[10,11,14] sonophotocatalysis by TiO_2,[11−15] and sonocatalytic hydrogen production.[16] However, less attention has been paid to understanding the detailed mechanism of catalysis by metal oxides, particularly by noble-metal-NP-loaded metal oxides, in sonolysis.

On the other hand, noble-metal-NP-loaded metal oxides such as Au/TiO_2 and Pt/TiO_2 have also attracted much attention in hydrogen production such as photocatalysis[17−21] and catalytic dehydrogenation.[18,22,23] In photocatalysis, to achieve high quantum yields, many model systems have included methanol as a sacrificial reagent to scavenge photogenerated holes and $^{\bullet}OH$ radicals, an intermediate generated by the reaction of holes with water molecules.[17−21] However, reactions of methanol (and other sacrificial reagents) in these systems are rather complicated. Recent studies have shown that H_2 is also formed in the reforming of methanol over metal-loaded TiO_2 materials such as Au/TiO_2, Pt/TiO_2, Cu/TiO_2, and Pd/TiO_2 under light irradiation.[18,22,23] Therefore, although sacrificial reagents are routinely used in hydrogen production, the pathways for hydrogen formation deserve careful consideration: How much of the evolved hydrogen is derived from water, and how important is each pathway for H_2 molecule formation? Both of these critical questions are also closely related to the function of Au NPs on the surface of TiO_2. However, so far, neither question has been addressed in detail.

In this study, Au/TiO_2 was used for the first time in the sonocatalytic production of hydrogen, and the details of hydrogen evolution under various conditions were examined. Based on the detection of intermediate radicals, products of methanol, and isotopic compositions of evolved hydrogen, pathways for H_2 formation during catalyzed and noncatalyzed sonolysis are proposed, and the sources of hydrogen atoms in the evolved hydrogen gas are addressed. All of the evidence points to a mechanism whereby Au NPs on the TiO_2 surface significantly enhance both the thermal cleavage of water and the reforming of methanol in the gas phase of the cavitation bubbles.

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2. Experimental Section

2.1. Chemicals. TiO_2 (P25, 80% anatase and 20% rutile; average diameter $\approx$ 21 nm, BET area $\approx$ 50 m^2 g^{-1}) was purchased from Degussa Co. $HAuCl_4 \cdot 4H_2O$ (AR), activated Al_2O_3 (for gas chromatography use, 60−80 mesh), methanol (AR), ethanol (AR), dimethyl sulfoxide (DMSO, AR), and glycerol (AR) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) and 3-carbamoyl-2,2,5,5-tetramethyl-1-pyrroline 1-oxide (CTMPO) were purchased from Sigma-Aldrich Co. D_2O (99.9% D) was obtained from CIL Inc. H_2, CO, and CH_4 standard gases were obtained from Beijing Hua Yuan Gas Chemical Industry Co., Ltd. Deionized water was used in all experiments.

2.2. Methods. Au NPs were loaded onto the surface of TiO_2 NPs (unless otherwise indicated, TiO_2 refers to Degussa P25 in this work) following the photoreduction method described previously[9] and summarized here. TiO_2 (1.0 g), methanol (0.50 mL), and a calculated amount of $HAuCl_4$ were dispersed in 100 mL of water in a Pyrex cylindrical bottle (final pH = 3.1). After the dispersion had been ultrasonicated for 15 min and stirred in the dark for 30 min, it was irradiated with a 500-W xenon lamp for 4 h to load Au nanoparticles onto the TiO_2. Next, the dispersion was filtered, and the as-prepared catalyst was washed with water three times. Conversion of $HAuCl_4$ to Au(0) was tracked by UV−vis spectroscopy. The sonocatalytic activity of Au/TiO_2 increased with gold content and reached a plateau at ~0.5 wt % (Figure S1 in the Supporting Information). Therefore, Au/TiO_2 with 0.75 wt % Au was used for this study. The average diameter of the Au NPs was 2.0 ± 0.5 nm as measured by transmission electron microscopy.[9] Citrate-stabilized Au NPs (3.5 ± 0.7 nm in diameter) were also prepared according to the literature method.[24]

Sonolysis reactions were carried out using a commercial 40-kHz transducer (UP2200H, Nanjing Panda Electronics Co. Ltd.) operating at 50 W. According to a calorimetric method,[25] the average power intensity of ultrasound was 0.045 W/mL. The reaction temperature was maintained at 21−25 °C using circulating water. Because rates of hydrogen evolution increased with Au/TiO_2 dosage and reached a plateau level at ~0.3 g L^{-1} (Figure S2 in the Supporting Information), 0.5 and 1.0 g L^{-1} catalyst dosages were chosen. A 250 mL Pyrex flask that was filled with 150 mL of the reactants and fixed close to the transducer was used as the reactor. The flask was sealed with a rubber stopper and purged with Ar for 30 min before each reaction. Unless otherwise emphasized, all reactions were performed under Ar.

For electron spin resonance (ESR, Bruker E500) experiments, 5 mL of water containing 5 mg of catalyst and 8 mM DMPO was irradiated with ultrasound; an Ar flow was maintained to keep the system isolated from air. After a certain regular interval, an aliquot was taken for EPR measurements immediately after sampling. Great care was taken to minimize experimental errors. Key parameters are as follows: center field = 3480 G, sweep width = 150.0 G, microfrequency = 9.77 GHz, and power = 12.6 mW. The WinSim program[26] was used for spectral simulation. Concentrations of DMPO−OH and DMPO−H were calculated based on the standard calibration curve of peak area vs concentration of CTMPO.[27]

Quantification of the evolved gas was performed with a gas chromatograph (GC, Techcomp GC7890) equipped with a thermal conductivity detector (TCD). A 5-Å molecular sieve packed column [3 m (length) × 3 mm (o.d.) × 2 mm (i.d.)] with Ar as the carrier gas was used to separate H_2, CH_4, and CO. To quantify H_2, HD, and D_2, a column [2 m (length) × 3 mm (o.d.) × 2 mm (i.d.)] packed with Fe_2O_3-modified activated Al_2O_3 was prepared following the published method[28] with some optimization. The protocol for modifying activated Al_2O_3 with Fe_2O_3 is summarized as follows: $FeCl_3$ solution (30 mL, 0.139 mol) was added dropwise to a dispersion of active Al_2O_3 (60 mL, 0.368 mol) under vigorous stirring; meanwhile, 4 M ammonium hydroxide was added to keep the pH between 3 and 4. Next, another 10 mL of concentrated ammonium hydroxide solution (~14 M) was added. More water was added when the dispersion turned viscous. The dispersion was stirred for 2 h, filtered, washed three times, and dried under reduced pressure. The solid material was dried at 120 °C for 24 h, was then rescreened to 60−100 mesh, and finally was calcined at 500 °C for 4 h to convert $Fe(OH)_3$ into Fe_2O_3. For the separation of H_2, HD, and D_2 by GC, temperatures of the inlet and the detector were both set to 50 °C; liquid nitrogen was used to maintain the temperature of the column (77 K), and highly purified Ne was used as the carrier gas. A typical chromatogram is shown in Figure S3 in the Supporting Information. D_2 standard gas was obtained by reaction of D_2O with Na metal. Because HD standard gas was unavailable, the algebraic average of the correction factors of H_2 and D_2 was used for quantifying HD. Formaldehyde in aqueous solutions was analyzed using the acetylacetone spectrophotometric method.

TABLE 1: Rates (μmol h^{-1}) of H_2 Evolution in Sonolysis Reactions[a]

catalyst	water	methanol/water[b]	ethanol/water[c]	glycerol/water[d]	DMSO/water[d]
no catalyst	0.4	3.4	0.8	1.0	2.8
TiO_2	1.3	15.1	25.0	9.5	12.8
Au/TiO_2	21.6	282.3	198.1	31.4	39.1

[a] Catalyst dosage = 0.5 g L^{-1}. [b] 4% (v/v). [c] 1.9% (v/v). [d] 0.67% (v/v).[29]

3. Results and Discussion

3.1. H_2 Evolution Catalyzed by Au/TiO_2. Au-nanoparticle-loaded TiO_2 (Au/TiO_2) was used in sonocatalytic H_2 production. Very fast H_2 evolution from water (21.6 μmol h^{-1}; see Table 1) was obtained in the presence of Au/TiO_2 during sonolysis, whereas in the presence of bare P25 TiO_2, H_2 evolution was much slower (1.3 μmol h^{-1}), and in the absence of any catalyst, the rate was extremely low (0.37 μmol h^{-1}). It should be noted here that no H_2 was detected without ultrasound, indicating that H_2 formation was caused by ultrasound rather than by indoor light. The effect of Au/TiO_2 was further examined in sonolysis of aqueous solutions of methanol, ethanol, glycerol, and DMSO, which are known to scavenge hydroxyl radicals and have been used as sacrificial reagents in H_2 production.[17−21] Au/TiO_2 significantly accelerated H_2 evolution in all of these cases, as expected. For example, compared to bare TiO_2, Au/TiO_2 accelerated H_2 evolution by 18-fold using a 4% (v/v) methanol/water solution. Clearly, Au/TiO_2 increased the energy efficiency of the ultrasonic treatment.

In the absence of a catalyst, the rate of H_2 evolution during sonolysis of pure water (0.37 μmol h^{-1}; see Table 1) was close to that reported by Sasikala et al,[16] where a total amount of ~0.14 μmol of H_2 was evolved within 50 min, showing that the experimental conditions were similar. However, the present Au/TiO_2 was ~20 times more effective than the previously reported (metal oxide) catalyst.[16] The enhancement of catalytic activity by Au loading also far exceeds the negative effect of a (modest) size increase that, according to Sasikala et al.,[16] might reduce the activity of the catalyst. Actually, as far as we know,

Au/TiO_2 has been the most efficient sonocatalyst for both H_2 formation and degradation of azo dyes.[9]

Data in Table 1 also show that methanol and ethanol were more efficient sacrificial reagents for H_2 evolution than glycerol and DMSO when Au/TiO_2 was used as the sonocatalyst. In contrast, in the presence of bare TiO_2 or in the absence of any catalyst, although the four sacrificial reagents also accelerated H_2 evolution, any differences in their effects on H_2 evolution were insignificant. This shows that the activity of Au/TiO_2 in sonocatalytic H_2 production strongly depends on the volatility of the sacrificial reagents.

To examine the stability of Au/TiO_2, three repeated runs of the reaction were performed (Supporting Information, Figure S4) in which H_2 evolution retained a high and reproducible rate. The total turnover number (TTN, molecules of H_2 per atom of surface-loaded Au) reached 506 (mol H_2/mol Au) within 15 h. These results indicate that Au/TiO_2 was very stable under our experimental conditions, in agreement with a previous study.[9]

Control experiments showed that (3.5 ± 0.7)-nm-diameter citrate-stabilized Au NPs[24] alone exhibited little sonocatalytic activity (data not shown). When citrate-stabilized Au NPs and bare TiO_2 were both used in the sonolysis of a 4.0 vol % methanol solution, the H_2 evolution rate was 14.5 μmol h^{-1}, close to that of bare TiO_2 (Table 1), suggesting that Au NPs have a high sonocatalytic activity for H_2 evolution only when attached to the TiO_2 surface.

3.2. Detection of Radicals during Sonolysis. The propagation of ultrasonic waves through water causes numerous tiny cavitation bubbles, which, during collapse, produce local "hot spots" of high temperature and high pressure (e.g., 5000 K, 1000 atm).[30] Under these extreme conditions, water molecules undergo homolytic cleavage and form $^{\bullet}OH$ and $H^{\bullet}$ radicals (eq 1). Subsequent recombination of $^{\bullet}OH$ and $H^{\bullet}$ radicals gives rise to H_2 and H_2O_2 (eqs 2−4).[11,31] A spin trap such as DMPO can be used to capture the radicals, resulting in the formation of long-lived spin adducts (eqs 5 and 6;[32] Figure S5 in the Supporting Information) that can be detected by the electron spin resonance (ESR) spectroscopy. As shown in Figure 1, DMPO−OH has a characteristic four-line hyperfine structure (peak height ratio 1:2:2:1, curve a), DMPO−H has nine lines (curve b), and a mixture of the two spin adducts is also composed of nine lines (curves c and d).

$$H_2O \xrightarrow{\text{heat}} H^{\bullet} + {}^{\bullet}OH \quad (1)$$

$$H^{\bullet} + {}^{\bullet}OH \rightarrow H_2O \quad (2)$$

$$H^{\bullet} + H^{\bullet} \rightarrow H_2 \quad (3)$$

$$2{}^{\bullet}OH \rightarrow H_2O_2 \quad (4)$$

$${}^{\bullet}OH + DMPO \rightarrow DMPO{-}OH, \quad k = 4.9 \times 10^9\ M^{-1}\ s^{-1} \quad (5)$$

$${}^{\bullet}H + DMPO \rightarrow DMPO{-}H, \quad k = 3.8 \times 10^9\ M^{-1}\ s^{-1} \quad (6)$$

Both $^{\bullet}OH$ and $H^{\bullet}$ radicals were generated in the sonolysis of water in the presence of Au/TiO_2, in the presence of bare TiO_2, and in the absence of a catalyst (Figure 2). In the presence of Au/TiO_2, average rates of formation of DMPO−OH and DMPO−H within the first 10 min were 0.32 and 0.12 μM min^{-1}, respectively, whereas in the presence of bare TiO_2, the corresponding rates were 0.11 and 0.033 μM min^{-1}. Because recombination of two $H^{\bullet}$ radicals forms a H_2 molecule (eq 3), a higher rate of formation of $H^{\bullet}$ in the presence of Au/TiO_2 than in the presence of bare TiO_2 is consistent with the results in Table 1, which shows that Au/TiO_2 greatly accelerated H_2 formation from pure water. Therefore, Au/TiO_2 greatly enhanced the thermal cleavage of water (eq 1) in sonocatalysis. It can also be seen from Figure 2 that bare TiO_2 actually enhanced the thermal cleavage of water, too, compared to the noncatalytic system.

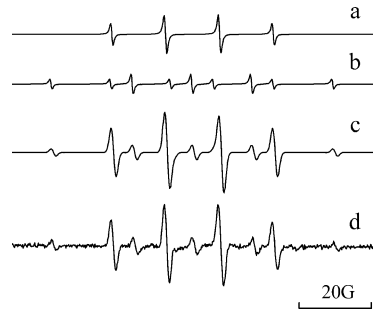

Figure 1. Simulated spectra of (a) DMPO−OH, (b) DMPO−H, and (c) a mixture of the two and (d) observed ESR signals.

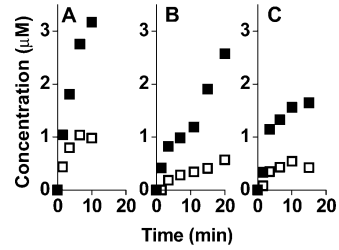

Figure 2. Evolution of (■) DMPO−OH and (□) DMPO−H by sonolysis of water (A) in the presence of Au/TiO_2, (B) in the presence of bare TiO_2, and (C) in the absence of a catalyst.[33] Conditions: Ar atmosphere, catalyst dosage of 1 g L^{-1}.

Complex mixtures of radicals were formed by the sonolysis of methanol/water mixtures under Ar atmosphere. These radicals included $H^{\bullet}$, $^{\bullet}OH$, $^{\bullet}CH_3$, and $^{\bullet}CH_2OH$ (see Supporting Information, Figure S6, for a typical ESR spectrum). The ESR spectra were fitted with the WinSim program, and concentrations of DMPO−OH and DMPO−H were extracted. Yields of DMPO−OH and DMPO−H within the first 10 min of sonolysis and rates of H_2 formation are plotted as functions of methanol concentration in Figure 3. At low methanol concentration [e.g., <10% (v/v)], both spin adducts were detected. The yield of DMPO−OH decreased sharply with methanol concentration, whereas the yield of DMPO−H decreased only slowly with methanol concentration. The rate of H_2 evolution increased steeply with methanol concentration when the methanol concentration was lower than ~5% (v/v), reaching a maximum at ~5% (v/v) and gradually decreasing with any further increase in methanol concentration.

One important reason for the large enhancement of H_2 evolution upon addition of methanol at methanol concentrations lower than 5% (v/v) (Figure 3) is that methanol efficiently captures $^{\bullet}OH$ radicals (eq 7[34]), resulting in the effective inhibition of recombination between $^{\bullet}OH$ and $H^{\bullet}$ (eq 2). This can be understood in terms of the high volatility of methanol and the large rate constant associated with the reaction between

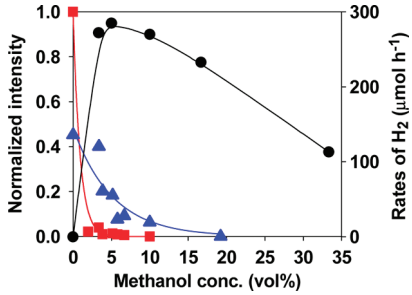

Figure 3. Formation of (■) DMPO−OH and (▲) DMPO−H after 10 min of sonolysis of water in the presence of Au/TiO_2 (0.5 g/L) and (●) rate of H_2 evolution as functions of methanol concentration.

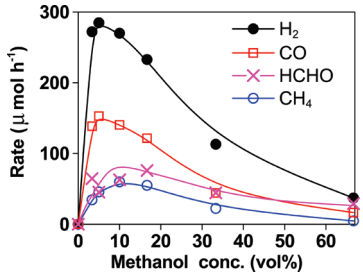

Figure 4. Rates of formation of major products in the sonolysis of water/methanol mixtures in the presence of Au/TiO_2 (0.5 g/L).

methanol and •OH (eq 7): Efficient scavenging of •OH by methanol occurs both in the interior and in the interfacial zone of the cavitation bubbles (see section 3.5). Further, the yield of DMPO−OH depends not only on the concentration of DMPO, but also on the concentration of other •OH scavengers. A rough calculation illustrated in Figure S7 (Supporting Information) shows that the fraction of •OH scavenged by DMPO decreased drastically with increasing methanol concentration. Our experimental observations (Figure 3) showed that the yield of DMPO−OH declined in line with a similar trend, but faster than the calculated results. In contrast to DMPO−OH, the weaker dependence of the yield of DMPO−H on methanol concentration (Figure 3) can be attributed to the inefficient scavenging of •H by methanol (eq 8[34]), which is consistent with the calculated results (Supporting Information, Figure S7).

$$^{\bullet}OH + CH_3OH \rightarrow H_2O + {}^{\bullet}CH_2OH, \quad k = 9.7 \times 10^8\ M^{-1}\ s^{-1} \qquad (7)$$

$$H^{\bullet} + CH_3OH \rightarrow H_2 + {}^{\bullet}CH_2OH, \quad k = 2.6 \times 10^6\ M^{-1}\ s^{-1} \qquad (8)$$

3.3. Products of Methanol during Sonolysis. Four major products, namely, H_2, CO, HCHO, and CH_4, were detected in the sonolysis of water/methanol mixtures under Ar atmosphere[35] in the presence of Au/TiO_2. Their formation rates varied similarly with the methanol concentration, that is, they all first increased steeply, passing through peak values at ~5% (v/v) of methanol (Figure 4).

During sonication, HCHO was formed by H-abstraction of methanol mainly by •OH and H• radicals (eq 9).[35,36] Meanwhile thermal cleavage of methanol generated methyl radicals which then formed CH_4 (eq 10).[35,36] Nevertheless, the four major products, H_2, CO, HCHO and CH_4, were actually derived from both oxidation (by •OH and H• by water cleavage, eq 1) and thermal reforming of methanol.

$$CH_3OH \xrightarrow{\text{H-abstraction}} HCHO \qquad (9)$$

$$CH_3OH \xrightarrow{\text{heat}} CH_3^{\bullet} + {}^{\bullet}OH \qquad (10)$$

The catalytic activity of Au NPs on the TiO_2 surface was then investigated by comparing the products of methanol in the sonolysis of methanol solutions in the presence of Au/TiO_2, bare TiO_2, and in the absence of a catalyst (Figure 4 and Figure S8 in the Supporting Information). As in the Au/TiO_2 system, the formation rates of H_2, CO, HCHO, and CH_4 in the other two systems also increased with methanol concentration and passed through their maxims at ~5% (v/v) methanol. At the methanol concentration for the fastest H_2 evolution, the ratio of the rates of H_2, CO, HCHO, and CH_4 was 1.0:0.53:0.16:0.16 for Au/TiO_2, 1.0:0.51:0.22:0.14 for bare TiO_2, and 1.0:0.54:0.22:0.15 without a catalyst. The ratio of HCHO (to H_2) for the Au/TiO_2 system was lower, whereas the ratio of CH_4 (to H_2) was slightly higher than those of the other two systems. It can also be seen that the ratios of CO (to H_2) in the three systems were close to one other. Numerous reports showed that 2−3-nm Au NPs attached to TiO_2 surfaces exhibited high catalytic activity for CO oxidation.[3,4] In the present work, carried out under Ar (i.e., no dioxygen was present), the selective oxidation of CO was not observed.

3.4. Tracking the Source of Hydrogen with H/D Isotope Evidence. Based on analysis of intermediate radicals and products during the sonolysis of methanol solutions, three pathways are proposed for the formation of dihydrogen (H_2). These are pathway 1, the recombination of two H• atoms formed by the cleavage of water molecules; pathway 2, H-abstraction from methanol by H• generated by water cleavage; and pathway 3, thermal reforming of methanol. In this section, the relative importance of each pathway is assessed. This was done by analyzing hydrogen-isotope compositions of the H_2 gas evolved from methanol solutions containing deuterated reagents. As a prerequisite, the effect of ultrasound on the hydrogen-isotope composition of the gas phase had to be examined. To do this, a small amount of H_2 (or D_2) gas was deliberately added to the headspace of the reactor prior to sonolysis (see Figure S9 and the discussion in the Supporting Information). Under ultrasound irradiation, the product of H/D isotopic exchange, HD, was effectively undetectable; as the reaction was prolonged, the headspace of the reactor was actually filled with a mixture of H_2, D_2, and Ar, but still no HD was detected. This and other evidence[37] indicates that H/D exchange of hydrogen in the gas phase should be ignored under the present experimental conditions. Therefore, the isotope profile of each gas (i.e., H_2, HD, and D_2) was used to calculate its rate of formation during sonolysis of solutions of CH_3OH/D_2O or CD_3OD/H_2O in the presence of Au/TiO_2, in the presence of bare TiO_2, and in the absence of a catalyst.

As can be seen in Figure 5, the amount of each gas increased linearly with reaction time. The average rates ranged from 57 μmol h^{-1} for HD, to 37 μmol h^{-1} for D_2 and to 16 μmol h^{-1} for H_2 from a CD_3OD/H_2O solution (1:19 v/v, Figure 5A). The rates were 61, 35, and 22 μmol h^{-1} for evolution of HD, H_2, and D_2, respectively, from a CH_3OH/D_2O solution (1:19 v/v, Figure 5B). These rates correspond to the three pathways for hydrogen molecule formation. H_2 in Figure 5A and D_2 in Figure 5B are the products of recombination of two H• (or D•) radicals from water cleavage (pathway 1). HD in both panels is the

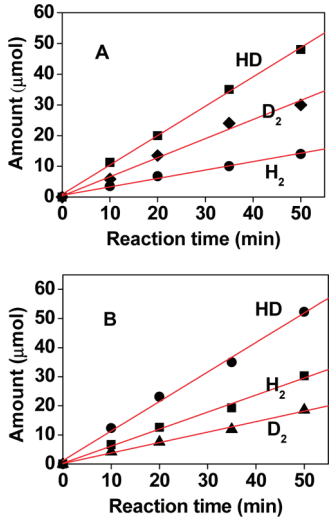

Figure 5. Formation of H_2, D_2, and HD by sonolysis of mixtures of (A) 19 mL of H_2O and 1 mL of CD_3OD and (B) 19 mL of D_2O and 1 mL of CH_3OH.[38] In both cases, Au/TiO_2 (1 g L^{-1}) was used.

product of H-abstraction (or D-abstraction) of methanol by H• (or D•) from cleavage of water (pathway 2). D_2 in panel A and H_2 in panel B are the products of thermal reforming of methanol (pathway 3). The total rates of all three pathways in panels A and B of Figure 5 were close (110 vs 118 μmol h^{-1}). This is reasonable, given that the deuterium kinetic effects become insignificant at the high temperatures [$k_H/k_D = \exp(-\Delta E_a/RT)$ approaches 1 as T increases] of the hot spots caused by ultrasound.[30] The ratio of the three pathways in Figure 5A is 1.0:3.5:2.3 for pathway 1 to pathway 2 to pathway 3. This also indicates that the ratio of H-atoms from H_2O to D-atoms from CD_3OD is 0.7:1.0. In Figure 5B, the ratio of the three pathways is 1.0:2.8:1.6 for pathway 1 to pathway 2 to pathway 3; the ratio of D-atoms from D_2O to H-atoms from CH_3OH is 0.8:1.0. Under sonication, isotope exchange between methanol and water was expected to occur. We speculate that its rate should be of the same order of magnitude as that of hydrogen evolution, so that, with respect to the time scale of the experiments of Figure 5, the isotopic composition of the liquid phase could be regarded as unchanged. Therefore, the above data indicate that all three pathways are important for hydrogen formation. During the sonolysis of aqueous methanol in the presence of Au/TiO_2, added methanol accelerated the rate of H_2 evolution by a factor of 12 (Table 1), but water was still an important source of hydrogen.

Anologously, sonolysis of CD_3OD/H_2O solutions in the presence of bare TiO_2 and in the absence of a catalyst was also performed (Supporting Information, Figure S10). The data indicated that pathway 3 was slightly more pronounced in the Au/TiO_2 system than in the other two systems, which suggested that the reforming of methanol was enhanced by Au NPs. Moreover, for both TiO_2 and noncatalytic systems, nearly half of the hydrogen atoms were also from water.

3.5. Mechanism of Au/TiO_2-Enhanced H_2 Evolution. The chemical effects of ultrasound are brought about by the high temperature and pressure during the violent collapse of the cavitation bubbles. The microbubbles are tens to hundreds of micrometers in diameter[30,39] and are filled with dissolved gas and solvent vapor. The interiors of these bubbles have the highest temperature—ca. 5000 K.[30] The interfacial zone is a liquid layer ca. 200−300 nm thick[30] that surrounds the collapsing cavitation bubbles. The temperature of the interfacial zone is over 1900 K.[30] The third region is the bulk solution, which is much less active.

Methanol is highly volatile and readily enters cavitation bubbles. It accelerates hydrogen evolution by capturing H• (eq 8) and scavenging •OH radicals (eq 7). Thermal reforming of methanol at the high temperatures present at the hot spots also generates H_2. Other sacrificial reagents, such as ethanol, glycerol, and DMSO in Table 1, also accelerated hydrogen evolution to different extents. Among them, ethanol is physically and chemically similar to methanol. It not only captures •OH and H• radicals but also readily enters cavitation bubbles for pyrolysis. Glycerol and DMSO are good •OH scavengers but are much less volatile (the boiling point of glycerol is 290 °C, and that of DMSO is 189 °C). Thus at low concentrations, both accelerate H_2 evolution mainly by scavenging •OH radicals in the interfacial zone, whereas the thermal reforming favored in the interior of the cavitation bubbles does not contribute significantly to hydrogen formation.[27] Therefore, higher rates of hydrogen evolution with methanol or ethanol than with glycerol or DMSO (see Table 1) as the sacrificial reagents are attributed to the enhanced thermal reactions (e.g., thermal cleavage of water and reforming of the alcohols) in the interior of the cavitation bubbles. For example, the rate of H_2 evolution in the presence of Au/TiO_2 was about 9 times larger with methanol than with glycerol. Furthermore, this acceleration was more significant in the presence of Au/TiO_2 than in the presence of bare TiO_2 (an increase of less than 2-fold) and in the absence of a catalyst (less than 3 times as fast). Therefore, thermal reactions in the interior of the cavitation bubbles were greatly enhanced by Au/TiO_2. This conclusion is also consistent with and supported by the facts that (1) hydrogen evolution was much faster by sonolysis of water in the presence of Au/TiO_2 than in the presence of bare TiO_2 and in the absence of a catalyst; (2) yields of •OH and H• were higher in the Au/TiO_2 system than in the other two systems; (3) deuterium isotope experiments indicated that, in all three systems, water was an important source of hydrogen; (4) deuterium isotope experiments also suggested that Au enhanced the thermal reforming of methanol; and (5) cleavage of water occurs mainly in the interior region, whereas the temperature of the interfacial zone (1900 K) is not high enough for water cleavage.[40]

The thickness of the interfacial zone of a cavitation bubble, 200−300 nm,[30] is 10−15 times the diameter of an individual TiO_2 NP (P25, $d = 21$ nm). Taking into account that each TiO_2 aggregate contains tens of individual particles (aggregation is often observed when a metal oxide material is dispersed in water, e.g., Au/TiO_2 in ref 9), Au/TiO_2 and TiO_2 are likely to extend through interfacial zones to the interiors of cavitation bubbles, thereby creating solid−gas interfaces. These solid−gas interfaces are responsible for the sonocatalytic activity. Therefore, the higher sonocatalytic activity of Au/TiO_2 compared to bare TiO_2 could be attributed to the high catalytic activity of gold NPs for the thermal reforming of methanol and cleavage of water.[41,42] This also explains why other noble-metal NPs such as Pt NPs on TiO_2 also exhibit sonocatalytic activity for hydrogen evolution (Supporting Information, Figure S11).

4. Conclusions

Au/TiO_2 greatly accelerates hydrogen evolution in the sonolysis of water and methanol solutions. To our knowledge, Au/TiO_2 is the most efficient sonocatalyst for H_2 formation and the degradation of azo dyes.[9] Three important pathways that are enhanced by using Au/TiO_2 are proposed for the formation of hydrogen molecules in aqueous methanol solutions. Although

the addition of methanol in the presence of Au/TiO_2 increased the rate of H_2 evolution by a factor of 12, nearly half of the hydrogen atoms were nevertheless derived from the water molecules. The high sonocatalytic activity of Au/TiO_2 can be attributed to its high activity for the thermal cleavage of water and the thermal reforming of methanol. The present study not only demonstrates the potential for applications of Au/TiO_2 in sonocatalysis, but also provides information relevant to understanding the mechanisms of hydrogen production in photocatalysis and catalytic dehydrogenation.

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Supporting Information Available: Chromatogram, data on H_2 evolution, analysis of ESR data, and more hydrogen isotope evidence. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Lett.* **1987**, 405.
(2) Daniel, M.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293.
(3) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.
(4) Min, B. K.; Friend, C. M. *Chem. Rev.* **2007**, *107*, 2709.
(5) Furube, A.; Du, L.; Hara, K.; Katoh, R.; Tachiya, M. *J. Am. Chem. Soc.* **2007**, *129*, 14852.
(6) Tian, Y.; Tatsuma, T. *J. Am. Chem. Soc.* **2005**, *127*, 7632.
(7) Yu, K.; Tian, Y.; Tatsuma, T. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5417.
(8) Chen, X.; Zhu, H.; Zhao, J.; Zheng, Z.; Gao, X. *Angew. Chem., Int. Ed.* **2008**, *47*, 5353.
(9) Wang, Y.; Zhao, D.; Ma, W.; Chen, C.; Zhao, J. *Environ. Sci. Technol.* **2008**, *42*, 6173.
(10) Wang, J.; Guo, B.; Zhang, X.; Zhang, Z.; Han, J.; Wu, J. *Ultrason. Sonochem.* **2005**, *12*, 331.
(11) Adewuyi, Y. G. *Environ. Sci. Technol.* **2005**, *39*, 3409.
(12) Harada, H. *Ultrason. Sonochem.* **2001**, *8*, 55.
(13) Davydov, L.; Reddy, E. P.; France, P.; Smirniotis, P. G. *Appl. Catal. B: Environ.* **2001**, *32*, 95.
(14) Adewuyi, Y. G. *Environ. Sci. Technol.* **2005**, *39*, 8557.
(15) Berberidou, C.; Poulios, I.; Xekoukoulotakis, N. P.; Mantzavinos, D. *Appl. Catal. B: Environ.* **2007**, *74*, 63.
(16) Sasikala, R.; Jayakumar, O. D.; Kulshreshtha, S. K. *Ultrason. Sonochem.* **2007**, *14*, 153.
(17) Chen, D.; Ye, J. *Chem. Mater.* **2007**, *19*, 4585.
(18) Wu, G.; Chen, T.; Su, W.; Zhou, G.; Zong, X.; Lei, Z.; Li, C. *Int. J. Hydrogen Energy* **2008**, *33*, 1243.
(19) Lu, D.; Hara, M.; Hisatomi, T.; Takata, T.; Domen, K. *J. Phys. Chem. C* **2009**, *113*, 17151.
(20) Higashi, M.; Abe, R.; Takata, T.; Domen, K. *Chem. Mater.* **2009**, *21*, 1543.
(21) Yao, W.; Huang, C.; Ye, J. *Chem. Mater.* **2009**, *22*, 1107.
(22) Meyer, S.; Saborowski, S.; Schäfer, B. *ChemPhysChem* **2006**, *7*, 572.
(23) Bowker, M.; Millard, L.; Greaves, J.; James, D.; Soares, J. *Gold Bull.* **2004**, *37*, 170.
(24) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Langmuir* **2001**, *17*, 6782.
(25) Wang, S.; Huang, B.; Wang, Y.; Liao, L. *Ultrason. Sonochem.* **2006**, *13*, 506.
(26) Duling, D. R. *J. Magn. Reson. B* **1994**, *104*, 105.
(27) Kondo, T.; Kirschenbaum, L. J.; Kim, H.; Riesz, P. *J. Phys. Chem.* **1993**, *97*, 522.
(28) Zhou, J.; Gao, L. *Atom. Energy Sci. Technol.* **2007**, *41*, 356.
(29) The volatility of DMSO is much lower than those of methanol and water. At [DMSO] < 20 vol %, the concentration of DMSO steam in the gas phase of the cavitation bubbles is low, and decomposition of DMSO occurs mainly by $^{\bullet}OH$ attack in the interfacial zone (see ref 27). The rate of this reaction increases with the concentration of DMSO and reaches the maximum at [DMSO] = 0.2 vol %. Therefore, 0.67 vol % (instead of 4.0 vol %) DMSO was used. With the same consideration, 0.67 vol % glycerol was also used.
(30) Suslick, K. S.; Hammerton, D. A.; Cline, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 5641.
(31) Halstead, C. J.; Jenkins, D. R. *Combust. Flame* **1970**, *14*, 321.
(32) Faraggi, M.; Carmichael, A.; Riesz, P. *Int. J. Radiat. Biol. Relat. Stud. Phys., Chem. Med.* **1984**, *46*, 703.
(33) Although H_2O is split into $^{\bullet}OH$ and $^{\bullet}H$ radicals in a 1:1 ratio (eq 1), the measured ratio of the concentrations of DMPO−OH and DMPO−H is ∼3:1. Similar results were also found in the following works: Makino, K.; Mossoba, M. M.; Riesz, P. *J. Phys. Chem.* **1983**, *87*, 1369. Makino, K.; Mossoba, M. M.; Riesz, P. *J. Am. Chem. Soc.* **1982**, *104*, 3537. This can be explained by the higher reactivity of $^{\bullet}OH$ with DMPO and other species and by the longer lifetime of DMPO−OH.
(34) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
(35) Buettner, J.; Gutierrez, M.; Henglein, A. *J. Phys. Chem.* **1991**, *95*, 1528.
(36) Krishna, C. M.; Lion, Y.; Kondo, T.; Riesz, P. *J. Phys. Chem.* **1987**, *91*, 5847.
(37) Fischer, C. H.; Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1986**, *90*, 222.
(38) The non-symmetrical results in panels A and B could be due to (1) small differences in methanol concentrations, arising from changes in the densities of H_2O, D_2O, CH_3OH, and CD_3OD (1.00, 1.11, 0.78, and 0.89 g mL^{-1}, respectively) and (2) a small kinetic isotope effect.
(39) Hung, H.; Hoffmann, M. R. *J. Phys. Chem. A* **1999**, *103*, 2734.
(40) Baykara, S. Z. *Int. J. Hydrogen Energy* **2004**, *29*, 1459.
(41) Haruta, M.; Ueda, A.; Tsubota, S.; Torres Sanchez, R. M. *Catal. Today* **1996**, *29*, 443.
(42) Nuhu, A.; Jorge, S.; Monica, G.; Andrew, W.; Ghulam, H.; Bowker, M. *Top. Catal.* **2007**, *44*, 293.

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