

## Supplementary information

### **A heterogeneous palladium catalyst hybridised with a titanium oxide photocatalyst for direct C–C bond formation between an aromatic ring and acetonitrile**

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## Experimental

TiO<sub>2</sub> powder sample was donated from the Catalysis Society of Japan as JRC-TIO-8 (anatase, BET specific surface area was 338 m<sup>2</sup> g<sup>-1</sup>). The hybridised palladium catalyst was prepared by an oxidative photodeposition method:<sup>S1</sup> the TiO<sub>2</sub> powder was dispersed in an aqueous solution of methanol (25%) containing a palladium dichloride (PdCl<sub>2</sub>, Kishida 99%, dissolved into water with the aid of HCl to prepare the stock solution), followed by photoirradiation for 3 h from a 300 W xenon lamp (Cermax PE300BUV, PerkinElmer) with magnetically stirring under air atmosphere. Other metal catalysts hybridised with a titanium oxide were also prepared in the same manner by using each metal precursor (H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O Wako 99.9%, RhCl<sub>3</sub>•3H<sub>2</sub>O Kishida 99%, or HAuCl<sub>4</sub>•4H<sub>2</sub>O Kishida 99.9%) for comparison. The loading amount of these metal catalyst on the titanium oxide was 0.1 wt %.

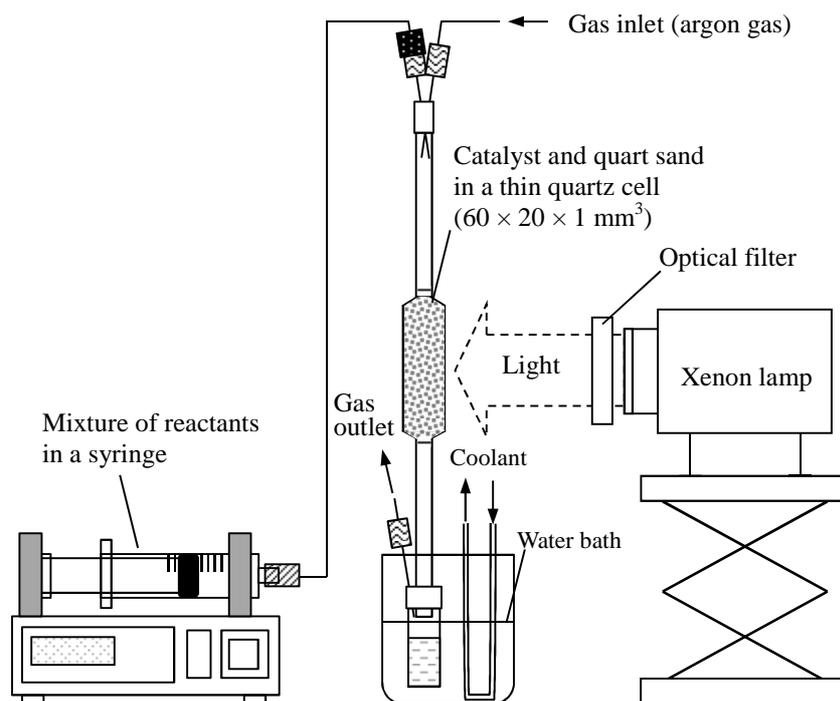
TEM images were recorded by a HITACHI H-800 electron microscope (200 kV) equipped with a CCD camera at High Voltage Electron Microscope Laboratory, Ecotopia Science Institute, Nagoya University. Diffuse reflectance (DR) UV–visible spectrum was recorded at room temperature on a JASCO V-570 equipped with an integrating sphere covered with BaSO<sub>4</sub>, where BaSO<sub>4</sub> was used as the reference. Pd K-edge XAFS (X-ray Absorption Fine Structure) spectra were recorded at the NW-10A station<sup>S2</sup> of KEK-PF (Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Japan) at room temperature with a Si(311) double crystal monochromator in a transmission mode for reference samples, and in a fluorescence mode by using the Lytle-detector<sup>S3</sup> (100 mm ion chamber filled with krypton) with a ruthenium filter ( $\mu\tau = 3$ ) for the catalyst samples. The spectra were analyzed with a REX 2000 software (Rigaku).

Before the catalytic reaction in a closed system, the catalyst (0.2 g) in a quartz photoreactor (46 cm<sup>3</sup>) was photoirradiated from beneath (20 cm<sup>2</sup>) by the xenon lamp under an air atmosphere for 1 h to clean up the catalyst surface. After the gas phase was purged by flowing argon for 1 h, benzene (0.1 mL, corresponding to 1.1 mmol, Kishida 99.5%) and acetonitrile (3.9 mL, corresponding to 74.7 mmol, Kishida 99.8%) were introduced unless otherwise stated. When the isotopic effects were examined, benzene-*d*<sub>6</sub> (TCI, 99.6%D) and CD<sub>3</sub>CN (Euriso-Top, 99.8%D) were employed instead. Then, the mixture of the reactants and the catalyst was photoirradiated by the xenon lamp from the bottom for 3 h around room temperature (313 K) with magnetically stirring in the absence of oxygen. When the irradiation light wavelength was limited, an optical band-pass filter was used. After the photoreaction, a part of the gas was collected by a gas tight syringe, and analyzed by a GC-TCD (Shimadzu, GC-8A). The liquid phase was diluted with methanol, and filtered. The filtrate was analysed by a GC-MS (Shimadzu, QP-5050A).

To demonstrate the stability of the continuous catalytic reaction over this hybrid catalyst, a fixed-bed flow reactor was employed. The apparatus setup is shown in Fig. S1. The catalyst sample (0.2 g) mixed with quartz sand in another quartz cell (60 × 20 × 1 mm<sup>3</sup>) was irradiated from the xenon lamp for 1 h under an air atmosphere, and then, the gas phase in the reactor was purged by argon for 1 h. After preliminary flowing a mixture of benzene (10%), acetonitrile (75%) and water (15%) with the aid of an argon gas flow (<1.0 mL/min), the photocatalyst was irradiated from the xenon lamp in the flow of the mixture (7.5 mL/h) and argon (<1.0 mL/min). The effluent (liquid phase) was periodically collected and analyzed with the GC-MS (Shimadzu, QP-5050A).

ESR measurement was carried out at room temperature with an X-band spectrometer (JEOL, JES-RE1X) by using a TM<sub>110</sub>-mode cavity with a quartz flat cell (JEOL ES-LC12) for an aqueous sample. After the Pd(0.1)/TiO<sub>2</sub> sample was photoirradiated under an air atmosphere with the xenon lamp for 2 h to clean up the surface, a part of the sample (0.2 g) was dispersed in the mixture of acetonitrile (1.7 mL) and water (0.3 mL)

with PBN (N-tert-Butyl- $\alpha$ -phenylnitron, Tokyo Chemical, 98%, 1 mmol). A portion of the obtained suspension was introduced into the quartz cell and photoirradiated in the cavity from an ultrahigh pressure Hg lamp (Ushio UI-501C) equipped with an optical cut-off filter permitting the light of longer than 350 nm for 40 min, followed by the ESR measurement at room temperature. ESR parameters for the measurements were microwave power of 1 mW, field modulation width of 0.025 mT at 100 kHz, time constant of 0.3 s, and sweep time of 8 min, respectively. We confirmed that the observed signals (Fig. 1) did not appear in the dark or in the absence of the catalyst.



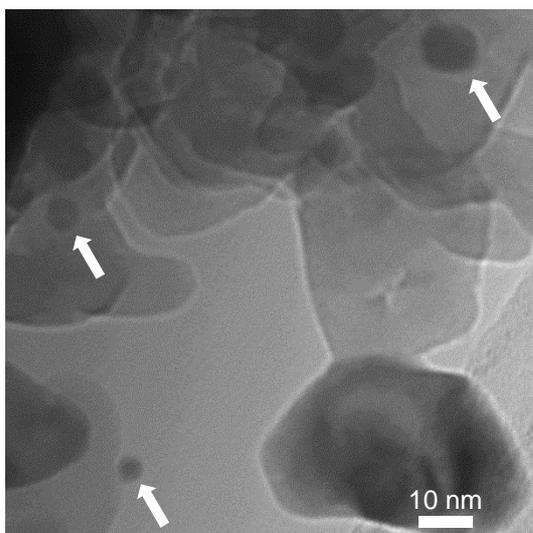
**Fig. S1** A fixed-bed flow reactor.

## Results and discussion

### 1. Characterization of the hybrid catalyst (Pd(0.1 wt%)/TiO<sub>2</sub>)

The prepared hybrid catalyst, Pd(0.1wt%)/TiO<sub>2</sub>, was characterised by transmission electron microscopy (TEM), diffuse reflectance UV-visible spectroscopy, and X-ray absorption spectroscopy (XAS).

Fig. S2 shows a TEM image of the Pd(0.1wt%)/TiO<sub>2</sub> hybrid catalyst. Some spherical palladium nanoparticles are clearly observed as indicated by the arrows, which are attached to larger titanium oxide particles. The sizes of the palladium nanoparticles was distributed from 3 nm to 11 nm in diameter, where the average was 5.8 nm in diameter.



**Fig. S2** TEM image of the Pd(0.1wt%)/TiO<sub>2</sub> hybrid catalyst.

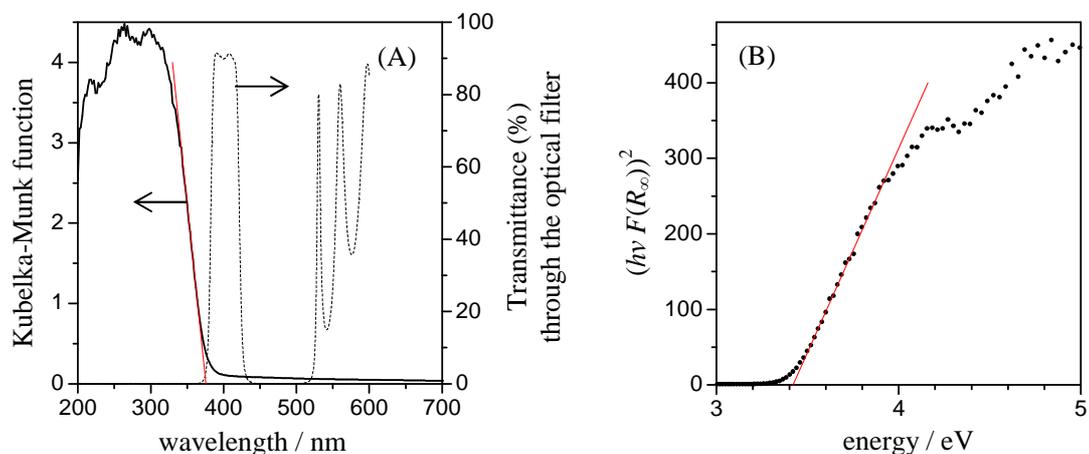
Fig. S3 shows the DR UV-vis spectrum of the Pd(0.1wt%)/TiO<sub>2</sub> sample (JRC-TIO-8, the Catalysis Society of Japan). The specific surface area is 338 m<sup>2</sup> g<sup>-1</sup>). This shows a broad absorption band due to anatase TiO<sub>2</sub>. The bandgap ( $E_g$ ) estimated from the edge in Fig. S3A was estimated as 3.30 eV (376 nm), while a Tauc plot for direct allowed transition according to eqn (S1)<sup>S4</sup> gives the  $E_g$  to be 3.42 eV (363 nm) in Fig. S3B:

$$(hv F(R_\infty))^2 = A(hv - E_g) \quad (\text{S1})$$

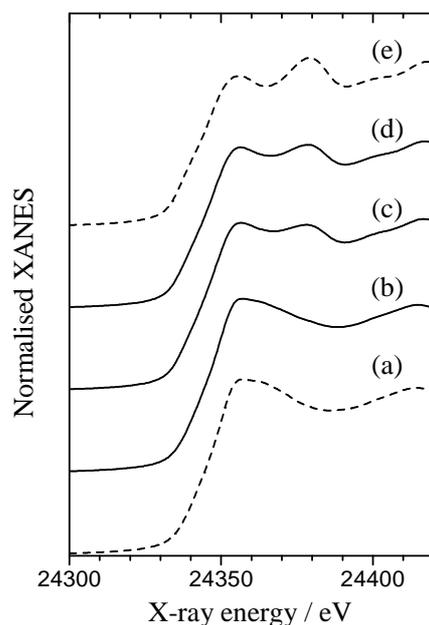
where  $hv$  is the energy of the incident light,  $F(R_\infty)$  is the value of Kubelka-Munk function,  $A$  is a constant, and  $E_g$  is the bandgap. It is clear that the light through the optical filter (405±20 nm) can excite the titanium oxide photocatalyst in the hybrid catalyst as shown in Fig. S3A.

Fig. S4 shows Pd K-edge X-ray absorption near-edge structures (XANES) of the Pd(0.1wt%)/TiO<sub>2</sub> hybrid catalyst sample before and after the reaction test, with those of palladium oxide and metal as references. The XANES spectrum of the catalyst sample before the reaction (Fig. S4b) is almost similar to that of palladium oxide (Fig. S4a), indicating that the palladium nanoparticles in the as-prepared hybrid catalyst were not completed but almost oxidised. The spectrum of the catalyst sample after the reaction test upon photoirradiation for 1 h shows the characteristic feature with the two peaks at 24,356 and 24,378 eV (Fig. S4c), while the sample after the reaction for 3 h (Fig. S4d) shows a spectrum similar to the metallic palladium foil

(Fig. S4e). This means that the palladium nanoparticles were gradually reduced to be more metallic during the reaction condition since the catalyst was photoirradiated in the organic solvent (acetonitrile with a small amount of water).



**Fig. S3** Diffuse reflectance UV-visible spectrum of the Pd(0.1wt%)/TiO<sub>2</sub> hybrid catalyst: (A) Kubelka-Munk function, and (B) Tauc plot. The broken line shows a transmission spectrum of the optical filter, which permits the light of 405±20 nm in wavelength.



**Fig. S4** Normalized XANES of PdO powder (a), the Pd(0.1wt%)/TiO<sub>2</sub> hybrid catalyst before the reaction (b), after the reaction for 1 h (c) and 3 h (d), and Pd foil (e). See Table S2 for the reaction condition.

## 2. Reaction tests

The cyanomethylation took place under the light of  $405 \pm 20$  nm in wavelength most selectively on the hybrid catalyst (Table S1, entry 1). The light around 365 nm in wavelength provided high yield of benzyl cyanide, although succinonitrile and hydrogen were more produced (Table S1, entry 2). Under the unrestricted light from the xenon lamp, these byproducts were predominantly produced (Table S1, entry 3). These results suggest that the light of short wavelength would produce an excess amount of cyanomethyl radical compared to the benzene under these reaction conditions, which promoted the production of succinonitrile and hydrogen through the homocoupling of the cyanomethyl radicals.

**Table S1** Results of the reaction tests over the Pd/TiO<sub>2</sub> hybrid catalyst<sup>a</sup>

Entry	Catalyst	$\lambda^b$ / nm	Products <sup>c</sup> / $\mu$ mol					$Y^d$ (%)	$S_b^e$ (%)	$S_a^e$ (%)
			BnCN	PhOH	BP	SN	H <sub>2</sub>			
1	Pd/TiO <sub>2</sub>	$405 \pm 20^f$	3.6	0.3	n.d. <sup>g</sup>	0.4	3.6	0.32	92	82
2	Pd/TiO <sub>2</sub>	$365 \pm 20^h$	6.0	0.7	n.d. <sup>g</sup>	6.6	19.0	0.55	90	31
3	Pd/TiO <sub>2</sub>	$>200^i$	2.4	0.2	n.d. <sup>g</sup>	23.7	62.1	0.22	$<92^j$	4.8

<sup>a</sup> Catalyst (Pd(0.1 wt %)/TiO<sub>2</sub>) 0.2 g, benzene 0.1 mL (1.1 mmol), acetonitrile 3.9 mL (74.7 mmol). Reaction time 3 h. <sup>b</sup> Wavelength of the incident light. <sup>c</sup> BnCN: benzyl cyanide, PhOH: phenol, BP: biphenyl, SN: succinonitrile, H<sub>2</sub>: hydrogen. <sup>d</sup> BnCN yield:  $Y(\%) = 100 \times Y_{\text{BnCN}} / I_{\text{benzene}}$ , where  $Y_x$  and  $I_{\text{benzene}}$  stand for the amount ( $\mu$ mol) of obtained X and the initial amount ( $\mu$ mol) of benzene, respectively. <sup>e</sup> BnCN selectivity: benzene-based,  $S_b(\%) = 100 \times Y_{\text{BnCN}} / (Y_{\text{BnCN}} + Y_{\text{PhOH}} + 2 \times Y_{\text{BP}})$ , and acetonitrile-based,  $S_a(\%) = 100 \times Y_{\text{BnCN}} / (Y_{\text{BnCN}} + 2 \times Y_{\text{SN}})$ . <sup>f</sup> The wavelength of the incident light was limited to  $405 \pm 20$  nm. The light intensity was 27 mW cm<sup>-2</sup> when measured at  $405 \pm 30$  nm. <sup>g</sup> n.d. = not detected. <sup>h</sup> The wavelength of the incident light was limited to  $365 \pm 20$  nm. The light intensity was 27 mW cm<sup>-2</sup> when measured at  $365 \pm 15$  nm. <sup>i</sup> No optical filter was used. The light intensities were 8, 50 and 120 mW cm<sup>-2</sup> when measured at  $250 \pm 10$ ,  $365 \pm 15$  and  $405 \pm 30$  nm, respectively. <sup>j</sup> The selectivity should be much less than the shown value because the amounts of many unknown products were not determined.

This photoassisted direct cyanomethylation with acetonitrile can be applied to other aromatic compounds as listed in Table S2. From several monosubstituted benzenes and pyridine, the corresponding cyanomethylation products were obtained in varying yield and selectivity. In addition, the trend of the isomer distribution of the obtained cyanomethylation products for each monosubstituted benzene was very unique.

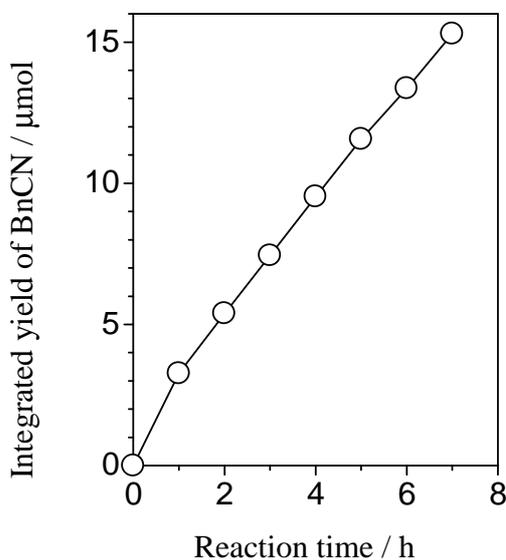
The result listed in Table S2, entry 1, corresponds to an examination for the successive reaction of the cyanomethylation of benzene over the hybrid catalyst. Even upon photoirradiation of a high intensity (70 mW cm<sup>-2</sup>), very small amounts of cyanomethylation products (m/e=156) were obtained. Thus, the reaction rate of the successive reaction should be very slow, which would originate from that the reaction proceeded on the catalyst surface and the adsorbed state would not be suitable for the reaction between the adsorbed benzyl cyanide and cyanomethyl radical. The position for the substitution (aromatic ring or methylene group) of the successively produced three compounds were unclear at present except for *o*-di(cyanomethyl)benzene.

**Table S2** Results of the reaction tests for various substrates <sup>a</sup>

Entry	Substrates	Products / μmol	Products / μmol				Y <sup>b</sup> (%)	S <sub>b</sub> <sup>c</sup> (%)
			<i>o</i> -	<i>m</i> -	<i>p</i> -	total		
1 <sup>d</sup>		Three kinds of compounds (m/e=156) <sup>e</sup>	0.05	-	-	0.47	0.05	-
2			0.7	tr. <sup>f</sup>	3.5	4.2	0.43	13
3			0.6	0.5	0.5	1.6	0.16	57
4			0.1	tr. <sup>f</sup>	tr. <sup>f</sup>	0.1	0.01	16
5			0.9	0.9	0.7	2.5	0.26	41
6			0.3	0.1	0.1	0.5	0.06	23
			2-	3-	4-	total		
7 <sup>g</sup>			13	0.7	n.d. <sup>h</sup>	14	1.1	78

<sup>a</sup> Catalyst (Pd/TiO<sub>2</sub>) 0.2 g, substrate 0.1 mL (0.92–1.1 mmol), acetonitrile 3.85 mL, water 0.05 mL, reaction time 1 h, wavelength of the incident light 365±20 nm, the light intensity 27 mW cm<sup>-2</sup>. <sup>b</sup> Yield of the cyanomethylation products. <sup>c</sup> Selectivity to cyanomethylation products determined from the amount of the obtained aromatic products. <sup>d</sup> Catalyst (Pd/TiO<sub>2</sub>) 0.2 g, benzyl cyanide 0.1 mL (0.87 mmol), acetonitrile 3.9 mL, water 0.0 mL, reaction time 3 h, wavelength of the incident light 405±20 nm, the light intensity 70 mW cm<sup>-2</sup>. <sup>e</sup> The three compounds included at least *o*-di(cyanomethyl)benzene. Other two were assumed as two compounds among the following three candidates, *m*-di(cyanomethyl)benzenes, *p*-di(cyanomethyl)benzene or 2-phenylsuccinonitrile. <sup>f</sup> tr. = trace. <sup>g</sup> Pyridine 0.1 mL (1.2 mmol), acetonitrile 2.9 mL, water 1.0 mL. <sup>h</sup> n.d. = not detected.

A reaction test in the fixed-bed flow reactor was carried out in the presence of water (Fig. S5). After the initial period less than 1 h, the product (BnCN) was produced at a constant rate (2.0  $\mu\text{mol/h}$ ) at least 6 h. TON (per the number of the Pd atom in the catalyst) reached 8.1 for 7 h. This result shows that the reaction can continuously progress without any catalyst deactivation.



**Fig. S5** The continuous cyanomethylation of benzene in the fix-bed flow reactor with the hybrid catalyst. For the reaction condition, see the experimental section in this ESI.

## References

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