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Light-induced formation of 2,5-dihydroxy-*p*-benzoquinone from hydroquinone in photoirradiated silver-loaded zirconium phosphate suspension
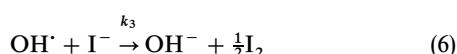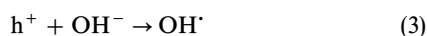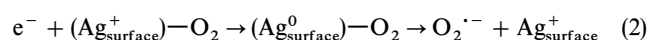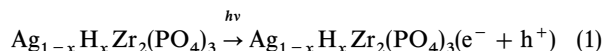
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Silver-loaded zirconium phosphate [$Ag_{1-x}H_xZr_2(PO_4)_3$] has shown photocatalytic activity concerning the generation of $OH^\cdot$ and the hydroxylation of hydroquinone (HQ) to 2,5-dihydroxy-*p*-benzoquinone ($DHQH_2$). HQ was initially oxidized to *p*-benzoquinone (BQ) by Ag^+ on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$ in the dark and by photogenerated $OH^\cdot$ during visible-light irradiation. As an intermediate, a semiquinone radical $BQH^\cdot$ was detected by EPR measurements in both cases. Furthermore, under visible-light irradiation, $DHQH_2$ was identified by its absorption spectrum and thin layer chromatography. The amount of $DHQH_2$ increased and BQ decreased with irradiation time. The total amount of BQ and $DHQH_2$ under visible-light irradiation agreed with that of BQ in the dark. Consequently, $DHQH_2$ appeared to form from $BQH^\cdot$ generated by the oxidation of HQ and the reduction of BQ by photogenerated e^-. From the XPS and FT-Raman technique analyses, it was found that the addition of the photogenerated $OH^\cdot$ to $BQH^\cdot$ occurred at the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$. This indicated that both the $OH^\cdot$ and $HBQ^\cdot$ were stabilized on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$.

Silver-loaded zirconium phosphate [$Ag_{1-x}H_xZr_2(PO_4)_3$] has been prepared as an antibacterial reagent by Kourai *et al.*[1] $Ag_{1-x}H_xZr_2(PO_4)_3$ was obtained by ion-exchanging Na^+ in sodium zirconium phosphate [$NaZr_2(PO_4)_3$] with Ag^+. $NaZr_2(PO_4)_3$ has been reported to be a three-dimensional structure composed of ZrO_6 and PO_4 by Goodenough *et al.*[2] Also, the crystal data has been indicated by Hagman and Kierkegaard.[3] Antibacterial action towards *Esherichia coli* K12 W 3110 occurred during visible-light irradiation.[1,4] The active species were found to be $OH^\cdot$ as a DMPO-OH adduct using a spin-trapping technique.[5] The generation mechanism of $OH^\cdot$ was investigated and it was clarified that a charge separation occurred as a result of light irradiation of zirconium phosphate. A photocathodic current was observed for the zirconium phosphate-modified Pt electrode in 0.1 mol dm^{-3} Na_2SO_4 aqueous solution using a 500 W Xe lamp.[5] The generation rate of DMPO-OH increased with the relative concentration of Ag/Zr on the surface. It seemed that Ag^+ on the surface acted as an electron pool like Ag[6] which leads to an effective charge separation. Furthermore, the addition of I^- to that suspension reduced the amount of $OH^\cdot$ and the signal of DMPO-$O_2^{\cdot-}$ appeared. This indicated that an electron and a hole generated by the charge separation reduced O_2 and oxidized OH^-, respectively. The reaction mechanism has been proposed to be as follows.[5]

$$Ag_{1-x}H_xZr_2(PO_4)_3 \xrightarrow{h\nu} Ag_{1-x}H_xZr_2(PO_4)_3(e^- + h^+) \quad (1)$$

$$e^- + (Ag_{surface}^+)\text{—}O_2 \rightarrow (Ag_{surface}^0)\text{—}O_2 \rightarrow O_2^{\cdot-} + Ag_{surface}^+ \quad (2)$$

$$h^+ + OH^- \rightarrow OH^\cdot \quad (3)$$

$$DMPO + O_2^{\cdot-} \xrightarrow{k_1} DMPO-O_2^- \quad (4)$$

$$OH^\cdot + DMPO \xrightarrow{k_2} DMPO-OH \quad (5)$$

$$OH^\cdot + I^- \xrightarrow{k_3} OH^- + \tfrac{1}{2}I_2 \quad (6)$$

where the rate constants k_1, k_2 and k_3 are known to be 16.9 dm^3 mol^{-1} s^{-1},[7] 3.4×10^9 dm^3 mol^{-1} s^{-1} [7] and 1.0×10^{10} dm^3 mol^{-1} s^{-1}.[8] $Ag_{surface}^+$ represents a semi-reduced Ag^+ on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$ as an electron pool.[5] DMPO-$O_2^{\cdot-}$ was only detected in the presence of I^-. In the absence of I^-, DMPO traps almost exclusively $OH^\cdot$ because the rate constant k_2 was much larger than k_1. If instead of DMPO, hydroquinone (HQ) was added to the suspension and irradiated by visible light then the rate constant for reaction of $HO^\cdot$ and HQ was reported to be 2.1×10^{10} dm^3 mol^{-1} s^{-1} at pH 6–7.[8] In this study, when a suspension $Ag_{1-x}H_xZr_2(PO_4)_3$ and HQ was irradiated by visible light, 2,5-dihydroxy-*p*-benzoquinone ($DHQH_2$) was formed. Generally, $DHQH_2$ is synthesized from hydroquinone in alkaline solution by addition of H_2O_2 at <323 K.[9] Since $BQH^\cdot$ is stable in alkaline solution, during the synthesis of $DHQH_2$, it seems that the stabilization of the semiquinone radical $BQH^\cdot$ as an intermediate of hydroquinone is required. Therefore, it seems that the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$ may stabilize both $OH^\cdot$ and $BQH^\cdot$.

In this study, trapping of the photogenerated $OH^\cdot$ was attempted using a hydroquinone. As a result, since $DHQH_2$ formed with BQ during irradiation and in the dark, only BQ was generated. Its irradiation time dependence was investigated with respect to the concentration of BQ and $DHQH_2$. Furthermore, the reaction mechanism and the role of the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$ were investigated using XPS, EPR and FT-Raman techniques. Also, the usefulness of $Ag_{1-x}H_xZr_2(PO_4)_3$ as a photocatalyst for the formation of $DHQH_2$ from HQ is discussed.

Experimental

Silver-loaded zirconium phosphate $Ag_{1-x}H_xZr_2(PO_4)_3$ (Ag content = 11 wt.%) was provided by Toa Gousei Co., Ltd. 5,5-Dimethylpyrrolidine-*N*-oxide (DMPO, LC-9130) and 2,2,6,6-tetramethyl-1-piperidine-*N*-oxyl nitroxide (TEMPO) were

obtained from Labotec Co., Ltd. Hydroquinone (reagent grade) was purchased from Wako Pure Chemical Industries, Ltd. These reagents have been directly used in our investigations without further purification. 2,5-Dihydroxy-p-benzoquinone (DHQH$_2$) as a standard was synthesized as previously reported[9] and was recrystallized from ethanol. A phosphate buffer solution of pH 6.0 was prepared with KH$_2$PO$_4$ and NaOH.

The oxidation of hydroquinone (HQ) was investigated in the dark and under irradiation. After the sample (2 mg) was dispersed in a 2.125 cm^3 phosphate buffer solution (pH 6.0) containing 5.9 mmol dm^{-3} HQ, this solution in a Pyrex tube was irradiated with a Xe lamp (UV-37 and UV-25 cut-off filters, Toshiba Glass Co., Ltd.) or allowed to stand in the dark for certain times. The absorption spectra of the solutions, which were diluted to 1/30 or undiluted ($\times$ 1), in 10 mm cells were measured using a Hitachi U-2000 spectrophotometer. The concentration of p-benzoquinone (BQ) was calculated from the absorbance at 246 nm[10] and its log $\varepsilon_{(\lambda = 246 \text{ nm})} = 4.4$[11] and that of DHQH$_2$ was from the absorbance at 490 nm and its log $\varepsilon_{(\lambda = 490 \text{ nm})} = 3.0$; log $\varepsilon_{(\lambda = 490 \text{ nm})}$ was determined using $A_{(\lambda = 490 \text{ nm})} = 0.087$ of 83.3 µmol dm^{-3} DHQH$_2$.

Thin layer chromatography was performed using a Merk Art. 15389 DC-Fertigplatten RP-18 F 254 S. Its 9.8 $\times$ 5.0 cm plate (the baseline is 0.1 cm from the bottom) was prepared and methyl alcohol, ethyl acetate and isopropyl alcohol were used as the developing solvents.

EPR spectral measurements were performed with a JEOL TE-300 and ESPRIT-425 data system. 5,5-Dimethylpyrrolidine-N-oxide (DMPO) was used as the spin trap reagent. The EPR spectra (X-band) of a semiquinone radical (HBQ˙) and DMPO adducts were measured with a JEOL DATUM LC12 quartz oblique cell (ca. 0.2 cm^3) for the aqueous solution. Concentrations of HBQ˙ and DMPO-OH were determined by comparing their peak area in their EPR spectra to that of a 3.2 µmol dm^{-3} TEMPO aqueous solution as the standard. A 0.2 mg/0.2 cm^3 sample of an Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ powder suspension was mixed with 0.02 cm^3 DMPO spin trapping reagent (9.0 mol dm^{-3}) and added to the cell. The concentration of DMPO in the suspension was 0.8 mol dm^{-3}. The EPR spectra were measured during irradiation with a 500 W Xe lamp (Ushio, UI-501C) with UV-25 and UV-37 cut-off filters (Toshiba Glass Co., Ltd.), UV-37 cut-off and KL-40 interference filters (Toshiba Glass Co., Ltd.), or in the dark at room temperature with the following conditions: 8 mW power, 79 µT modulation width, Mn$^{\text{II}}$/MgO external standard for g values, and $\pm$5 mT sweep width.

XPS spectra of the Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ (Ag content = 11 wt.%) powders were measured with a Shimadzu ESCA-1000AX instrument. Mg-Kα radiation (1253.6 eV) was employed as the X-ray source. Data processing[12] was carried out with an HP 340 computer (Hewlett-Packard Co., Ltd.), which was attached to the Shimadzu ESCA-1000AX. The ESCA-1000AX was operated at 10 kV and 30 mA under a pressure of 10^{-6}–10^{-7} Pa. The binding energy (E_b) was calibrated with C 1s = 285 eV from contaminant C. The sampling time was 200 ms and the number of accumulations was 20 for the Ag 3d$_{5/2}$ peak while for other elements, the number of accumulations was 1. The Savitzky method[13] was used for the smoothing. The sample was pelletized and attached to the sample probe with carbon tape.

Measurements of the FT-Raman spectra were performed with a Nihon Bunko NR-1800 instrument at room temperature. The FT-Raman spectra of the Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ (Ag content = 11 wt.%) powders were measured with an Ar ion laser (514.5 nm, 30 mW power) and triple monochromator. The sample powders were put on the glass plate and simply arranged on its surface with another glass plate: entrance slit 500 µm, sensitivity 1.0 (nA/full scale) $\times$ 100, scan speed 600 cm^{-1} min^{-1}, and accumulation number 3.

Results and Discussion

A visible-light irradiated silver-loaded zirconium phosphate Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ generated OH˙ and O$_2$˙$^-$ from aqueous solution in air as shown in eqn. (1)–(6) earlier.[5] Their radicals formed DMPO-OH and DMPO-O$_2^-$ adducts with DMPO as the spin trap reagent. However, since the reaction rate of DMPO and OH˙ is much larger than that of DMPO and O$_2$˙$^-$, only DMPO-OH was detected by the EPR measurement. In a separate experiment, instead of DMPO, HQ was added and its suspension was irradiated. The reaction rate of HQ and OH˙ has been reported to be 2.1 $\times$ 10^{10} dm^3 mol^{-1} s^{-1}.[8] After irradiation, the solution turned from yellow to red, Fig. 1(a) and (b) show the absorption spectra of HQ and the product. As shown in Fig. 1(a), in the dark, the absorption peak of BQ at 246 nm (log ε = 4.4, in hexane)[11] increased with the amount of Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ [0 mg (a) to 30 mg (e)] present. As shown in Fig. 2(b), during light irradiation, peaks at 490 and 246 nm grew. The peak at 490 nm corresponded to DHQH$_2$ in aqueous solution. The R_f value from a thin layer chromatogram for the solutions was measured using ethyl acetate and isopropyl alcohol as the developing solvents. Table 1 lists the R_f values of products in unirradiated and irradiated solutions. The R_f value (0) for the irradiated sample
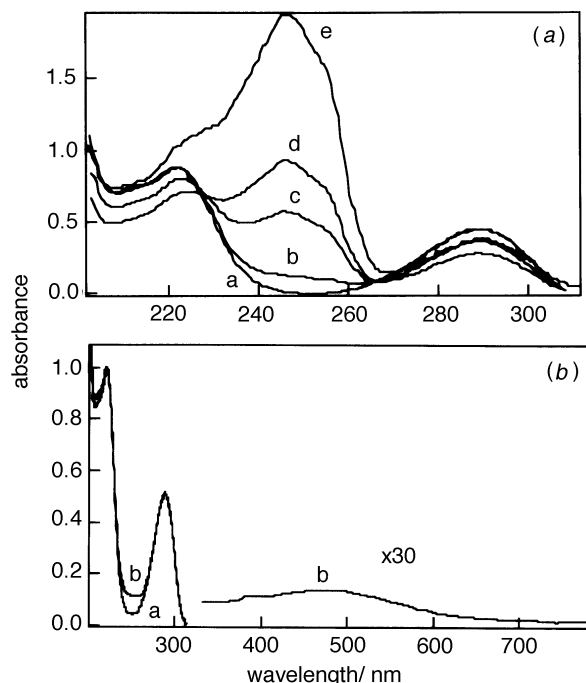

Fig. 1 (a) Absorption spectra of hydroquinone in supernatant after mixing with 0 mg (a), 2 mg (b), 10 mg (c), 20 mg (d) and 30 mg (e) Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ for 2–3 h in the dark. Each amount of Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ was suspended in 2.125 cm^3 of 5.9 mmol dm^{-3} hydroquinone phosphate buffer solution (pH 6.0) and mixed for 2–3 h in the dark. After the reaction, the suspension was centrifuged at 3000 rpm for 5 min. The obtained supernatant was diluted to 1/30 and its absorption spectrum was measured. The concentration of p-benzoquinone was calculated using log $\varepsilon_{(\lambda = 246 \text{ nm})} = 4.4$ to be 4.8 µmol dm^{-3}, 22.9 µmol dm^{-3}, 36.9 µmol dm^{-3} and 75.5 µmol dm^{-3}, respectively. (b) Absorption spectra of hydroquinone in supernatant after mixing with 0 mg (a) and 2 mg (b) Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ for 1 h under light irradiation. 2 mg of Ag$_{1-x}$H$_x$Zr$_2$(PO$_4$)$_3$ was suspended in 2.125 cm^3 of 5.9 mmol dm^{-3} hydroquinone phosphate buffer solution (pH 6.0) and mixed for 1 h under light irradiation using a 500 W Xe lamp (UV-25 and UV-35 cut-off filters). After the reaction, the suspension was centrifuged at 3000 rpm for 5 min. The absorption spectra of the supernatant, which was diluted to 1/30 and undiluted ($\times$ 1), were measured. The concentration of p-benzoquinone was calculated to be 2.3 µmol dm^{-3} and that of 2,5-dihydroxy-p-benzoquinone using log $\varepsilon_{(\lambda = 490 \text{ nm})} = 3.0$ to be 12.5 µmol dm^{-3}.

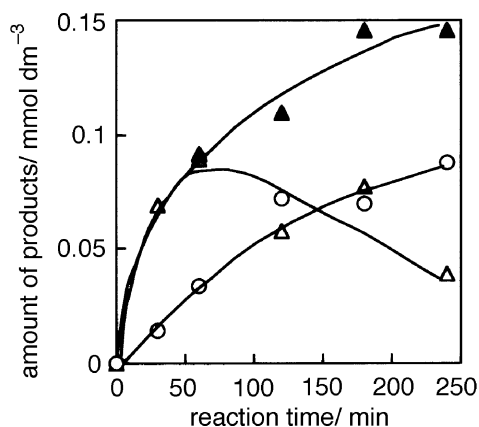**Fig. 2** Plot of amount of products *vs.* the reaction time in the dark and during irradiation. The products were *p*-benzoquinone in the dark (▲), *p*-benzoquinone during light irradiation (△) and 2,5-dihydroxy-*p*-benzoquinone during light irradiation (○). $Ag_{1-x}H_xZr_2(PO_4)_3$ (2 mg) was suspended in 2.125 cm³ phosphate buffer solution (pH 6.0) containing 5.9 mmol dm⁻³ HQ and irradiated using a 500 W Xe lamp with UV-37 and UV-25 cut-off filters.

indicated the presence of DHQH₂ which was absent in the unirradiated sample. Although the R_f values of HQ and BQ could not be distinguished in this experiment, the formation of BQ could be identified from the absorption peak at 246 nm. In the dark the generation of BQ was due to the oxidation of HQ by Ag^+ on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$ (the redox potential for Ag^+/Ag^0 [14] is +0.799 V *vs.* NHE and that for BQ/HQ[15] is +0.70 V *vs.* NHE). Consequently, as shown in Fig. 1(*a*), the formation of BQ depended on the amount of $Ag_{1-x}H_xZr_2(PO_4)_3$.

Fig. 2 shows the relation between the amount of products and the reaction time in the dark and during irradiation. In the dark, the amount of BQ increased with reaction time. During irradiation, the amount of BQ decreased and that of DHQH₂ increased with irradiation time. Up to *ca.* 50 min, the amount of BQ was the same as that in the dark. Since DHQH₂ was also generated with BQ at the same time, the formation of BQ during irradiation would be due to the oxidation by Ag^+ and the photogenerated OH· on the surface. On the other hand, a decrease in the concentration of BQ was seen from 0.08 to 0.04 mmol dm⁻³ for an irradiation time of 50 to 240 min. The generated BQ was re-reduced by the photogenerated e^- from $Ag_{1-x}H_xZr_2(PO_4)_3$ and HBQ· was reformed. Subsequently, HBQ· was hydroxylated to DHQH₂ by the photogenerated OH· on the surface and the HBQ· that originated from BQ would be consumed. Therefore, the amount of BQ tended to decrease with the formation of DHQH₂. These facts indicate that HBQ· needs to form DHQH₂ and HBO· increases with irradiation time (see Fig. 4). The total of BQ and DHQH₂ almost agreed with that of BQ in the dark as shown in Fig. 2. The formation of BQ is known to occur by a disproportionation of HBQ· as an intermediate. HBQ· was detected by EPR measurements in both irradiated and non-irradiated suspensions. Fig. 3 shows the observed radicals formed during irradiation of

Table 1 R_f values of products in $Ag_{1-x}H_xZr_2(PO_4)_3$ suspension containing 5.9 mmol dm⁻³ HQ in the dark and under irradiation using thin layer chromatography[a]

	R_f	
light	0	0.9
dark	—	0.89
HQ	—	0.9
DHQH₂	0	—

[a] Developing solvent: ethyl acetate or isopropyl alcohol.
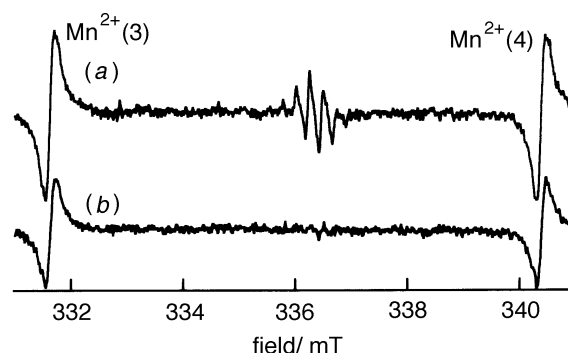
Fig. 3 EPR spectra of semiquinone free radical in $Ag_{1-x}H_xZr_2(PO_4)_3$ (*a*) and $HZr_2(PO_4)_3$ (*b*) suspensions containing 5.9 mmol dm⁻³ hydroquinone during 500 W Xe lamp (UV-37 and UV-25 cut-off filters) irradiation. $Ag_{1-x}H_xZr_2(PO_4)_3$ (2 mg) or $HZr_2(PO_4)_3$ was suspended in 2.125 cm³ of the phosphate buffer solution (pH 6.0) containing 5.9 mmol dm⁻³ hydroquinone. $Mn^{2+}(3)$ and $Mn^{2+}(4)$ occur at g = 2.033 and 1.981, respectively. Sampling time was 10 s and accumulation was 30.

$Ag_{1-x}H_xZr_2(PO_4)_3$ and $HZr_2(PO_4)_3$. Spectrum (*a*) was assigned to that of the *p*-semiquinone free radical.[16] For $HZr_2(PO_4)_3$ in the dark or during irradiation, the semiquinone radical could not be detected. Fig. 4 shows the reaction time dependence of the concentration of HBQ· in the dark and during irradiation. The concentration of HBQ· was estimated from the peak area and compared to that of TEMPO as a standard. Its concentration upon irradiation was higher than that in the dark and saturated at *ca.* 0.24 µmol dm⁻³ whereas in the dark, its concentration was *ca.* 0.05–0.06 µmol dm⁻³. This indicates that HBQ· is stabilized on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$. In the absence of $Ag_{1-x}H_xZr_2(PO_4)_3$, direct light-irradiation to an HQ solution (pH 6.0) led to the formation of HBQ·, but as soon as the light was turned off, HBQ· immediately disappeared. Therefore, the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$ stabilizes the radical. Such stabilization was also observed in the case of the photogenerated OH·. Fig. 5 shows the relation between the concentration of DMPO-OH and the amount of $Ag_{1-x}H_xZr_2(PO_4)_3$. The spectra of DMPO-OH were measured immediately after the addition of DMPO to the 45 min pre-irradiated $Ag_{1-x}H_xZr_2(PO_4)_3$ suspension. The signal of DMPO-OH appeared and its concentration depended on the amount of $Ag_{1-x}H_xZr_2(PO_4)_3$. This indicates that the photogenerated OH· is stabilized on the surface in the dark. Therefore, both HBQ· and photogenerated OH· are stabilized on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$. Generally, DHQH₂ is prepared from

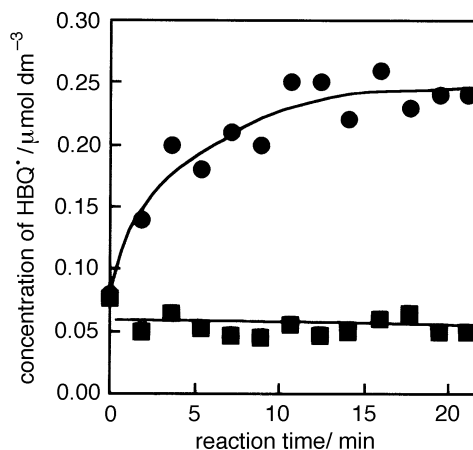**Fig. 4** Plot of concentration of semiquinone radical *vs.* the reaction time in the dark (■) and during irradiation (●) using a 500 W Xe lamp with UV-37 and UV-25 cut-off filters. $Ag_{1-x}H_xZr_2(PO_4)_3$ (2 mg) was suspended in 2.125 cm³ of 5.9 mmol dm⁻³ hydroquinone phosphate buffer solution at pH 6.0.
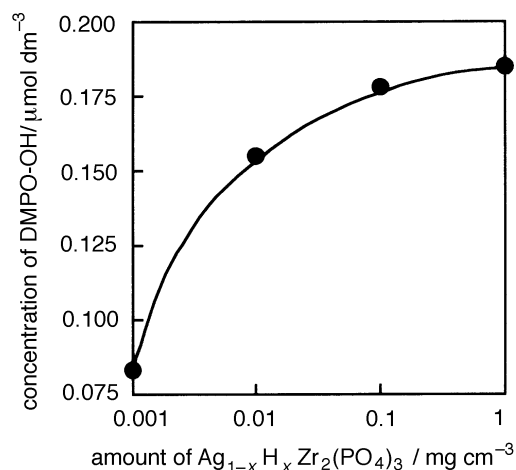
Fig. 5 Plot of concentration of DMPO-OH *vs.* amount of $Ag_{1-x}H_xZr_2(PO_4)_3$. Each amount of $Ag_{1-x}H_xZr_2(PO_4)_3$ was dispersed in 0.2 cm^3 of distilled water and irradiated using 400 nm light from a 500 W Xe lamp (UV-37 cut-off and KL-40 interference filters) for 45 min. Then, 0.02 cm^3 of DMPO (9 mol dm^{-3}) was added to the suspension and the EPR spectrum was measured. The concentration of DMPO in the suspension was 0.8 mol dm^{-3}. Sampling time was 5 s and accumulation was 40.

the sodium salt of HQ and H_2O_2 in alkaline solution in which HBQ$^{\cdot}$ is stable. Thus the addition of OH$^{\cdot}$ to the stabilized HBQ$^{\cdot}$ seems to be important and supports the above result in this study, and a reaction scheme is proposed in Fig. 6. HQ is oxidized by Ag$^+$ or photogenerated OH$^{\cdot}$ on the surface to form HBQ$^{\cdot}$ [eqn (7)]. The two generated HBQ$^{\cdot}$ molecules disproportionate to BQ and HBQ$^-$ in the dark [eqn (9)] whereas under irradiation they disproportionate to DHQH$_2$,
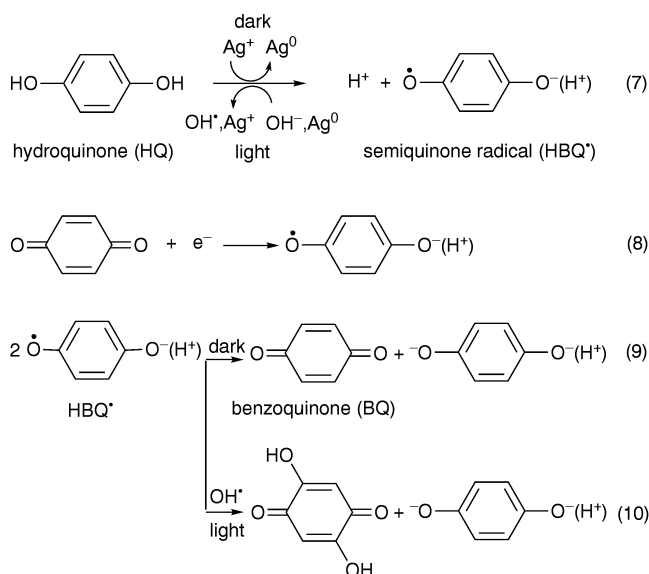
which was formed by the addition of OH$^{\cdot}$ to HBQ$^{\cdot}$ and HBQ$^-$ [eqn. (10)]. The amount of DHQH$_2$ linearly increased and that of BQ decreased with irradiation time as shown in Fig. 2, and this indicates that HBQ$^{\cdot}$ is also formed from the reduction of BQ by photogenerated e$^-$ [eqn. (8)].

After the reaction in the dark or during irradiation, surface analysis of the used $Ag_{1-x}H_xZr_2(PO_4)_3$ powders was performed using XPS. The C 1s XPS spectra for the used sample was different from that of the original sample (*c*) as shown in Fig. 7 in which the peak at 285 eV was due to contaminant C used as a reference. Peaks at 293 and 296 eV were assigned to K 2p$_{3/2}$[17] appearing to originate from the KH$_2$PO$_4$ phosphate buffer solution (pH 6.0). A new peak was observed at *ca.* 280 eV in the dark and decreased in intensity in the irradiated sample. After the reaction in the dark and during irradiation, HQ, BQ and DHQH$_2$ may be adsorbed on the surface. From the result shown in Fig. 2, the concentration of BQ increased in the dark while during irradiation it decreased. Therefore, the peak at 280 eV appears to be due to that of BQ. The binding energy E_b of C 1s for C_6H_6 has been reported to be 284.9 eV.[17] The lower E_b of BQ compared to that of C_6H_6 would be due to the high reactivity of BQ. Table 2 lists the binding energies of Ag 3d$_{5/2}$, O 1s, P 2p and Zr 3s$_{1/2}$ and the atomic ratio of the surface region determined by the XPS technique. In the unirradiated sample, E_b values were *ca.* 0.6 eV higher than that of the unreacted sample. In the irradiated sample, only the E_b value of Zr 3s$_{1/2}$ was shifted to higher energy by +0.4 eV. The atomic ratios of Ag/P, Zr/P and Ag/Zr were the same values for the unreacted and the irradiated samples. In the dark Ag/P and Zr/P decreased while Ag/Zr was unchanged. The high E_b values for the unirradiated sample and the decrease in the atomic ratio seems to be due to the adsorption of BQ on the surface, because the surface atoms constituting $Ag_{1-x}H_xZr_2(PO_4)_3$ were recovered by adsorbed species and were stabilized. The decrease in Ag/P
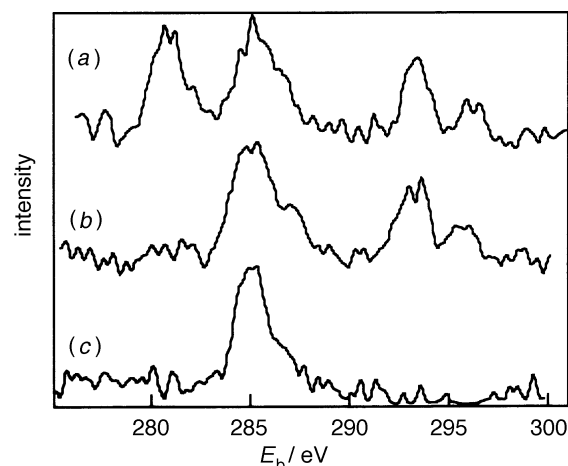

Fig. 6 Reaction scheme of conversion of HQ to BQ and DHQH$_2$ in the $Ag_{1-x}H_xZr_2(PO_4)_3$ suspension in the dark and during irradiation

Fig. 7 XPS spectra of C 1s on $Ag_{1-x}H_xZr_2(PO_4)_3$ powders used in the experiment of Fig. 2; (*a*) after the reaction in the dark, (*b*) after the reaction during irradiation and (*c*) before the reaction. The peak at 285 eV was due to contaminant C, those at 293 and 295 eV were due to K 2p$_{3/2}$.

Table 2 Binding energies and the atomic ratio of surface region determined by XPS

	Ag 3d$_{5/2}$	O 1s	P 2p	Zr 3s$_{1/2}$			
		eV			Ag/P	Zr/P	Ag/Zr
$Ag_{1-x}H_xZr_2(PO_4)_3$[a]							
dark	369	532.2	134.3	434.5	0.054	0.32	0.17
light	368.3	531.7	133.7	434.4	0.062	0.36	0.17
unreacted	368.4	531.6	133.6	434	0.06	0.36	0.17

[a] $Ag_{1-x}H_xZr_2(PO_4)_3$ powder after reaction in the dark, during irradiation, and before the reaction shown in Fig. 2.

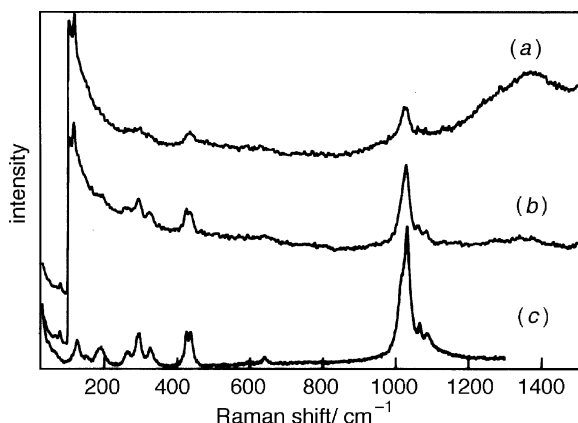**Fig. 8** Raman spectra of $Ag_{1-x}H_xZr_2(PO_4)_3$ powders used in the experiment of Fig. 2; (*a*) after the reaction in the dark, (*b*) after the reaction during irradiation and (*c*) before reaction

and Zr/P suggests that BQ was adsorbed on the Ag and Zr atoms on the surface.

Raman spectra of the adsorbed species were measured by the FT-Raman technique. Fig. 8 shows the Raman spectra of $Ag_{1-x}H_xZr_2(PO_4)_3$ powders before and after reaction in the dark and under irradiation. As shown in Fig. 8, compared to the unreacted sample, both samples in the dark and during irradiation showed enhanced peak intensities at 104 and 119 cm^{-1} due to zirconium phosphate.[5] The reason why these peaks were enhanced could not be determined. In the dark, a new broad peak at *ca.* 1370 cm^{-1} appeared, and for the irradiated sample, its peak intensity decreased. These Raman shifts are characteristic of BQ and HQ;[18,19] for BQ, peaks at 1394 and 1299 cm^{-1} are assigned to C—C stretching vibrations while for HQ, peaks at 1370 and 1260 cm^{-1} are assigned to the C—H bending and C—O stretching vibrations, respectively. These indicate the existence of the adsorbed species in the dark. Considering XPS and the Raman spectra of the sample in the dark, the peak at 280 eV in the XPS spectrum and that at 1370 cm^{-1} in the Raman spectra seemed to originate from the same species. Since the product in the dark was BQ (Fig. 2), the peak in the Raman and XPS spectra is due to BQ. On the other hand, the peaks based on $Ag_{1-x}H_xZr_2(PO_4)_3$ in the Raman spectra decreased in the dark, but during irradiation, clearly remained. Furthermore, since the surface had few adsorbed species during irradiation according to the surface analysis by XPS and FT-Raman spectroscopy, $Ag_{1-x}H_xZr_2(PO_4)_3$ was concluded to be able to act as a photocatalyst for the formation of $DHQH_2$ from HQ.

Conclusion

2,5-Dihydroxy-*p*-benzoquinone formed *via* HBQ· from HQ upon irradiation of an $Ag_{1-x}H_xZr_2(PO_4)_3$ suspension. HBQ· was generated from HQ by the oxidation of Ag^+ and the pho-

togenerated OH· and from BQ by the reduction of the photogenerated e^- on the surface. The formation of $DHQH_2$ was required in order to stabilize both OH· and HBQ· on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$. Surface analysis indicated the characteristic peaks of the products in the XPS and FT-Raman spectra after the reaction in the dark. The peaks were assigned to BQ considering the products formed in the dark. Therefore, the peak of BQ adsorbed on the surface of $Ag_{1-x}H_xZr_2(PO_4)_3$ was observed at 280 eV in the XPS spectra. Since these spectra showed no peaks for products during irradiation, $Ag_{1-x}H_xZr_2(PO_4)_3$ was indicated to be able to act as a photocatalyst for the formation of $DHQH_2$ from HQ.

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