Catalysis Letters Vol. 92, Nos. 1–2, January 2004 (© 2004)

Photocatalytic properties of TiO_2 modified with gold nanoparticles in the degradation of 4-chlorophenol in aqueous solution

Alexander Orlov, David A. Jefferson, Norman Macleod, and Richard M. Lambert*

Chemistry Department, Cambridge University, Lensfield Road, CB2 1EW, UK

Received 29 May 2003; accepted 20 October 2003

The degradation in aqueous solution of 4-chlorophenol photocatalyzed by band-gap-irradiated TiO_2 modified with nanoscopic gold particles has been studied as a function of Au particle size by means of HREM, DRIFTS, BET, and reactor measurements. 4-chlorocatechol is observed as a reaction intermediate, and the results indicate that gold particle size is an important parameter. At low metal loadings, very small Au particles (<3 nm diameter) are particularly effective in enhancing the pseudo first-order rate constant. Higher Au loadings result in much larger particles and a loss of catalytic efficiency. These findings are discussed in terms of possible effects on the rate of production and recombination of photogenerated electrons and holes. It is shown that elimination of adsorbed hydroxyl groups that act as effective hole traps has a deleterious effect on the catalytic efficiency.

KEY WORDS: gold; TiO_2; photocatalytic decomposition; 4-chlorophenol; HRTEM; DRIFTS.

1. Introduction

Studies of the photocatalytic degradation of organic compounds on semiconductor surfaces have become an important area of catalytic research. Titanium dioxide, commonly regarded as one of the most active and stable photocatalysts for environmental applications, has been studied extensively (see e.g. [1–3] and references therein). Similarly, the photodegradation on various semiconductor surfaces [4–7] of the prototypical toxic groundwater pollutant 4-chlorophenol has attracted much attention. Efforts to improve the intrinsic efficiency of TiO_2 have included doping by transition metals, sensitization, application of composite semiconductors, and addition of noble metals [8]. The latter strategy shows promise and most efforts have focused on Pt/TiO_2 systems [9], although Au/TiO_2 and Ag/TiO_2 have also been investigated [10–16]. However, these studies have involved relatively large metal particles (~10 nm or more) and have tended not to address the effects of metal particle size. Moreover, they were primarily concerned with the use of colloidal titania rather than P-25 titania—which is one of the most active commercial materials available in large quantities at low cost.

Following the pioneering work of Haruta and his coworkers [17], it is now well known that ultradispersed Au particles (≤3.6 nm) can display unusual catalytic properties for a range of reactions. Subsequently, Goodman and coworkers elegantly demonstrated that this behavior correlates with the onset of a metal to nonmetal electronic transition in the Au particles [18]. The effects of Au nanoparticles of size <5 nm on the photocatalytic activity of titania are largely unknown. Here, we report on the photocatalytic decomposition by Au/TiO_2 of 4-chlorophenol in aqueous solution, particular attention being given to the effects of metal particle size. We show that small Au particles can induce a significant improvement in performance even at low gold loadings.

2. Experimental methods

2.1. Catalyst preparation and characterization

TiO_2 modified by gold particles was prepared by the deposition precipitation method established by Haruta *et al.* [17]. P-25-TiO_2 was obtained from Degussa Corporation (70% anatase and 30% rutile) and used without further treatment. After adjusting the pH of an aqueous solution of $HAuCl_4$ to the desired value with Na_2CO_3, the titania support was added and the mixture was stirred for 3 h. Most preparations were carried out at pH 7 (intended to produce below 5-nm gold particles [19]); some were also performed at pH <7 in order to vary the Au particle size. The solid product was washed with distilled water until the traces of chloride were undetectable by titration with silver nitrate. It was then calcined in air for 5 h at 300 °C, ground, and sieved to give catalyst grains below 45 μm. Unmodified TiO_2 was also subjected to similar heat and size-separation procedures to serve as a benchmark of the activity.

2.2. Photocatalytic experiments

The photocatalytic system was based on a 1000-W Xe lamp (ORIEL), the radiant flux from which was

---

* To whom correspondence should be addressed.
E-mail: rml1@cam.ac.uk

collimated, filtered once to remove infrared radiation, then again to eliminate radiation below 300 nm. Experiments in which a long-wavelength pass filter was used to eliminate UV radiation <400 nm confirmed that no photocatalytic activity was induced by the visible portion of the spectrum. Control experiments confirmed that (i) volatilization of 4-chlorophenol from aqueous solution and (ii) photolytic reactions in the absence of the catalyst were negligible. An on-line intensity monitor was used to compensate for intensity variation due to aging of the lamp. Reactions were carried out in a well-mixed heterogeneous batch reactor, which incorporated ports for sampling, oxygen injection, and a thermocouple. The system temperature was stabilized at 20 °C by a water recirculation bath connected to the outer jacket of the reactor. Oxygen was delivered to the reactor at the constant rate of 18 mL/min by means of a mass-flow controller.

In a typical experiment, the reactor was loaded with 100 mL of 200 mg/L of 4-chlorophenol solution and 100 mg of catalyst. The system was stirred in the dark for approximately 1.5 h to establish sorption/desorption equilibria before switching the lamp on. In line with common practice [1], progress of the reaction was followed by observing the rate of decay of the reactant. However, we also identified and monitored the time dependence of a reaction intermediate, 4-chlorocatechol. After starting the photocatalytic reaction, 0.4-mL aliquots were periodically withdrawn from the reactor over the course of the reaction, filtered through an acetate membrane, and transferred to vials for analysis.

Samples of 5 μL were analyzed by liquid chromatograph with UV–vis detector (HP-1050). The composition of the mobile phase was 95% H$_2$O with 0.1% of trifluoroacetic acid (TFA), and 5% acetonitrile with 0.1% of TFA; the flow rate was 0.6 mL/min. Analysis was carried at two wavelengths (282 and 254 nm) with a column temperature of 22 °C. 4-chlorocatechol was identified as a reaction intermediate by means of HPLC, in agreement with earlier work [1], its time dependence showing the characteristic maximum expected for such species.

2.3. *HRTEM, DRIFTS, and BET surface area measurement*

Specimens for electron microscopy were prepared by suspending them in acetone and transferring to a copper grid coated with an amorphous carbon support. HRTEM images were recorded on a JEOL JEM-3011 electron microscope operated at 300 keV. The JEM-3011 was fitted with a PGT energy-dispersive X-ray (EDX) solid-state detector incorporating Excalibur software. Particle size was determined by counting at least 50 particles.

Infrared spectroscopy experiments were performed with a Perkin-Elmer GX2000 spectrometer equipped with an MCT detector and a high-temperature DRIFTS cell (Thermo Spectra-Tech). Spectra were acquired at a resolution of 4 cm^{-1} typically averaging 32 scans. Catalyst samples were conditioned at 250 °C in flowing helium prior to data acquisition in order to remove weakly adsorbed water (the broad O–H stretch peak associated with this species masked other spectral features in this region).

Surface area measurements were carried out with Micromeretics Gemini 2360 surface area analyzer. Samples were degassed for at least 12 h prior to the measurements. BET surface area measurements on the catalyst samples and on pure untreated P-25 titania showed that the deposition precipitation technique had no measurable effect on the total surface area, which was ~48 m^2/g in every case.

3. Results

3.1. *Catalyst characterization*

Catalysts with a range of gold loadings were prepared at pH 7, and four of these with loadings of 0.55, 0.83, 2.78, and 5.58 at% Au were characterized by HRTEM/EDX, yielding information about chemical composition and metal particle-size distributions. Figure 1(a) shows a representative image obtained with a 5.58 at% Au catalyst—note the apparently good wetting interaction between the cubo-octahedral gold particle and the titania surface. EDX analyses indicated no detectable impurities; a typical spectrum is shown in figure 1(b). The labeled signals are all attributable to gold; the unlabeled signals on figure 1(b) can be attributed to either the titania support or the copper grid supporting the sample.

Figure 2(a) and (b) show HRTEM images obtained with 0.55 and 5.58 at% Au samples, respectively, which were examined in detail to obtain metal particle-size distributions, which are also shown in the figure. Similar observations were made on catalysts with 0.83 and 2.78 at% Au, and the results are summarized in figure 3 from which it can be seen that the mean Au particle size varied from 3.6 (lowest Au loading) to 4.8 nm (highest loading). These findings are consistent with the results obtained by Haruta *et al.* [19]. The average gold particle size obtained in our experiments was ~1 nm larger than that of comparable samples studied by Haruta *et al.*, who also found the Au particle-size dependence on gold loading [19]. The particle-size distribution remained relatively narrow except at the highest loading (5.58 at% Au) where significant agglomeration of gold nanoparticles was observed, resulting in the formation of composite particles up to 11 nm in size.

The DRIFTS data (figure 4) show that increased gold loading resulted in attenuation of the 3651 cm^{-1} band intensity, indicating elimination of hydroxyl groups from the titania surface at high Au loadings. This

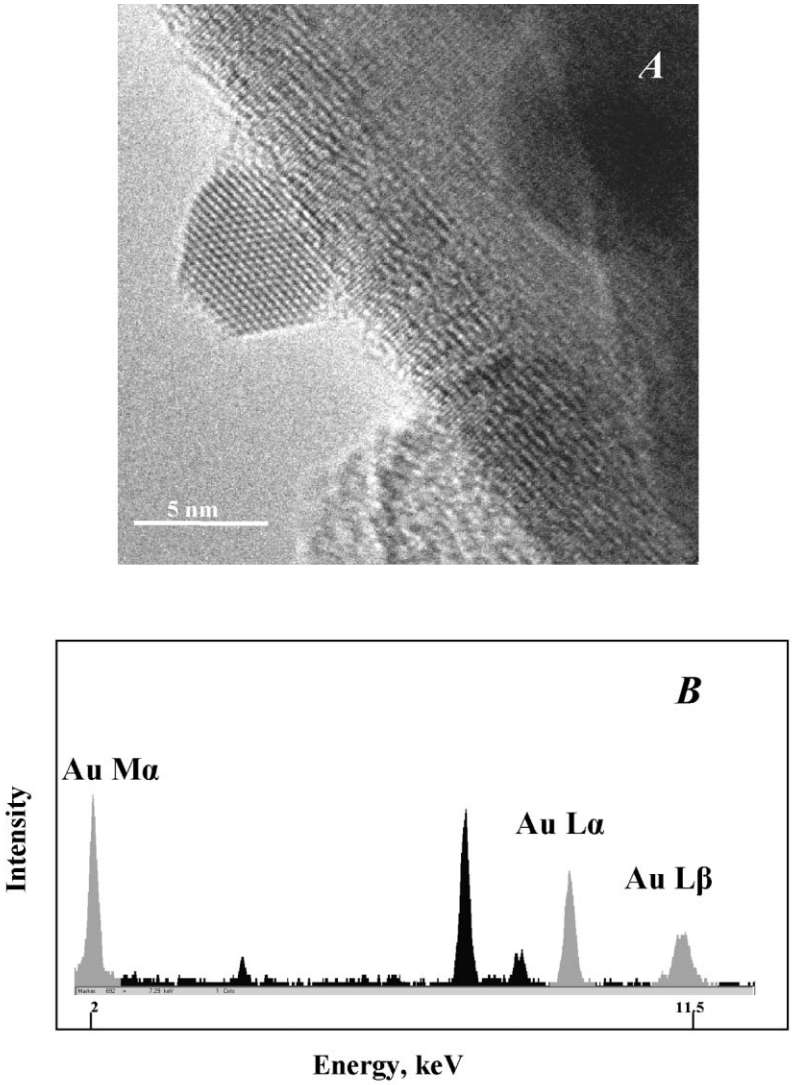

Figure 1. (a) TEM image of 5.58 at% Au sample. (b) EDS spectrum of 5.58 at% Au sample.

conclusion is strongly supported by the accompanying decrease in intensity of the 3413 cm^{-1} band, which is due to hydrogen-bonded water in interaction with surface hydroxyl groups [20].

3.2. Catalytic testing

Eight samples, synthesised at pH 7 but with different gold loadings, were prepared for testing: 0.0074, 0.06, 0.12, 0.42, 0.55, 0.83, 2.77, and 5.58 at% Au. A significant increase in catalytic activity relative to unmodified titania was observed for all samples, as illustrated in figure 5. Enhancement of 4-chlorophenol degradation was detectable, even at extremely low gold loading. A maximum in catalytic activity was observed at 0.42 at% Au, the pseudo first-order reaction rate exceeding that of bare titania by a factor of 2. Note that this corresponds to a very significant enhancement of performance and is of the same order or better than results reported by others for 4-chlorophenol and phenol degradation on Pt-loaded P-25 titania [21,22]. At the highest gold loadings, the activity fell, approaching that of unmodified titania. Additionally (figure 6), we observed a significant enhancement of 4-chlorocatechol production (a reaction intermediate), confirming that the observed enhancement of 4-chlorophenol disappearance is not due to light-induced hydrophilicity [23].

3.3. Effect of catalyst preparation conditions on catalytic activity

Given the observation that chloride impurity can adversely affect the catalytic activity of Au/TiO$_2$ catalysts for certain reactions [17], we examined one sample that was not subjected to the extensive washing/

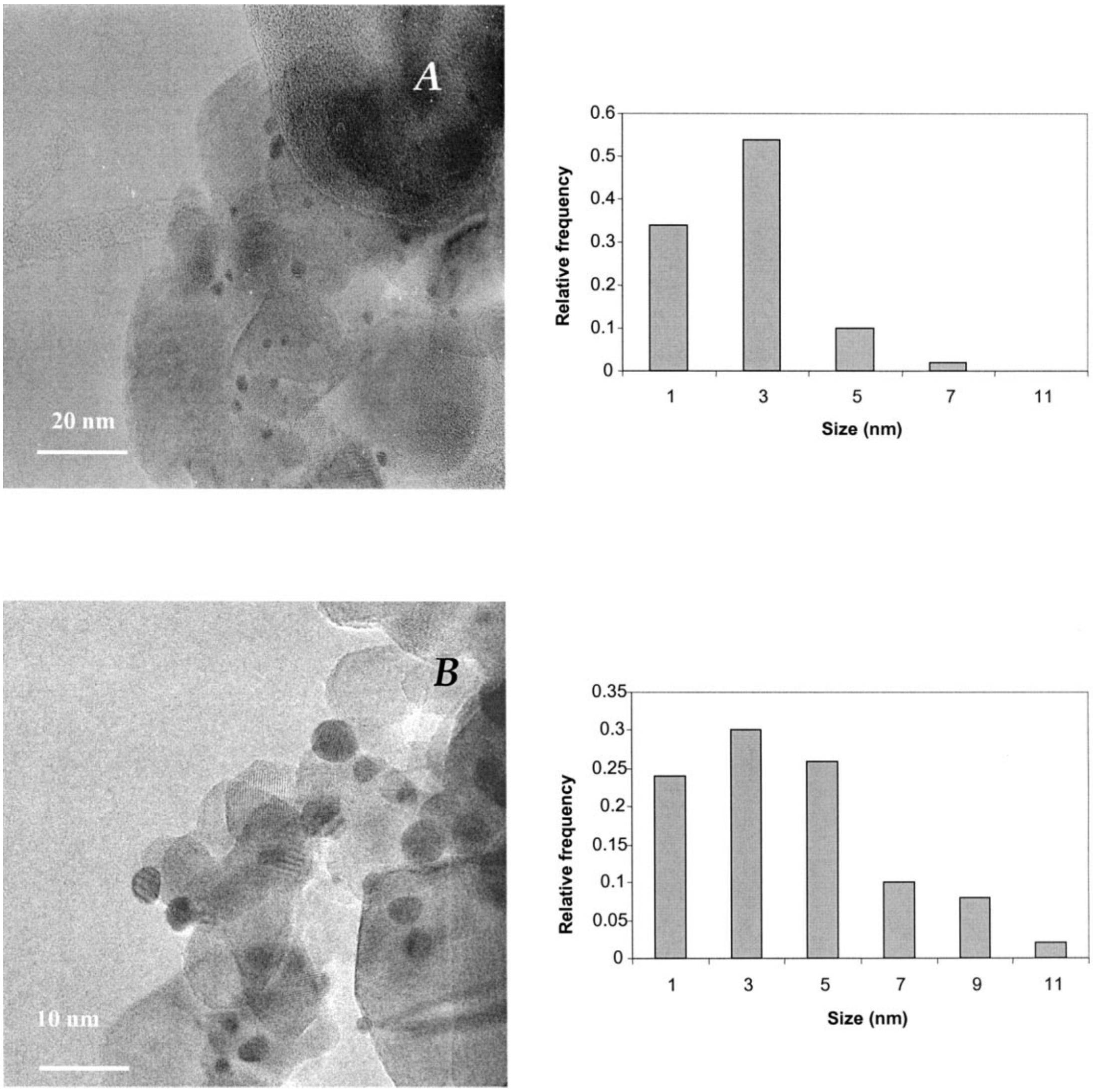

Figure 2. (a) TEM image of 0.55 at% Au sample and particle-size distribution. (b) TEM image of 5.58 at% Au sample and particle-size distribution.

chloride-elimination procedure used for the other catalysts. A small statistically insignificant increase in activity of the unwashed sample was observed.

Having established the variation of performance with Au loading at (nominally) constant particle size (all samples prepared at pH = 7), we attempted to examine the effect of Au particle size at constant Au loading. Accordingly, following the procedure of Haruta *et al.*

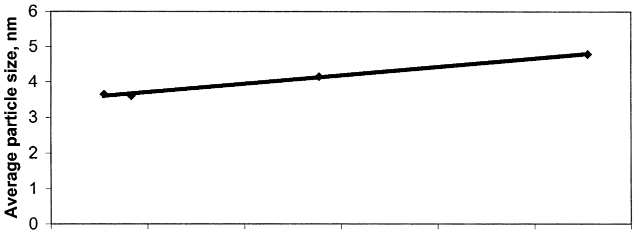

Figure 3. Dependence of gold average particle size on gold loading.

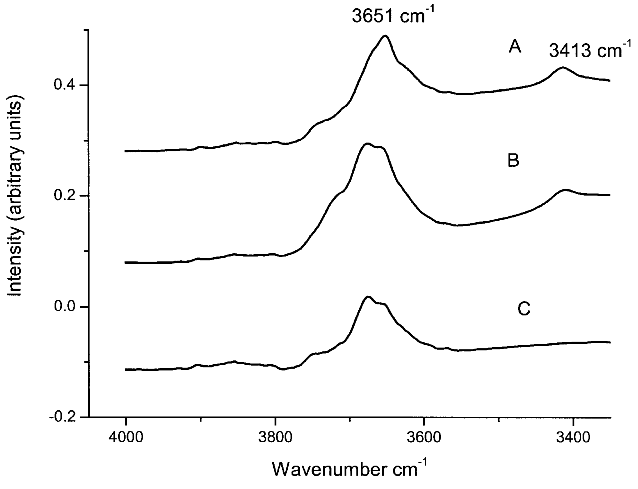

Figure 4. DRIFTS spectra of (a) TiO_2, (b) 0.42 at% Au sample, and (c) 5.58 at% Au sample.

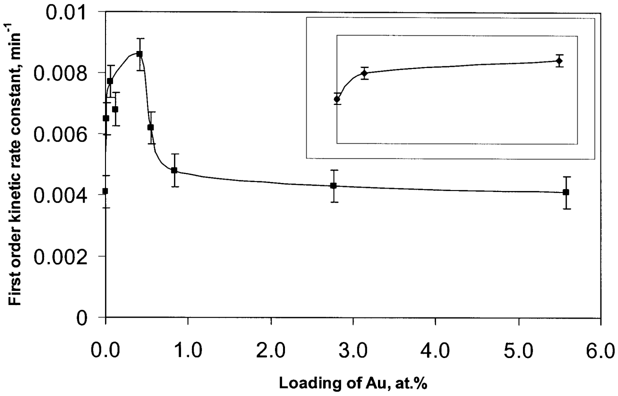

Figure 5. Dependence of the rate of photocatalytic degradation of 4-chlorophenol on gold loading. Insert shows the initial part of the curve.

[19], the effect of varying Au particle size on catalytic activity was investigated by changing the pH of gold precursor solution. Four 0.12 Au at% samples were prepared at unadjusted pH, pH = 4, pH = 5, and pH = 7. HRTEM analysis indicated that the gold particle size varied from ~5–6 nm for the sample prepared at pH = 7 to >17 nm for the sample prepared without pH control (figure 7). However, the low Au loading resulted in a very low gold particle density and consequently relatively large error bars on the average particle-size values. Nevertheless, it was clear that the catalytic activity of these samples increased with increasing pH of the precursor solution, that is, increasing activity with *decreasing* particle size. Thus, these data also indicate that Au particle size plays a role in catalytic activity. In this case, the effect was fairly small (~15%) over the size range accessed by these experiments, probably due to the significant width of the particle-size distribution.

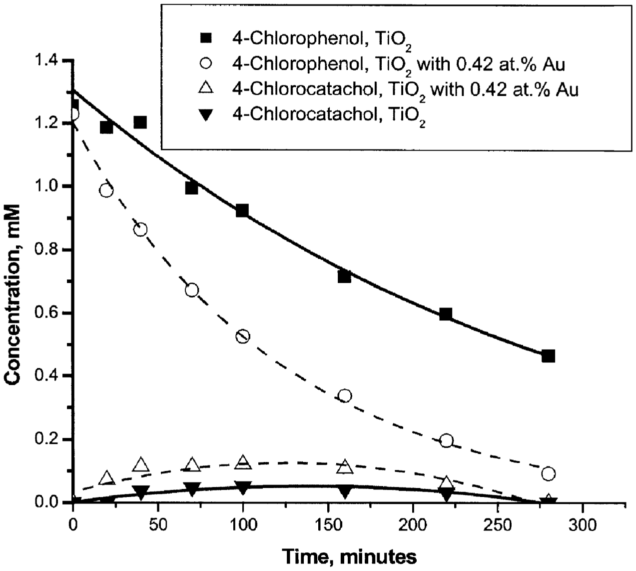

Figure 6. Photocatalytic degradation of 4-chlorophenol and production of 4-chlorocatechol for unmodified and 0.42 at% Au-modified TiO_2 samples.

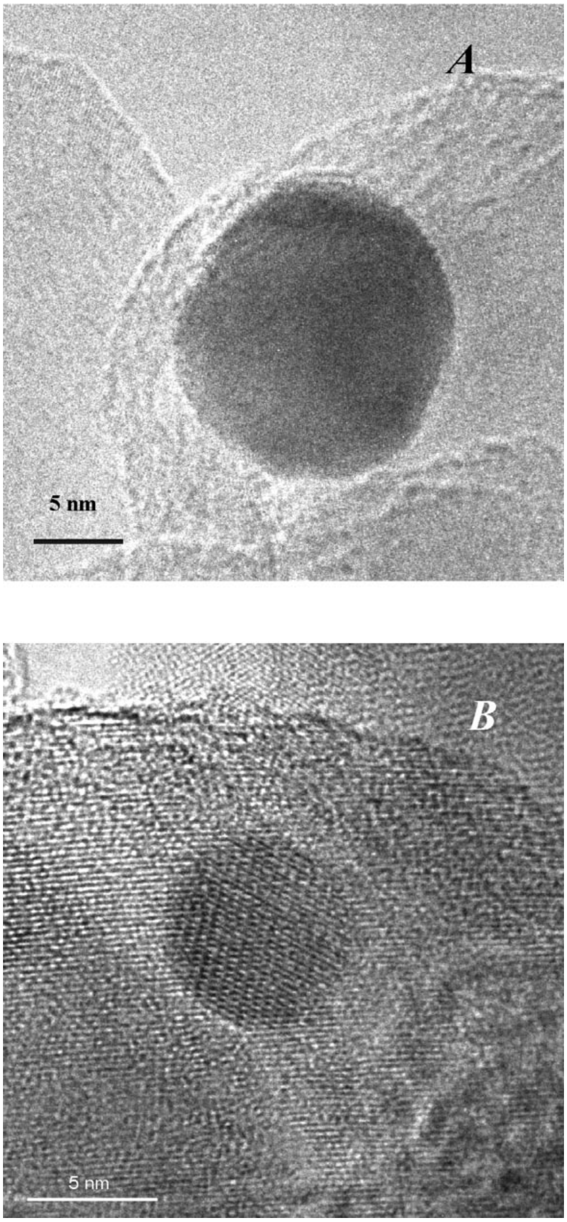

Figure 7. TEM images of samples prepared at (a) unadjusted pH and (b) pH = 7.

4. Discussion

The reactor and TEM results obtained with catalysts prepared at fixed pH = 7 indicate that increasing Au particle density is likely to be an important factor in determining performance. However, it is clear that there are other effects at work. An indication of these is provided by comparing the catalytic activities and measured particle-size distributions of the 0.55 and 5.58 at% Au catalysts (figures 2 and 5). Unlike the 0.55 at% Au catalyst, the 5.58 at% Au catalyst contains a high proportion of particles ≥5 nm. It seems quite possible that these $\geq$5-nm Au particles have a different impact on catalyst performance compared to that of smaller particles [18] as discussed below. Both samples contain a significant proportion of particles with diameters in the 1–3 nm range: $\sim$34 and 24% of the total distribution for the 0.55 and 5.58 at% Au samples respectively. This suggests that the role of very small Au particles in the photocatalysis may be substantial. In particular, it could be that extremely small Au particles, invisible to HRTEM, are critically important, and it seems reasonable to suppose that there could be a higher proportion of these in the 0.55 at% Au catalyst than in the 5.58 at% Au catalyst.

Recall that our BET measurements show the specific surface areas of pure P-25 titania and those of the catalysts derived from this material to be identical. Therefore, observed changes in the pseudo first-order rate constants are not merely due to variations in intrinsic surface area between the different samples. As a working hypothesis, since pure titania alone is effective, it is reasonable to assume that the catalytic chemistry occurs on the TiO$_2$ surface [16], whose properties are modified by the Au. Adsorbate decomposition is initiated by encounters with photogenerated electrons and holes, which trigger oxidation/reduction reactions [1]. Thus, any process that accelerates the electron–hole recombination rate will be detrimental for catalytic activity. Conversely, effects that inhibit electron–hole recombination should enhance photocatalytic activity.

How does Au initially affect the photocatalytic rate (figure 5)? Three possible effects could occur involving (i) larger Au particles, (ii) very small gold particles, and (iii) the titania surface itself.

4.1. Larger (metallic) Au particles

If a Schottky junction were formed so that the metal and oxide phases are in electronic communication [12], the Au particle could act as a sink for photogenerated electrons, thus reducing the e^-/h^+ recombination rate and enhancing the photocatalytic rate [8]. The overall rate of this process would depend on the length of the boundary between Au and TiO$_2$. In the case of methanol decomposition on Pd/TiO$_2$, Bowker *et al.* [24] have argued that the rate-limiting step occurs at the metal/oxide phase boundary. As a consequence, the rate passed through a maximum and fell to zero when the "effective perimeter" of the gold particles on the TiO$_2$ surface approached zero, due to coalescence. Our system differs from that described by Bowker *et al.,* since even at the highest Au loadings only a small fraction of the titania surface was shadowed by gold particles. Therefore, even if the phase boundary plays a role in the present case, a rate maximum could occur without the rate subsequently falling to zero. Shadowing of the titania by large Au particles would act to reduce the surface area available for 4-chlorophenol adsorption and photoexcitation [12]. Again, as indicated by figure 2(b), this factor could not have been very large, even at the highest Au loadings we used. There is no doubt that at sufficiently high Au loadings, the rate would eventually fall to zero because of a combination of gold "perimeter" and "area" effects.

4.2. Very small Au particles ($<$1–3 nm)

Recall that these are no longer metallic but semiconducting, as elegantly demonstrated by Valden *et al.* by means of tunneling spectroscopy [18]. In this case, one may invoke an alternative mechanism [8] based on semiconductor–semiconductor contact in which photoexcited electrons are injected from Au into the TiO$_2$ conduction band, creating separated electrons and holes that then undergo charge-transfer reactions with adsorbates. Wavelength-dependent photocatalytic measurements could provide a means of distinguishing between this possibility and the previous one, and such experiments are planned for the future.

4.3. Hydroxyl groups on the titania surface

A third factor that may contribute to loss of activity with increased Au loading is suggested by the DRIFTS spectra. These show a substantial decrease (by $\sim$40%) in the intensity of the OH band at 3650 cm^{-1} when the Au loading increases from 0.42 to 5.58%. Hydroxyl groups are efficient hole traps, and since holes are thought to initiate the oxidative processes that lead to degradation of adsorbed organic species [1], their elimination should decrease the photocatalytic rate.

Our results indicate that the *average* gold particle size of the catalysts did not vary hugely for the samples characterized by TEM (figure 3); the actual variation was $\sim$40%. However, the average particle size does not reflect the width of the cluster-size distribution, leaving the possibility that the smallest particles are the most photocatalytically active. Increased loading is likely to markedly decrease the fraction of the smallest and most effective Au particles, without substantially affecting the average Au particle size. Indeed, the data shown in figures 3 and 5 indicate that the most catalytically active samples contain a substantial fraction of Au particles with dimensions $<\sim$4 nm, where the metal to nonmetal transition of gold occurs.

5. Conclusions

1. At very low metal loadings, gold nanoparticles significantly enhance the catalytic activity of P-25 titania toward the photodegradation of 4-chlorophenol; 4-chlorocatechol is a reaction intermediate in this process.

With increasing Au loading, the activity falls again toward a value, characteristic of unmodified titania.

2. The observed Au particle-size distributions indicate that it is the very smallest Au particles that are responsible for the enhanced catalytic performance—probably by increasing the rate of production of separated electrons and holes.

3. DRIFT spectra indicate that the principal cause of the rate decrease observed at the highest Au loadings is progressive elimination of hole-trapping OH groups on the TiO_2 surface.

Acknowledgments

This work was supported under Research Grant GR/R03082/01 awarded by the UK Engineering and Physical Sciences Research Council. AO thanks the Environmental Research and Education Foundation for the award of an International Scholarship and Schlumberger Cambridge Research for additional financial support.

References

[1] M.R. Hoffmann, S.T. Martin, W.Y. Choi and D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

[2] G.L.L. Puma and P.L. Yue, Ind. Eng. Chem. Res. 41 (2002) 5594.

[3] L. Millard and M. Bowker, J. Photochem. Photobiol., A: Chem. 148 (2002) 91.

[4] N.J. Peill and M.R. Hoffmann, Environ. Sci. Technol. 29 (1995) 2974.

[5] C. Guillard, J. Disdier, J.M. Herrmann, C. Lehaut, T. Chopin, S. Malato and J. Blanco, Catal. Today 54 (1999) 217.

[6] S.M. Fonseca, A.L. Barker, S. Ahmed, T.J. Kemp and P.R. Unwin, Chem. Commun. (2003) 1002.

[7] A. Mills and J.S. Wang, J. Photochem. Photobiol., A: Chem. 118 (1998) 53.

[8] A.L. Linsebigler, G.Q. Lu and J.T. Yates, Chem. Rev. 95 (1995) 735.

[9] U. Siemon, D. Bahnemann, J.J. Testa, D. Rodriguez, M.I. Litter and N. Bruno, J. Photochem. Photobiol., A: Chem. 148 (2002) 247.

[10] F.B. Li and X.Z. Li, Appl. Catal. A: Gen. 228 (2002) 15.

[11] P.V. Kamat, J. Phys. Chem. B 106 (2002) 7729.

[12] V. Subramanian, E.E. Wolf and P.V. Kamat, Langmuir 19 (2003) 469.

[13] M. Jakob, H. Levanon and P.V. Kamat, Nano. Lett. 3 (2003) 353.

[14] A. Dawson and P.V. Kamat, J. Phys. Chem. B 105 (2001) 960.

[15] D. Lahiri, V. Subramanian, T. Shibata, E.E. Wolf, B.A. Bunker and P.V. Kamat, J. Appl. Phys. 93 (2003) 2575.

[16] H. Haick and Y. Paz, J. Phys. Chem. B 107 (2003) 2319.

[17] M. Haruta, Catal. Today 36 (1997) 153.

[18] M. Valden, X. Lai and D.W. Goodman, Science 281 (1998) 1647.

[19] T. Hayashi, K. Tanaka and M. Haruta, J. Catal. 178 (1998) 566.

[20] C. Morterra, J. Chem. Soc., Faraday Trans. I 84 (1988) 1617.

[21] B. Sun, A.V. Vorontsov and P.G. Smirniotis, Langmuir 19 (2003) 3151.

[22] D. Hufschmidt, D. Bahemann, J.J. Testa, C.A. Emilio and M.I. Litter, J. Photochem. Photobiol., A: Chem. 148 (2002) 223.

[23] L. Sirghi and Y. Hatanaka, Surf. Sci. 530 (2003) L323.

[24] M. Bowker, D. James, P. Stone, R. Bennett, N. Perkins, L. Millard, J. Greaves and A. Dickinson, J. Catal. 217 (2003) 427.