Supplement to: Selective Photocatalytic Oxidation of Benzene for the Synthesis of Phenol Using Engineered Au-Pd Alloy Nanoparticles Supported on Titanium Dioxide

Ren Su,{a} Lokesh Kesavan, b Mads M. Jensen, c Ramchandra Tiruvalam, d Qian He, d Nikolaos Dimitratos, b,e Stefan Wendt, a Marianne Glasius, c Christopher J. Kiely, d Graham J. Hutchings, b,e,* and Flemming Besenbacher a,*

Sample preparation

Colloid Preparation

Monometallic Au and Pd and three distinct Au–Pd (Au-Pd, Pdshell-Auccore, and Aushell-Pdcore) sols were prepared, as described below. Aqueous solutions of PdCl₂ and HAuCl₄·3H₂O (Johnson Matthey) of the desired concentration were first prepared. Fresh aqueous solutions of poly vinyl alcohol (PVA) (1 wt% aqueous solution, Aldrich, MW=10000, 80% hydrolyzed) and of 0.1 M NaBH₄ were also prepared.

(a) Au-Pd sol: The PdCl₂ and HAuCl₄ stock solutions were mixed in the desired ratio and the required amount (1 wt%) of a PVA solution was added (m[PVA]/m[Au + Pd] = 1.2); the freshly prepared solution of NaBH₄ (n[NaBH₄]/n[Au + Pd] = 5) was then added to the solution to form a dark-brown sol.

(b) Pdshell-Auccore sol: Firstly, the required amount of a PVA solution (1 wt%) was added (m[PVA]/m[Au + Pd] = 1.2) to an aqueous HAuCl₄ solution of the desired concentration; a freshly prepared solution of NaBH₄ (0.1 M, n[NaBH₄]/n[Au] = 5) was then added to form a red sol. The solution was then stirred for 30 minutes to allow the complete reduction of all Au³⁺ in the solution. Then the required amount of the stock aqueous PdCl₂ solution was added, followed by the desired amount of NaBH₄ (0.1 M, n[NaBH₄]/n[Pd] = 5) to produce a dark brown sol. The solution was stirred for a further 30 minutes.

(c) Aushell-Pdcore sol: The Aushell-Pdcore sol was prepared in a similar way to that presented in (b). The required amount of PdCl₂ solution was added and reduced prior to the addition and reduction of the HAuCl₄ solution.

Colloid immobilisation

The afore-mentioned sols were immobilised onto the TiO₂ support (Degussa P25). Immobilisation of the sol was accomplished by adding TiO₂ (acidified to pH 1 by H₂SO₄) after a 30 min of sol-generation under vigorous stirring conditions. The total metal loading was maintained at 1% wt. For the random alloy series, samples having Au:Pd molar ratios of 7:1, 3:1, 1:1, 1:3 and 1:7 were prepared. After 2 h the slurry was filtered, washed thoroughly with deionized (DI) water and dried at 120 °C for 16 h.

Details of the preparation procedures are also available from our previous work.¹

Photocatalyst characterisations

TEM/STEM

The as-prepared sol-immobilised catalysts were prepared for TEM/STEM analysis by dry dispersing the catalyst powder onto a holey carbon TEM grid. HRTEM and HAADF imaging was carried out using a 200kV JEOL 2200FS TEM equipped with a CEOS probe aberration corrector. Figure S1 shows the representative HRTEM images of the Au₇Pd₁ and Pdshell-Auccore NPs supported on TiO₂ and the derived particle size distributions of the metal NPs. Details of the analysis can be found in some of our previous publications.¹⁻³

XRD & BET

Crystallographic information relating to the TiO₂ support material after sol-immobilisation was acquired via X-ray diffractometry (SmartLab, Rigaku employing Cu-Kα radiation). The metal decoration did not change the crystallographic polymorph distribution of the TiO₂ support (Fig. S2a), and the TiO₂ polymorph composition was identical for all samples (Fig. S2b). The metal loading and particle size was too low to be
detected by XRD. The N₂ adsorption analysis (Figs. S2c and S2d) of selected samples shows they have very similar surface areas and are very close, within experimental error, to that of the pure TiO₂ support (~50 m²·g⁻¹).³

Figure S2. (a) XRD patterns of Au, Au₄Pd₄, Au₄Pd₄Au₄Pd₄, and Pd NPs supported on TiO₂. XRD from a pristine TiO₂ support (P25) is also presented for comparison. (b) Derived polymorph composition of the TiO₂. (c) N₂ adsorption isotherms and (d) BET plots from selected catalyst samples. The derived surface areas are 33.6, 48.7, 45.8, and 46.8 m²·g⁻¹ for Pd/TiO₂, Au₄Pd₄/TiO₂, Au₄Pd₄Au₄Pd₄/TiO₂, and Pd/Pd₄Au₄Pd₄/TiO₂, respectively.³

Methodology for photocatalytic tests

Optical property of the samples

The light responses of the samples are summarized in Fig. S3(a) by means of diffuse reflectance spectroscopy (DRS). Only the Au/TiO₂ sample showed a considerable reduction of the reflectance in the 450 – 650 nm wavelength range compared to the rest of the samples (Fig. 2a), which originated from the Au surface plasmon. The spectra indicate that no visible light absorption (λ > 400 nm) was observed any other samples except Au/TiO₂.

Light source

A UV LED (365 nm, Optimax 365) light source was used in all photocatalysis experiments. The light source has a peak emission at 365 nm with a full-width-at-half-maximum (FWHM) of 10 nm, as shown in Fig. S3(b). This eliminated the possibility of visible light photoactivity of the Au/TiO₂ sample (if any) and allowed for direct comparison with the other samples.

The average photon flux of the light source was measured using a standard ferrioxalate actinometry method and was found to be ~4 × 10¹⁷ photons·s⁻¹.³

Apparatus and protocols for photocatalytic benzene oxidation

Photo-oxidation of benzene was carried out under aerated conditions at room temperature. A leak-tight reactor that was designed for in-situ UV-vis spectrometry analysis is shown in Fig. S4. The cuvette and the viewport were made of quartz. The total volume of the reactor was 125 mL. Magnetic stirring was applied throughout the reaction, and we have confirmed that the equilibrium of the diffusion can be achieved within 30 s under our stirring conditions. A 100 mg·L⁻¹ photocatalyst-water suspension was prepared, sonicated for 1 min, and UV cleaned for 2 h under continuous stirring to remove the capping ligands. Then the concentrated suspension was diluted 20 times (catalyst loading of 5 mg·L⁻¹) and transferred into the reactor to prepare a 100 mL of diluted suspension for photocatalytic reactions. The reactor was then mounted to the UV-vis spectrometer with continuous stirring (see Fig. S4). A series of UV-vis spectra were sequentially recorded for 1 h with a time interval of 5 min. A stable background was achieved after ~30 min, indicating the equilibrium state of the suspension. A 8.9 µL of benzene (≥ 99%, Sigma Aldrich) was subsequently added into the suspension to form the 1 mM benzene-catalyst suspension. Then all valves were closed to prevent the evaporation of benzene. The UV-vis spectra were continuously recorded for another 30 min with a time interval of 5 min until the benzene peaks stabilised. The UV irradiation was then commenced and UV-vis spectra were recorded in-situ at regular time intervals for all samples, as shown in Fig. S5.

Figure S4. Apparatus for recording UV-vis spectra time sequences during benzene oxidation with our photocatalysts.
Liquid phase products analysis

The absorption spectra of phenolic compounds along with benzene are shown in Fig. S6(a). A characteristic sextet of absorption peaks for benzene are located at ~250 nm with absorption coefficients ($\epsilon$) of 19 (233 nm), 31 (238 nm), 48 (243 nm), 76 (248 nm), 90 (254 nm), and 64 (260 nm) M$^{-1}$cm$^{-1}$, respectively (Fig. S6b). The light absorption of benzene at $\lambda >$ 270 nm was found to be negligible. The absorption peaks of phenol, hydroquinone, and catechol are located at 270, 289, and 275 nm, respectively, and all $\epsilon$ values were orders of magnitude higher than that of benzene, as shown in Fig. S6(c)-(e) and listed in Table S1.4 Note that the absorption peak of benzoquinone ($\lambda_{\text{max}} = 246$ nm) overlaps with that of benzene; however, it should be relatively easy to observe the evolution of benzoquinone (if any is generated) due to its extremely large $\epsilon$ value (16649 M$^{-1}$cm$^{-1}$) and distinct peak shape compared to that of benzene. Therefore, in our in-situ UV-vis experiments, the formation of benzoquinone was determined to be negligible and the concentrations of the phenolic products can be estimated using the following equations that have been reported in our previous work.$^5$

$$A_{289} = \epsilon_H^{289} \times C_H + \epsilon_C^{289} \times C_C + \epsilon_P^{289} \times C_P$$  
$$A_{275} = \epsilon_H^{275} \times C_H + \epsilon_C^{275} \times C_C + \epsilon_P^{275} \times C_P$$  
$$A_{270} = \epsilon_H^{270} \times C_H + \epsilon_C^{270} \times C_C + \epsilon_P^{270} \times C_P$$  

where $\epsilon$ is the absorption coefficient; $C$ is the concentration; Subscripts H, C, and P denote hydroquinone, catechol, and phenol, respectively. The absorption coefficients were are listed in Table S1.

Ultra high performance liquid chromatography coupled by an electrospray ionisation inlet to a quadrupole time-of-flight mass spectrometer (UHPLC-ESI-QTOF-MS, Dionex Ultimate 3000 UHPLC+ coupled to Bruker microOTOF-Q) was utilised to determine any other possible liquid phase byproducts (i.e., polycarboxylic acids).

The liquid samples for UHPLC-ESI-QTOF-MS were prepared using the following procedure:

First, a 100 mg·L$^{-1}$ photocatalyst-water suspension was prepared using the Au@core-Pd@shell/TiO$_2$ sample, sonicated for 1 min, and UV cleaned for 2 h under continuous stirring to remove the capping ligands. Then 8.9 µL of benzene ($\geq$ 99%, Sigma Aldrich) was added into the suspension to form the 1 mM benzene-catalyst suspension. Subsequently, the suspension was continuously stirred in dark conditions for 30 min to reach adsorption equilibrium. The reactor was sealed to prevent the evaporation of benzene. UV irradiation was then commenced.

---

**Table S1.** Absorption coefficients of phenol, hydroquinone, catechol, and benzoquinone at a series of specific wavelengths.

<table>
<thead>
<tr>
<th>Products</th>
<th>Coefficient / M$^{-1}$cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>246 nm</td>
</tr>
<tr>
<td></td>
<td>270 nm</td>
</tr>
<tr>
<td></td>
<td>275 nm</td>
</tr>
<tr>
<td></td>
<td>289 nm</td>
</tr>
<tr>
<td>Benzoquinone</td>
<td>16649</td>
</tr>
<tr>
<td>Catechol</td>
<td>255</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>231</td>
</tr>
</tbody>
</table>

---

Figure S5. In situ UV-vis spectra time sequences recorded during benzene oxidation for all photocatalysts in this study. P and H denote phenol and hydroquinone, respectively.

Figure S6. (a) Absorption spectra of phenolic compounds and benzene. (b)-(f) Absorption coefficients of benzene and the phenolic compounds at a series of specific wavelengths determined using various concentrations.
and 3 mL of aliquots were taken at given time intervals (0, 10, 20, 30, and 60 min) and immediately centrifuged to remove the photocatalysts. Finally, the clear liquid samples were filtered through syringe filters (0.22 µm pore size Q-Max PTFE/L) prior to analysis.

The following parameters were used for UHPLC analysis. A Waters ACQUITY UPLC HSS T3 column was kept at 45 °C during the analysis (particle size 1.8 µm, C18 phase, 100 x 2.1 mm), and the sample injection volume was 20 µL. Eluents A and B were 0.1% acetic acid and 0.1% acetic acid in acetonitrile, respectively, and the flow rate was 0.3 mL min⁻¹. The applied 17 min eluent gradient was eluent B kept at 3% for 1 min, increased to 25% in 9 min, increased to 95% in 2.5 min and kept at 95% for 2.5 min before returning to 3% B. The analysis of carboxylic acids was achieved by MS detection in negative ESI mode in a m/z range of 50-1000 using a modified method described by Kristensen and Gläsium. Positive ESI mode revealed neither significant peaks nor differences between samples (data not shown).

Extracted ion chromatograms (EICs) of significant peaks from negative ESI mode are shown in Fig. S7. Table S2 lists all possible by-products. It was clear that the most intense peak was identified as catechol, which has been determined to be less than 6 µM after UV irradiation of 60 min by UV-vis spectrometry. Since all the rest of the peaks were much less intense than that of catechol, it indicates the concentrations of these compounds should be far less than 6 µM based on the assumption that they have similar relative sensitivity factors.

<table>
<thead>
<tr>
<th>ID</th>
<th>m/z</th>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>109.03</td>
<td>catechol</td>
<td>&lt; 6 µM (a)</td>
</tr>
<tr>
<td>B</td>
<td>117.02</td>
<td>succinic acid</td>
<td>&lt; 10 µM (b)</td>
</tr>
<tr>
<td>C</td>
<td>N/A</td>
<td>carboxylic acids</td>
<td>&lt; 10 µM (b)</td>
</tr>
<tr>
<td>D</td>
<td>123.01</td>
<td>hydroxy-benzoquinone</td>
<td>&lt; 6 µM (c)</td>
</tr>
<tr>
<td>E</td>
<td>125.02</td>
<td>hydroxy-hydroquinone</td>
<td>&lt; 6 µM (c)</td>
</tr>
<tr>
<td>F</td>
<td>109.03</td>
<td>resorcinol</td>
<td>&lt; 6 µM (c)</td>
</tr>
<tr>
<td>G</td>
<td>492.06</td>
<td>unknown (d)</td>
<td>&lt; 6 µM (c)</td>
</tr>
<tr>
<td>H</td>
<td>172.10</td>
<td>unknown (f)</td>
<td>&lt; 6 µM (c)</td>
</tr>
</tbody>
</table>

(a): The concentration determined by UV-vis.  
(b): Quantified by malonic acid reference.  
(c): Based on the assumption that these molecules have similar relative sensitivity factor.  
(d): Expected to be resorcinol due to the identical mass to catechol.  
(e): Expected to be benzenediol polymer.  
(f): Only observed in the liquid sample before irradiation.

**Gas phase product analysis**

The CO₂ evolution from the complete oxidation of benzene and phenol was carried out in a leak-tight reactor that was connected to a mass spectrometer (MS, Hiden HPR-20). The same amount of photocatalyst that was used in the in-situ UV-vis reactor was dispersed in 25 ml of 1 mM benzene/phenol solution and kept in the dark for 30 min to establish adsorption equilibrium prior to experiment. A 5.5 hour irradiation was employed for the CO₂ evolution process under continuous stirring and the partial pressures of m/e = 18 (H₂O), 28 (N₂), 32 (O₂), and 44 (CO₂) were monitored in-situ. Deionised (DI) water and the same UV LED light was used throughout the experiments. Details of the photo-reactivity measurements and related calculations have been reported in detail in our previous work.3,4

**High loading test & evaluation of quantum efficiency**

We have discussed the effect of metal co-catalyst using a low catalyst loading, which avoided the excessive scattering of light that originated from the TiO₂ NPs during the in-situ UV-vis measurements. The advantages of in-situ UV-vis analysis are obvious; however, one downside is that the light cannot be fully absorbed by the photocatalysts due to their low concentration. In order to evaluate the performance under a more realistic conditions, we performed benzene oxidation using the best photocatalyst, Au₃Pd₁₋₅/TiO₂ at a much higher loading of 100 mg·L⁻¹ (20 times higher than the low loading test). Note that at such high photocatalyst loading, in-situ UV-vis spectrometry method cannot be used due to the strong scattering by the TiO₂ NPs. Therefore, we have to use ex-situ UV-vis spectrometry instead. In this case, 2 mL of aliquots were withdrawn at given time intervals, centrifuged for 10 min and measured immediately by UV-vis, as shown in Fig. S8(a). Evolution of the phenolic products that were derived from the UV-vis spectra is shown in Fig. S8(b). It is clear that the...
production of phenol was significantly enhanced (~7 times) compared to that of at low catalyst loading case, as ~140 μM of phenol have been produced within 30 min of irradiation. We also observed the evolution of benzoquinone (B) instead of hydroquinone (H) during the ex-situ UV-vis measurement, which was evolved from the oxidation of hydroquinone during the time elapsed before ex-situ UV-vis measurements.

We have also estimated the apparent quantum efficiency (AQE) for the generation of phenolic products at different times. Clearly, the Au shellPdcore/TiO2 photocatalyst showed decent AQEs within the irradiation period. A drop of AQE was observed after prolonged irradiation time, which may arise from the complete oxidation of benzene and the produced phenolic compounds.

Notes and references