

Preparation of Hydroxynaphthalene-Modified TiO₂ via Formation of Surface Complexes and their Applications in the Photocatalytic Reduction of Nitrobenzene under Visible-Light Irradiation

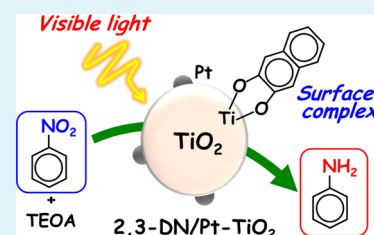
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S Supporting Information

ABSTRACT: Visible light-sensitive photocatalysts were designed by the surface modification of TiO₂ using hydroxynaphthalenes, i.e., mono- and dihydroxy derivatives of naphthalene, via formation of surface complexes. The differences in the coordination ability on TiO₂ were confirmed depending on the numbers and substitution patterns of hydroxy groups. The relatively intense visible light absorption was observed after modification of TiO₂ surface by colorless 2,3-dihydroxynaphthalene (2,3-DN) having two neighboring hydroxy groups. Platinized TiO₂ (Pt-TiO₂) modified with suitable amount of 2,3-DN showed higher photocatalytic performances and good reusability in the reduction of nitrobenzene to aminobenzene with relatively high selectivity under irradiation of visible light ($\lambda > 420$ nm).

KEYWORDS: surface complex, TiO₂, photocatalyst, hydroxynaphthalenes



1. INTRODUCTION

Over the last several decades, TiO₂-based photocatalysts have been investigated by many researchers for their practical uses in reduction technology of undesired organics as well as their applications in the production of clean energies.^{1–6} The functional coatings are also studied for accumulating multiple functions such as self-cleaning and surface hydrophilic properties.^{3,7–9} For efficient removal of dilute organics in air and water, controlling of TiO₂ architectures as well as combinations of TiO₂ with adsorbents such as porous siliceous materials and carbon materials have been widely researched.^{10–14} Moreover, unique photocatalytic reactions for production of important chemicals can occur on TiO₂ under controlled reaction conditions.^{15–20}

On the other hand, the development of photocatalytic systems, which work not only under UV light but also under visible light, has been a great concern regarding the efficient utilization of solar light and the need to address the world's energy problems. The doping of transition metals, nitrogen, and other elements into TiO₂ has contributed greatly to photocatalytic reactions under visible light.^{21–25} The loading of metal nanoparticles and metal ions is also effective for giving the sensitivity to visible light.^{26–28} The combination of TiO₂ with precious organic dyes such as derivatives of ruthenium-bipyridyl complexes is also a promising method for achieving the design of visible light-sensitive TiO₂-based materials.^{29–31} Another method for enabling the uses of visible light is surface modification of TiO₂ by colorless aromatics with phenolic hydroxyl or carboxylic groups such as catechol and salicylic acid.^{32–39} The direct electron transfer from coordinated aromatics to the conduction band of TiO₂ upon absorption

of visible light has the potential to induce various photocatalytic reactions under controlled conditions.^{36–39} In the present study, hydroxynaphthalenes, i.e., mono- and dihydroxy derivatives of naphthalene, with different substitution patterns were adopted as surface-attached ligands of TiO₂ and Pt-TiO₂ for the design of visible-light-sensitive TiO₂-based materials. The coordination abilities of hydroxynaphthalenes on TiO₂ as well as the light absorption properties of prepared samples were investigated in detail. We also explored their photocatalytic performances in the reduction of nitrobenzene (NB) to aminobenzene (AB) under visible light ($\lambda > 420$ nm) irradiation.

2. EXPERIMENTAL SECTION

TiO₂ (Ishihara Sangyo, Ltd., ST-01) used in this study was supplied from the Catalysis Society of Japan as a reference catalyst. Mono- and dihydroxy derivatives of naphthalene, i.e., 1-naphthol (abbreviated as 1-NAP), 2-naphthol (2-NAP), 1,2-dihydroxynaphthalene (1,2-DN), 1,3-dihydroxynaphthalene (1,3-DN), 1,4-dihydroxynaphthalene (1,4-DN), and 2,3-dihydroxynaphthalene (2,3-DN), were purchased from Tokyo Kasei Kogyo Co., Ltd. Hydrogen hexachloroplatinate(IV) hexahydrate (H₂PtCl₆·6H₂O), nitro benzene (NB), aminobenzene (AB), acetonitrile, and acetone were purchased from Nacalai Tesque, Inc. Triethanolamine (TEOA) was obtained from Aldrich. All chemicals were used without further purification.

The loading of Pt nanoparticles on TiO₂ was carried out by photodeposition from a deaerated aqueous methanol solution of H₂PtCl₆·6H₂O under UV light irradiation ($\lambda > 290$ nm). The Pt content of the obtained sample (Pt-TiO₂) was determined to be 1 wt

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% by inductively coupled plasma (ICP) analysis. The surface treatment of TiO_2 and Pt-TiO_2 for formation of surface complexes was performed using mono- and dihydroxy naphthalene derivatives as surface-attached ligands. For preparation of surface treated samples, a given amount of NAP and DN in acetone was poured into TiO_2 and Pt-TiO_2 , and the mixture was stirred at 298 K for 1 h. Samples were then centrifuged, repeatedly washed with acetone, and then dried under vacuum for 12 h. Samples prepared using 2,3-DN as the surface attached ligand were denoted as 2,3-DN(*n*)/ TiO_2 and 2,3-DN(*n*)/ Pt-TiO_2 , where *n* describes the contents of 2,3-DN (*n* wt%).

Each sample was characterized by various methods. Diffuse reflectance UV–vis spectra were measured at 298 K using a Shimadzu UV-2450A double-beam digital spectrophotometer. FT-IR spectra were recorded with a resolution of 4 cm^{-1} using a JASCO FT/IR-6100. XRD measurements were performed using a Rigaku Ultima IV X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) micrographs were obtained with a Hitachi Hf-2000 FE-TEM operated at 200 kV. Nitrogen adsorption–desorption isotherms were recorded by using a BEL-SORP max (BEL Japan, Inc.) at 77 K after degassing of samples under vacuum for 2 h.

The coordination ability of NAP and DN on TiO_2 was evaluated from the concentration changes in solution before and after surface treatment. The initial concentration of NAP and DN in acetone was adjusted to 10 mmol/L. Pt-TiO_2 (300 mg) was added to 30 mL of the NAP and DN solution and vigorously stirred at 298 K for 1 h. After separation of colored Pt-TiO_2 , the residual quantities of NAP and DN in acetone were monitored by gas chromatography (Shimadzu GC-2014 with flame ionization detector equipped with TC-1 capillary column).

Photocatalytic reduction of NB in the presence of TEOA was carried out under visible-light irradiation ($\lambda > 420\text{ nm}$). Fixed amounts of catalysts (50 mg) and 10 mL of acetonitrile solution of NB (0.1 mmol) and TEOA (1 mmol) were charged into a Pyrex reaction vessel. After bubbling an argon into the solution for 30 min, visible light ($\lambda > 420\text{ nm}$) irradiation was carried out using a 500 W Xe arc lamp through a colored filter (HOYA; L-42). The analysis of product was performed on the gas chromatograph (Shimadzu GC-2014). The solid catalysts were recovered by centrifugation, washed three times with deionized water, dried under vacuum at 298 K, and subjected to the next photocatalytic reaction.

3. RESULTS AND DISCUSSION

The change in the light absorption properties of Pt-TiO_2 before and after treatment with an acetone solution of hydroxynaphthalenes (NAP and DN) was investigated by UV–vis spectroscopy. As shown in Figure 1a, Pt-TiO_2 exhibited an absorption band below 380 nm corresponding to the band gap energy of TiO_2 (anatase). After treatment of Pt-TiO_2 with the solution of hydroxynaphthalenes, a new absorption was observed in the visible-light region below 600 nm (Figure 1b–i). These visible-light absorbances could be assigned to the ligand-to-metal charge transfer (CT) of the surface complexes formed between the surface Ti atoms and the phenolic compounds (surface-attached ligands).^{32–34} The color change upon immersion of Pt-TiO_2 into the solution of hydroxynaphthalenes indicates clearly the formation of surface complexes. Hydroxynaphthalenes (1-NAP, 2-NAP, and 2,3-DN) showed no absorption in the visible light region (Figure 1j, k, o). A clear spectral change was thus observed after formation of surface complexes between TiO_2 and these hydroxynaphthalenes. The powder color of Pt-TiO_2 immediately changed to yellowish gray. As compared to the uses of 1,2-dihydroxybenzene (catechol) as surface-attached ligands, intense absorption in the visible-light region was observed after modification by 2,3-DN having additional aromatic ring.³⁵ In the case of the treatment of Pt-TiO_2 with 1,2-DN, 1,3-DN, and 1,4-DN solutions, similar spectral changes were observed; however, the

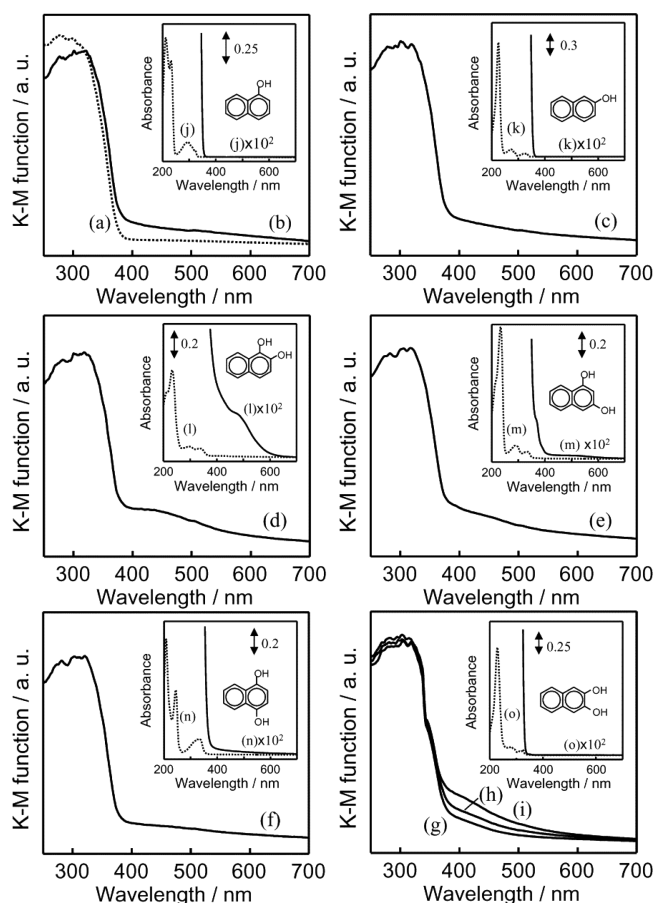


Figure 1. Diffuse reflectance UV–vis spectra of (a) Pt-TiO_2 , (b) 1-NAP(1)/ Pt-TiO_2 , (c) 2-NAP(1)/ Pt-TiO_2 , (d) 1,2-DN(1)/ Pt-TiO_2 , (e) 1,3-DN(1)/ Pt-TiO_2 , (f) 1,4-DN(1)/ Pt-TiO_2 , (g–i) 2,3-DN(*n*)/ Pt-TiO_2 (*n* = (g) 0.5, (h) 1, and (i) 3). Inset shows transmission UV–vis spectra of corresponding hydroxynaphthalenes ((j) 1-NAP, (k) 2-NAP, (l) 1,2-DN, (m) 1,3-DN, (n) 1,4-DN, (o) 2,3-DN in acetonitrile (0.02 mmol/L)).

changes were relatively small. The intrinsic visible-light absorption of these hydroxynaphthalenes overlapped with the CT absorption of the surface complexes (Figure 1l–n). As shown in Figure 1g–i, visible-light absorption also became larger with the increase in 2,3-DN coordinated on Pt-TiO_2 .

The coordination ability of NAP and DN, which have different numbers and substitution patterns of hydroxyl groups, was also evaluated by the treatment of Pt-TiO_2 with the NAP and DN solution. Figure 2 shows the amounts of hydroxynaphthalenes coordinated on TiO_2 surface after treatment of Pt-TiO_2 by their acetone solution. The amounts of coordinated 1-NAP and 2-NAP having one hydroxyl group on TiO_2 were small compared to those of hydroxynaphthalenes with two hydroxyl groups. Hydroxynaphthalenes possessing two neighboring hydroxyl groups, i.e., 1,2-DN and 2,3-DN, showed relatively large amounts coordinated on TiO_2 . The adjacent hydroxyl groups of 1,2-DN and 2,3-DN are more suited for formation of stable bidentate structures such as mononuclear chelating and binuclear bridging, as shown in Figure 3. The formation of surface complexes occurred through dehydration between Ti-OH with the phenolic hydroxyl groups of 2,3-DN in the same manner as the reported mechanisms in other phenolic compounds.^{32–37}

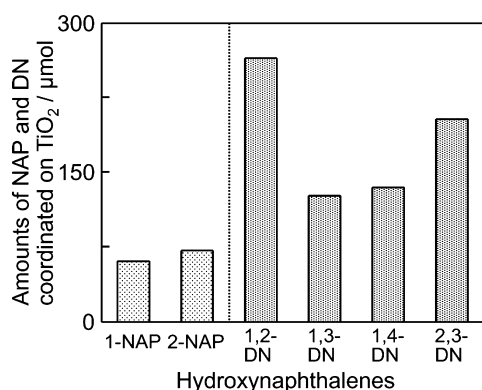


Figure 2. Amount of hydroxynaphthalenes coordinated on TiO₂ after treatment of Pt-TiO₂ with their acetone solutions at 298 K.

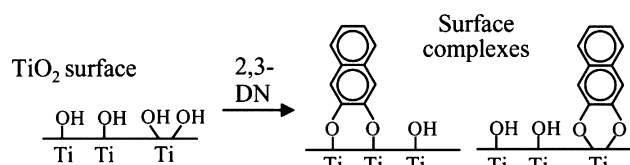


Figure 3. Schematic illustration of surface complexes formed by the coordination of 2,3-DN on TiO₂ surface.

Figure 4 shows transmission FT-IR spectra of free 2,3-DN and as the difference in the spectrum before and after surface

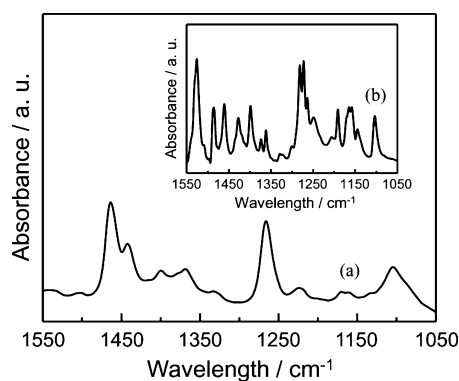


Figure 4. Transmission FT-IR spectra of (a) 2,3-DN(1)/Pt-TiO₂ and (b) free 2,3-DN.

treatment of Pt-TiO₂. Free 2,3-DN exhibits many FT-IR peaks assigned to the stretching vibrations of aromatic ring ($\nu(\text{C}-\text{C})/\nu(\text{C}=\text{C})$; 1484, 1459, and 1425 cm^{-1}), bending vibration of C-H groups ($\delta(\text{C}-\text{H})$; 1102 cm^{-1}), and the stretching or bending vibrations of phenolic groups ($\nu(\text{C}-\text{OH})$, $\delta(\text{C}-\text{OH})$; 1523 and 1400–1130 cm^{-1}).³⁵ The disappearance of FT-IR peaks due to the existence of phenolic groups was observed in the case of 2,3-DN(1)/Pt-TiO₂, suggesting the formation of surface complexes through the dehydration reaction as shown in Figure 3. The formations of surface complexes also lead to the decreases and broadening of other FT-IR peaks, which can be ascribed to the influence of different perturbations in the vibrations of the coordinated 2,3-DN.³⁵

The observation of Pt particles supported on TiO₂ by photodeposition method was carried out by TEM measurement (Figure 5). Many Pt metal particles were formed and homogeneously dispersed on TiO₂. The average diameter of the Pt particles was determined to be ca. 3.4 nm from analysis

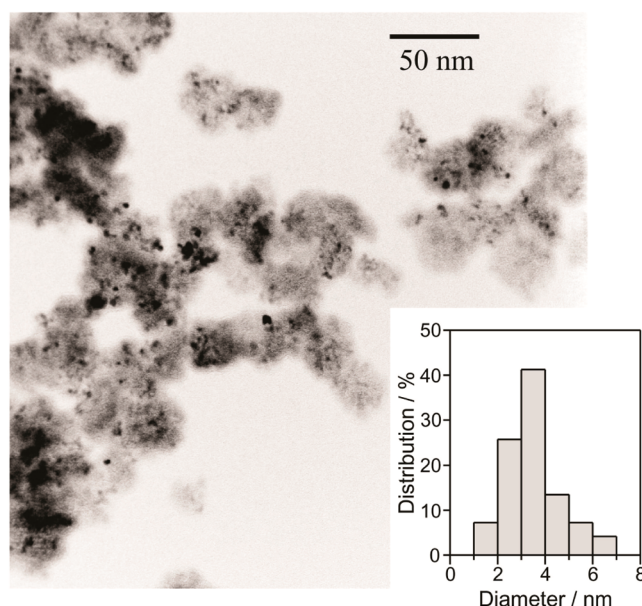
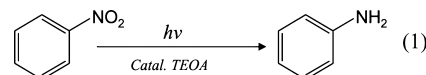


Figure 5. TEM image of Pt-TiO₂ and size distribution diagram of Pt metal.

of TEM images. XRD peaks attributed to the face-centered cubic (fcc) Pt metal and/or oxide could not be confirmed because of the smaller Pt nanoparticles dispersed on the TiO₂ surface. Moreover, the crystalline structure of TiO₂ (anatase) as well as surface area (ca. 240 m^2/g) of Pt-TiO₂ was hardly changed even after formation of surface complexes.

The catalytic performances of prepared samples were investigated under visible light irradiation ($\lambda > 420 \text{ nm}$). The photocatalytic reduction of NB to AB was adopted as a model reaction in the presence of TEOA as a sacrificial reagent (eq 1).



Amino aromatics are important chemicals as intermediates for syntheses of dyes and other compounds.^{18,19} As shown in Figure 6, the formation of AB was observed on NAP or DN-modified Pt-TiO₂, although this reaction hardly occurred in the case of original TiO₂ and Pt-TiO₂. These results clearly suggest that the catalytic activities under visible light are induced by

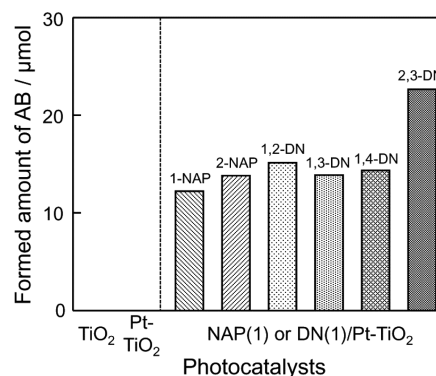
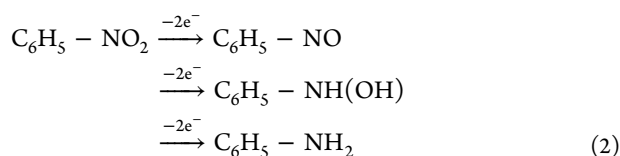


Figure 6. Amount of aminobenzene formed in the photocatalytic reduction of nitrobenzene on each photocatalyst under visible light ($\lambda > 420 \text{ nm}$) irradiation for 2 h ([Catal.] = 50 mg, [NB] = 0.1 mmol, [TEOA] = 1 mmol, [CH₃CN] = 10 mL).

surface complexes. It was also found that 2,3-DN(1)/Pt-TiO₂ showed a higher yield of AB compared to that on other samples. The turnover number calculated by the ratio of produced amount of AB to the content of 2,3-DN as surface-attached ligands also exceeded 7 after visible light irradiation for 2 h, indicating that this reaction firmly proceeded photocatalytically. The large absorption ability of visible light originated from the formation of surface complexes lead to the higher catalytic performances in this reaction. The selectivity of AB calculated by the ratio of produced amount of AB to consumed amount of NB on 2,3-DN(1)/Pt-TiO₂ was ca. 75% after visible light irradiation for 2 h. It has been reported that the photocatalytic reduction of nitro group to amino group consists of several reaction steps (eq 2).⁴⁰



Further reactions lead to the formation of oligomers of AB as minor products. As a consequence, the yield of AB is reduced in this reaction system.

Considering the better coordination ability and light absorption property of each hydroxynaphthalene, we mainly focused hereafter on the uses of colorless 2,3-DN as surface-attached ligands for designing visible light-sensitive systems. The effect of 2,3-DN content and the presence of supported Pt nanoparticles on the conversion of NB and yield of AB was also investigated on 2,3-DN(*n*)/Pt-TiO₂ (*n* = 0, 0.5, 1, 3 wt %) and DN(1)/TiO₂. The conversion of NB (selectivity of AB) on 2,3-DN(1)/TiO₂ and 2,3-DN(1)/Pt-TiO₂ was 26.5% (ca. 30%) and 42.7% (ca. 75%), respectively. The efficient separation of photoformed electrons and holes by loading of Pt on the TiO₂ surface played an important role for enhancement of this reaction with relatively high AB selectivity. The visible light absorption in the wavelength region from 400 to 600 nm was increased upon increasing content of 2,3-DN as surface attached ligands (Figure 1(g-i)). Although 2,3-DN(1)/Pt-TiO₂ showed the highest yield of AB (Figure 7), the selectivity of AB was comparable in each sample. Analogous to ruthenium complexes,³¹ the charge-separated pairs formed by the electron

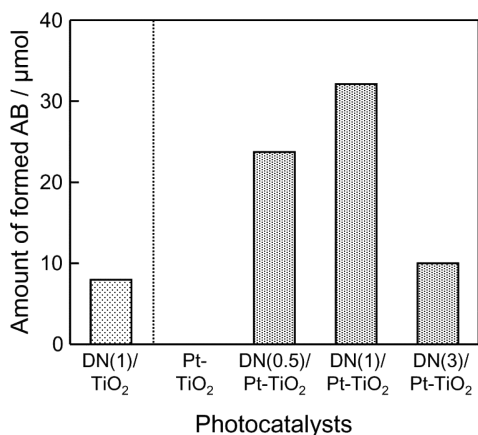


Figure 7. Amount of aminobenzene formed in the photocatalytic reduction of nitrobenzene on each photocatalyst under visible light ($\lambda > 420$ nm) irradiation for 4 h ([Catal.] = 50 mg, [NB] = 0.1 mmol, [TEOA] = 1 mmol, [CH₃CN] = 10 mL).

injection from 2,3-DN to TiO₂ (positive site), as well as the transformation of the thus formed electron into another 2,3-DN (negative site), may lead to a recombination into the original ground state. Considering the relatively large amount of 2,3-DN loaded on the Pt-TiO₂ surface, this process might affect the photocatalytic performance of 2,3-DN(3)/Pt-TiO₂. The shapes of coordinated aromatic molecules also contributed to the photocatalytic activity. Even though the loading amount was almost the same, aromatic molecules with phenolic hydroxyl groups and bulky alkyl substituents such as the 4-*tert*-butyl group reduced the yield of AB. Therefore, surface modification with a suitable amount of 2,3-DN is also effective for the enhancement of AB production due to the easy access of substances without the steric hindrances of surface-attached ligands. The photocatalytic performance of 2,3-DN(1)/Pt-TiO₂ was repeatedly evaluated to confirm the stability of surface complexes in this reaction (see Figure S1 in the Supporting Information). This sample was recyclable at least three times without the large decrease of photocatalytic performance for production of AB under irradiation of visible light ($\lambda > 420$ nm).

4. CONCLUSIONS

For designing of visible-light-sensitive photocatalysts through the formation of surface complexes, we investigated light absorption capacity of samples treated by mono- and dihydroxy derivatives of naphthalene in detail. Among them, colorless 2,3-DN having two neighboring hydroxy groups showed good coordination property for formation of surface complex with relatively intense visible light absorption. Photocatalytic reduction of NB to AB proceeded upon irradiation of visible light ($\lambda > 420$ nm), while no photocatalytic activities were observed in the case of pure TiO₂ and Pt-TiO₂. The modification of Pt-TiO₂ by suitable amount of 2,3-DN is effective for photocatalytic reduction of NB to AB due to the constraints of absorption capacity of visible light and accessibility of substances. This catalyst is also recyclable at least three times without the large decrease in photocatalytic performance.

■ ASSOCIATED CONTENT

Supporting Information

Multicycle test results of photocatalytic reaction on 2,3-DN(1)/Pt-TiO₂ (Figure S1). This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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