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2018

Ghosh, D., Febriansyah, B., Gupta, D., Ng, L. K. S., Xi, S., Du, Y., Baikie, T., Dong, Z., & Soo, H. S. (2018). Hybrid nanomaterials with single-site catalysts by spatially controllable immobilization of nickel complexes via photoclick chemistry for alkene epoxidation . ACS Nano, 12(6), 5903-5912. doi:10.1021/acsnano.8b02118

<https://hdl.handle.net/10356/87619>

<https://doi.org/10.1021/acsnano.8b02118>

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[<http://dx.doi.org/10.1021/acsnano.8b02118>].

Hybrid Nanomaterials with Single-Site Catalysts by Spatially Controllable Immobilization of Nickel Complexes *via* Photoclick Chemistry for Alkene Epoxidation

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KEYWORDS: hybrid nanomaterials, single-site heterogeneous catalysts, photoclick anchoring,
X-ray absorption spectroscopy, mesoporous nanoparticles, alkene epoxidation.

ABSTRACT: Catalyst deactivation is a persistent problem not only for the scientific community but also in industry. Isolated single-site heterogeneous catalysts have shown great promise to overcome these problems. Here, a versatile anchoring strategy for molecular complex immobilization on a broad range of semiconducting or insulating metal oxide (e.g. titanium dioxide, mesoporous silica, cerium oxide, and tungsten oxide) nanoparticles to synthesize isolated single-site catalysts has been studied systematically. An oxidatively stable anchoring group, maleimide, is shown to form covalent linkages with surface hydroxyl functionalities of metal oxide nanoparticles by photoclick chemistry. The nanocomposites have been thoroughly characterized by techniques including UV-visible diffuse reflectance spectroscopy (UV-DRS), high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), and X-ray absorption spectroscopy (XAS). The IR

spectroscopic studies confirm the covalent linkages between the maleimide group and surface hydroxyl functionalities of the oxide nanoparticles. The hybrid nanomaterials function as highly efficient catalysts for essentially quantitative oxidations of terminal and internal alkenes, and show molecular catalyst product selectivities even in more eco-friendly solvents. XAS studies verify the robustness of the catalysts after several catalytic cycles. We have applied the photoclick anchoring methodology to precisely control the deposition of a luminescent variant of our catalyst on the metal oxide nanoparticles. Overall, we demonstrate a general approach to use irradiation to anchor molecular complexes on oxide nanoparticles to create recyclable, hybrid, single-site catalysts that function with high selectivity in a broad range of solvents. We have achieved a facile, spatially and temporally controllable photoclick method that can potentially be extended to other ligands, catalysts, functional molecules, and surfaces.

Catalyst deactivation is a perennial problem for homogeneous inorganic catalysts supported by organic ligands. Catalyst oligomerization, ligand oxidation, and demetallation are some of the commonly reported pathways for the degradation of catalytic activity.^{1,2} Heterogenization of molecular compounds on high surface area nanoparticulate solid supports to form isolated single-site catalysts can potentially overcome many of these inactivation pathways.³ Moreover, highly reactive intermediates such as early transition metal hydrides,⁴ iron-based water oxidation catalysts,⁵ and molecular-imprinted cavities with ruthenium catalysts,⁶ which would otherwise be unstable in solution, have been characterized and utilized through catalyst immobilization on bulk metal oxide surfaces. The anchoring of molecular compounds to produce isolated single-site hybrid heterogeneous nanocatalysts⁷ is thus still a

nascent field that can address a number of catalyst deactivation problems and also offer alternative reactivity and longevity in eco-friendly solvents for highly selective, nominally homogeneous catalysts.

Several approaches have been presented for the immobilization of molecules on surfaces, especially metal oxides. Some of the most popular strategies include physisorption by electrostatic attraction or non-covalent π - π stacking in applications such as proton reduction by hydrogels⁸ or CO₂ reduction with graphitic carbon electrodes,⁹ respectively. However, physisorption is typically reversible, especially under aqueous and/or aerobic conditions. Chemisorption can be more robust and often involves hydrolysis of silyl esters or alkynes,¹⁰⁻¹² dealkylation of metal alkyls and hydrides⁴ as well as deposition of carboxylates, phosphonates,¹³ hydroxamates, and amines on metal oxides.^{11,14,15} Nonetheless, the functional groups required are often incompatible with metallation of the ligand and there is little spatial and temporal control, since the same functional groups such as phosphonates and carboxylates are also excellent donors to Lewis acidic catalytic centers. Consequently, protection-deprotection protocols will be necessary to prevent the anchoring groups from binding and interfering with the metal catalytic activity.

Photochemical grafting of molecules by UV radiation has emerged as a strategy for the orthogonal deposition of small molecules on surfaces such as silicon, diamond, and numerous metal oxides.¹⁶⁻¹⁹ Especially notable is the work by Hamers and co-workers, where *terminal* alkenes have been grafted on hydrogen-terminated metal oxides and diamond, and employed in applications such as nanomaterial self-assembly, molecular electronics, and chemical sensing.¹⁹⁻

²¹ This strategy is attractive in having a good surface substrate scope, and is often orthogonal to the catalytic and metallation reactivity since alkenes are relatively innocuous functional groups,

although terminal alkenes can be vulnerable under oxidative conditions. Also, spatial and temporal control is possible with established masking approaches. To the best of our knowledge, however, even though there has been some precedence for reductive chemistry,²² there has not been any report of photochemical covalent immobilization of molecular oxidation catalysts on metal oxide nanoparticle surfaces and their applications in catalysis.

Recently, the electron-deficient maleimide group with an internal instead of a terminal alkene has been shown to be a dipolarophile that reacts rapidly with tetrazoles in a “photoclick” modification of DNA strands.²³ The maleimide group is more oxidatively robust than terminal alkenes, and can be installed at the periphery of ligands with a reasonably small number of synthetic steps. Furthermore, metal oxide semiconductor nanocrystals readily absorb UV or visible radiation, leading to effective charge extraction from the semiconductor surfaces.

Herein, we describe an exceptionally mild protocol to use UV radiation to immobilize molecular complexes on the surface of metal oxide nanoparticles through a maleimide group. The maleimide is saturated by addition of surface hydroxyl groups to the alkene to form the hydrolytically more robust succinimide group. We have further demonstrated that the functional molecular nickel (Ni) catalysts anchored on the nanoparticles can be used as heterogeneous oxidation catalysts for the epoxidation of styrene and other alkenes, with comparable reactivity *vis a vis* their homogeneous congeners. Moreover, we show that the operational stability of the catalysts increases since we are able to recycle the heterogeneous nanomaterials more effectively, and more eco-friendly non-halogenated solvents can be used. Apart from the deposition of Ni epoxidation catalysts, the photoclick methodology has been successfully applied to attach a luminescent variant of the Ni catalyst on the metal oxide nanoparticles. Our work thus illustrates a proof of concept that this orthogonal, facile, photoclick protocol can create

functional nanomaterials with improved single-site catalytic activity and lifetime, using modular, independently optimized components. In addition, we can realize spatial and temporal attachment of catalysts, luminophores, and potentially other functional molecules in specifically desired amounts on nanomaterials.

RESULTS AND DISCUSSION

Salicylaldehyde ligands are known for their relative ease of synthesis and ability to stabilize multiple transition metal oxidation states.²⁴ In particular, Ni salicylaldehyde complexes have been reported to homogeneously catalyze reactions such as the asymmetric aldol reaction of β -keto esters,²⁵ tetralin oxidation,²⁶ Michael addition reactions,²⁷ and epoxidation of alkenes.²⁸⁻³⁰ Some Ni alkene oxidation catalysts had been encapsulated in zeolites previously, but there was no structural characterization, the epoxide selectivity was low, and there was little evidence that the catalyst could be recycled.³¹ Here, we have prepared a Ni^{II} salicylaldehyde complex, **Ni-1** (Figure 1a) *via* a templated condensation of 5-chloro-2,3-diamino pyridine, a maleimide-substituted salicylaldehyde, and Ni^{II} acetate (Scheme S1, Supporting Information). A variant **Ni-3** was also prepared as a luminescent reporter. Another Ni^{II} congener, **Ni-2** (Figure 1b), without the maleimide anchoring group was synthesized in a similar fashion for comparison in control experiments.

Figure 1. a) Chemical structures of **Ni-1** bearing the maleimide anchoring group and b) **Ni-2**, without the maleimide group. c) Reaction scheme of the anchoring experiment. Covalent anchoring *via* the maleimide group is shown.

Titanium(IV) oxide (TiO₂), silica (SiO₂), cerium oxide (CeO₂), and tungsten oxide (WO₃) nanoparticles were chosen as the hydroxy-terminated solid supports due to their high surface area, ease of synthesis, oxidative stability, and relative abundance. Furthermore, nanomaterials

offer the versatility of photocatalysis in the future since charge extraction is expected to be more expedient. Each of the photochemical anchoring reactions was carried out using a 254 nm (125 W) UV lamp in a sealed quartz Schlenk tube under an argon atmosphere. Briefly, **Ni-1** was added into a dispersion of TiO₂ nanoparticles in anhydrous dichloromethane (DCM) under argon and the mixture was stirred vigorously for 15 minutes before the solvent was removed under reduced pressure. The flask was then filled with argon and subjected to UV irradiation for 12 hours under stirring (Figure 1c). Likewise, **Ni-2** was also irradiated with TiO₂ nanoparticles under the same conditions. Upon UV irradiation, the hydroxyl groups on the nanoparticle surfaces form covalent linkages by reacting with the C=C double bonds of the maleimide groups to convert into alkoxy succinimides. Both product mixtures were then washed several times with DCM and characterized by UV-visible diffuse reflectance spectroscopy (DRS).

The DRS spectrum of the reaction product between **Ni-1** and TiO₂ (**Ni-1@TiO₂**) exhibits an absorption maximum at 515 nm and a shoulder at 370 nm (black, Figure 2a), which corresponds to the d-d transitions and ligand-to-metal charge transfer, respectively, in **Ni-1** (red, Figure 2a).^{32,33} On the other hand, the sample from the reaction between **Ni-2** and TiO₂ (**Ni-2+TiO₂**) shows almost no visible light absorption (navy blue, Figure 2a), indicating that **Ni-1** is not merely physisorbed on the TiO₂ surface and also the critical role of the maleimide group for the covalent anchoring. Similar spectral signatures were observed in the DRS spectra when TiO₂ nanoparticles were replaced by SiO₂ nanoparticles (Figure 2c), commercially available CeO₂ nanoparticles (Figure 2e), and WO₃ nanoparticles (Figure 2g) under similar reaction conditions. This highlights the generality and effectiveness of our approach on insulating, semiconducting, and visible light absorbing oxide materials. The DRS spectrum of the hybrid composite between **Ni-1** and CeO₂ nanoparticles (**Ni-1@CeO₂**) exhibits a broad absorption shoulder at 515 nm,

corresponding to the same Ni centered d-d transition (sky blue, Figure 2e), and likewise for the molecular-nanoparticle hybrid between **Ni-1** and WO_3 (**Ni-1@WO₃**, light green, Figure 2g).

Figure 2. a) DRS spectra of **Ni-1** (red), **Ni-1@TiO₂** (black), TiO₂ P25 nanoparticles (green), **Ni-2** (grey), and **Ni-2+TiO₂** (navy blue). b) The FT-IR spectra of **Ni-1** (red), **Ni-1@TiO₂** (black), TiO₂ P25 nanoparticles (green), and **Ni-1+TiO₂** (royal blue) in absorbance mode. c) DRS spectra of **Ni-1** (red), **Ni-1@SiO₂** (orange), SiO₂ nanoparticles (magenta), **Ni-2** (grey), and **Ni-2+SiO₂** (dark cyan). d) The FT-IR spectra of **Ni-1** (red), **Ni-1@SiO₂** (orange), SiO₂ nanoparticles (magenta), and **Ni-1+SiO₂** (light cyan) in absorbance mode. e) DRS spectra of **Ni-1** (red), **Ni-1@CeO₂** (sky blue), **Ni-2+CeO₂** (brick red), and CeO₂ nanoparticles (violet). f) The FT-IR spectra of **Ni-1** (red), **Ni-1@CeO₂** (sky blue), CeO₂ nanoparticles (violet), and **Ni-1+CeO₂** (olive green) in absorbance mode. g) DRS spectra of **Ni-1** (red), **Ni-1@WO₃** (light green), **Ni-2+WO₃** (dark yellow), and WO₃ nanoparticles (beige). h) The FT-IR spectra of **Ni-1** (red), **Ni-1@WO₃** (light green), WO₃ nanoparticles (beige), and **Ni-1+WO₃** (light grey) in absorbance mode. For **Ni-1** and all the **Ni-1@MO_x** samples (MO_x = TiO₂, SiO₂, CeO₂, and WO₃), the absorbance band at 515 nm corresponds to the Ni centered d-d transition.

To confirm the UV stability of **Ni-1** and verify that the maleimide group was involved in covalent bond formation with the surface hydroxyl groups during the photoclick reaction, we conducted FT-IR spectroscopic measurements. The FT-IR spectra of **Ni-1** in the solid state before and after 254 nm UV irradiation remained essentially identical (Figure S6a, Supporting Information), suggesting that the Ni^{II} complex was stable under our photochemical deposition conditions. The FT-IR spectra in the range 1400–1800 cm⁻¹ reveal that a vibrational stretching band at 1608 cm⁻¹ for **Ni-1@TiO₂** (black, Figure 2b) has diminished, whereas for a control reaction in which **Ni-1** and TiO₂ have been physically mixed without any UV irradiation (**Ni-1**+TiO₂), this stretching band remains intact (royal blue, Figure 2b). We propose that this vibrational band at 1608 cm⁻¹ corresponds to the C=C stretch of the maleimide group, which is lost upon covalent anchoring on the nanoparticle surface.³⁴ We observed similar spectral changes for **Ni-1@SiO₂** (orange, Figure 2d), **Ni-1@CeO₂** (sky blue, Figure 2f), and **Ni-1@WO₃** (light green, Figure 2h) in comparison to the controls (Figure S7, Supporting Information), fully consistent with our model that the **Ni-1** had become covalently attached by conversion of the maleimide group to a succinimide after reacting with the surface hydroxyls.

To further ascertain the coordination environment and oxidation state of the Ni center upon anchoring to the nanoparticle surface, we conducted X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) measurements on **Ni-1@TiO₂**, **Ni-1@SiO₂**, and **Ni-1**. The Ni K-edge X-ray absorption near-edge structure (XANES) spectra of **Ni-1** (red, dashed line, Figure 3a), **Ni-1@TiO₂** (black, dash-dotted line, Figure 3a), and **Ni-1@SiO₂** (orange, dotted line, Figure 3a) show very similar profiles. This suggested that the oxidation state and coordination environment of Ni remained unchanged after covalent anchoring to the nanoparticle surface. In addition, no pre-edge was observed in all the XANES spectra (Figure 3a), which

concluded with the symmetrical square planar geometry around the Ni coordination sphere, as observed in the single crystal X-ray diffraction (XRD) structure (Figure S35, Supporting Information). The Fourier transform of the extended X-ray absorption fine structure (EXAFS) data in *R*-space of **Ni-1** (red, dashed line), **Ni-1@TiO₂** (black, dash-dotted line), and **Ni-1@SiO₂** (orange, dotted line, Figure 3b and Figure S9b, Supporting Information) show similar, almost overlapping profiles, indicating that the Ni-O and Ni-N bond parameters in the samples are likely to be very close to those in the crystal structure of **Ni-1**. The XAS data thus confirms that no significant change in the oxidation state and coordination environment around Ni occurred upon anchoring.

Figure 3. a) Ni *K*-edge XANES for the region 8300-8400 eV of **Ni-1** (red, dashed), **Ni-1@TiO₂** (black, dash dotted), **Ni-1@SiO₂** (orange, dotted), and **Ni-1@TiO₂** after catalysis (light brown, solid) showing almost identical spectral features and no pre-edge. b) Fourier transforms of the EXAFS in *R*-space (*k*-weight = 3 and *k* range = 2 - 10) of **Ni-1** (red, dashed), **Ni-1@TiO₂** (black, dash dotted), **Ni-1@SiO₂** (orange, dotted), and **Ni-1@TiO₂** after catalysis (brown, solid). The grey vertical dashed line is a guide for the eye and indicates that the average bond distances of the first coordination shell around Ni appear invariant in all the samples.

The XPS spectra of **Ni-1@TiO₂** (Figures 4a, 4b and S1, Supporting Information) show the presence of Ni 2p, Cl 2p, and Ti 2p signals in the sample. Similarly, the XPS spectra of **Ni-1@SiO₂** (Figures 4d, 4e, and S2, Supporting Information) show the presence of Ni 2p, Cl 2p, and

Si 2p signals in the sample. The Ni 2p binding energies of **Ni-1@TiO₂** (Figure 4b), **Ni-1@SiO₂** (Figure 4e), and **Ni-1** (Figure S3a, Supporting Information) were found to be similar (Figure S4, Supporting Information), confirming the presence of Ni^{II} on the nanoparticle surfaces. The Ni 2p_{3/2} signals for **Ni-1**, **Ni-1@TiO₂**, and **Ni-1@SiO₂** appear at 853.8 eV, 853.7 eV, and 853.8 eV, respectively. The slight differences in the binding energies are likely within experimental error, although there have been reports of interfacial interactions between nanoparticles and surface-attached Ni complexes.³⁵⁻³⁷ In aggregate, we are confident that the molecular Ni^{II} catalysts remain structurally intact and are covalently anchored on the different metal oxide supports.

Figure 4. a) XPS survey spectrum of **Ni-1@TiO₂** showing the binding energies corresponding to Ni 2p, Ti 2p, and Cl 2p. b) Ni 2p XPS data for **Ni-1@TiO₂** with the Ni 2p_{3/2} signal at 853.7 eV and Ni 2p_{1/2} signal at 870.9 eV. c) HRTEM image of **Ni-1@TiO₂**. d) XPS survey spectrum of **Ni-1@SiO₂** showing the binding energies corresponding to Ni 2p, Si 2p, and Cl 2p. e) Ni 2p XPS data for **Ni-1@SiO₂** with Ni 2p_{3/2} signal at 853.8 eV and the Ni 2p_{1/2} signal at 871.1 eV. f) HRTEM image of **Ni-1@SiO₂**.

The catalysts were then employed in catalytic alkene epoxidation reactions to evaluate their activities and stabilities. The conditions were first optimized with **Ni-1** as a homogeneous catalyst. Different oxidants including hydrogen peroxide (H₂O₂), (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO), sodium periodate, sodium hypochlorite (NaOCl), and oxygen were screened (Table S2, Supporting Information). Moreover, since **Ni-1** is poorly soluble in ethyl acetate, methanol, and acetonitrile, they are unsuitable solvents for homogeneous catalysis. The combination of **Ni-1** (5 mol%), NaOCl (8 equivalents) as the oxidant, and DCM as the solvent

gave the highest (>99%) conversion of styrene (Table S3, Supporting Information). This performance is comparable with or better than previously reported alkene epoxidation catalysis.^{28, 31} We also found that less than 8 equivalents of NaOCl relative to the substrate resulted in incomplete conversions of the alkenes. Using these same optimized conditions, a number of internal and terminal alkene substrates were successfully oxidized at room temperature using **Ni-1** (Table S3, Supporting Information). The homogeneous reactions showed very high conversions and the selectivity for the epoxides were found to vary from moderate for cyclooctene oxide (54%) to good (78%) for 4-chlorostyrene oxide.

Ni-1@TiO₂, **Ni-1@SiO₂**, **Ni-1@CeO₂**, and **Ni-1@WO₃** were all then applied as heterogeneous catalysts for alkene oxidation under similar reaction conditions, although notably, we were no longer limited by the solubility constraints of **Ni-1** in the solvents mentioned above. The conversions of the substrates in the heterogeneous reactions and selectivities were found to be similar to the homogeneous version, with the highest epoxide selectivity of 68% for 4-chlorostyrene oxide (Table 1, Entry 3). **Ni-1@TiO₂** performed better than **Ni-1@SiO₂**, **Ni-1@CeO₂**, and **Ni-1@WO₃** (Table 1, Entries 8, 9, and 10, respectively) both in terms of substrate conversion and selectivity for the epoxide products. Notably, all of the heterogeneous catalysts displayed higher substrate conversion as well as epoxide selectivity compared to the best previously reported metal organic framework (MOF) heterogeneous catalysts embedded with Ni salicylaldimine complexes.³⁸ This could be due to better accessibility of the Ni catalytic centers, which are on the surface of the nanoparticles (Figures 4c, 4f, S8, and S10, Supporting Information) unlike the MOF-based catalysts that have Ni centers embedded deep inside the porous framework.

Table 1. Conversion, selectivity, and substrate scope of alkene epoxidation by heterogeneous catalysts.

Entry	Substrate	% conversion of substrate ^a	Time (h)	Epoxide product	% GC yields of epoxide product ^{a,h}	TOF (h ⁻¹)
1 ^b		92	4		53	2.64
2 ^b		96	2.5		63	5.04
3 ^b		95	5.5		68	2.47
4 ^b		93	8		54	1.35
5 ^b		96	3.5		62	3.54
6 ^b		84	5		42	8.40
7 ^c		85	4		45	2.25
8 ^c		88	5.5		64	2.32
9 ^d		90	5.5		61	2.21
10 ^e		94	5		66	2.64
11 ^f		<1	6		-	-
12 ^{b,g}		<1	6		-	-

^a Compound *n*-decane was used as the GC internal standard. ^b **Ni-1@TiO₂** was used as the catalyst. ^c **Ni-1@SiO₂** was used as the catalyst. ^d **Ni-1@CeO₂** was used as the catalyst. ^e **Ni-1@WO₃** was used as the catalyst. ^f Control reaction with TiO₂ P25 nanoparticles as catalyst. ^g Control reaction without NaOCl. ^h Other products obtained were aldehydes and 1,2-diols.

To use more environmentally benign solvents,³⁹ we performed the heterogeneous catalysis using NaOCl as the oxidant in ethyl acetate, 2-methyltetrahydrofuran, dimethyl carbonate, and water (Table S4, Supporting Information). In ethyl acetate, **Ni-1@TiO₂** showed slightly higher conversion of alkene and almost identical selectivity towards the epoxide product compared to the reaction in DCM. The reaction in water was remarkably fast likely due to the hydrophobic effect (Figure S13, Supporting Information), since the substrates and **Ni-1@TiO₂** are both hydrophobic. However, high selectivity towards 1-(4-chlorophenyl) ethane-1,2-diol as the product (GC yield 79%) was observed instead with 4-chlorostyrene as the substrate in water.

After the reaction, the heterogeneous catalysts could be recovered by centrifugation, and the residue was rinsed with solvent, dried, and recycled. Remarkably, the reused catalyst showed essentially quantitative conversions of the substrate for the first few recycling experiments, although the conversion and the epoxide selectivity decreased over extended reuse (Figure 5a). Despite the fact that the heterogeneous catalyst sample could not be completely recovered after every experiment (some remained in the reaction flasks and the centrifuge tubes) and some sample was also lost for FT-IR spectroscopic analysis, **Ni-1@TiO₂** could still be used for at least 10 consecutive cycles with 4-chlorostyrene as the substrate. In contrast, the physical mixtures of **Ni-1** and TiO₂ or SiO₂ do not survive after the first catalytic cycle and neither the supernatant (containing the dissolved Ni by-products) nor the recovered nanoparticles showed any catalytic activity in the second run (Figure S14 and Table S5, Supporting Information). The decrease in the catalytic activity of **Ni-1@TiO₂** could be due to inactivation of some of the Ni catalysts as insoluble Ni oxides on the nanoparticle surface. We observed that the Ni concentrations in the reaction aliquots were below the detection limit of our inductively coupled plasma optical emission spectroscopy (ICP-OES) experiments, indicating that little Ni leached out during the

catalytic process. To demonstrate the robustness and scalability of **Ni-1@TiO₂**, we performed four cycles of 4-chlorostyrene oxidations (0.277 g, 2.00 mmol in each cycle) since the percentage conversion remained fairly high, and isolated 0.655 g of 4-chlorostyrene oxide (53%) by reusing the same catalyst.

Figure 5. a) Percentage conversion of 4-chlorostyrene (black) and selectivity for epoxide (red) obtained over 10 cycles by reusing the **Ni-1@TiO₂** catalyst. b) FT-IR spectra of **Ni-1@TiO₂** before (black), and after four (light brown), eight (lilac), and 10 cycles of catalysis (light green) .

Based on previously presented mechanisms for alkene epoxidations by Ni^{II} complexes, we expected the catalyst to access higher valent nickel intermediates that could potentially be unstable.²⁸ Thus, we conducted XAS experiments on the used **Ni-1@TiO₂** sample to investigate the oxidation state and coordination environment of the Ni center after catalysis. The Ni K-edge XANES spectrum of **Ni-1@TiO₂** after four cycles of catalysis (light brown, solid line, Figure 3a) was essentially identical with that of pristine **Ni-1@TiO₂** (black, dash-dotted line, Figure 3a), and **Ni-1** (red, dashed line, Figure 3b), indicating that there was no change in the Ni coordination environment and oxidation state of **Ni-1@TiO₂** even after four catalytic cycles. Furthermore, it is evident from the Fourier transform of the EXAFS in *R*-space (light brown, solid line, Figure 3b and Figure S9b, Supporting Information) that the average Ni-O and Ni-N bond distances, and hence the overall coordination environment, remained unchanged between the **Ni-1@TiO₂** after catalysis compared to **Ni-1** and pristine **Ni-1@TiO₂**. Likewise, the FT-IR spectroscopic fingerprint region of the recycled **Ni-1@TiO₂** samples (Figure 5b) displayed similar, but attenuating vibrational bands as the sample before catalysis. Evidently, some of the **Ni-1@TiO₂** survived up to 10 cycles under the harsh oxidative conditions for our alkene epoxidation reaction.

This selective photoclick reaction of the maleimide anchoring group could be utilized to spatially and temporally attach luminescent reporters on the metal oxide nanoparticles, which is an advantage over indiscriminate grafting functionalities like carboxylates and phosphonates. We have been able to successfully graft a different luminescent nickel salicylaldehyde complex (**Ni-3**, Figure 6a), bearing the maleimide anchoring group, on SiO₂ and TiO₂ coated fluorine-doped tin oxide (FTO) films (**Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO**, respectively) using 254 nm UV radiation. The designs (Figures 6b and 6c) were achieved by using a simple paper mask, which

allows the photoclick reaction to occur only at specifically exposed areas of the coated FTO films. The DRS spectra of **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** (Figure 6d) shows the absorbance maxima corresponding to **Ni-3**, indicating the presence of the complex after the photoclick reaction. The successful grafting was again confirmed by the FT-IR spectra of **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** (Figure 6e), which show the loss of the 1605 cm⁻¹ peak, corresponding to the maleimide C=C stretch present in the **Ni-3** (wine red) spectrum.

Figure 6. a) Chemical structure of **Ni-3** bearing the maleimide anchoring group. Photograph of the spatially controlled photoclick deposition of **Ni-3** on b) SiO₂ and c) TiO₂ coated FTO plate. In each figure, the mask is shown on the top right. The dashed lines highlight the boundaries of the deposited patterns. A ruler has been provided to facilitate size comparison. d) DRS spectra, e) FT-IR spectra from 1400 cm⁻¹ to 1800 cm⁻¹ in absorbance mode, and f) photoluminescence spectra with 395 nm excitation of **Ni-3** (wine red), **Ni-1@SiO₂-FTO** (light magenta), and **Ni-1@TiO₂-FTO** (light violet).

The solid state photoluminescence (PL) spectra of the films exhibit the luminescent behavior of the parent **Ni-3** complex (Figure 6f). The PL spectrum of **Ni-3** shows an emission maximum at 530 nm when excited at 395 nm. A small blue-shift of 3 nm in the emission maximum was observed in each of the **Ni-3@SiO₂-FTO** and **Ni-3@TiO₂-FTO** samples. The **Ni-3** coated regions in the **Ni-3@SiO₂-FTO** sample were found to show PL when irradiated with a TLC lamp emitting 365 nm UV light (Figure S16, Supporting Information). However, the PL intensity for **Ni-3@TiO₂-FTO** was found to be attenuated compared to **Ni-3** and **Ni-3@SiO₂-FTO** (Figures 6f and S16, Supporting Information). This could be due to PL quenching after charge injection into the semiconducting TiO₂ layer, in contrast to the insulating SiO₂, a feature that will be further investigated for catalytic applications.

CONCLUSION

In conclusion, we have utilized maleimide as an oxidatively stable, photoactivated anchoring group to synthesize several hybrid single-site catalysts comprising covalently grafted Ni complexes on SiO₂, TiO₂, CeO₂, and WO₃ nanoparticles. Characterization by DRS, FT-IR spectroscopy, XAS, and XPS verified that the Ni salicylaldehyde complexes remained intact and were anchored covalently. Remarkably, the heterogeneous catalysts displayed conversions and selectivities for alkene epoxidation similar to their corresponding homogeneous molecular congener, but were found to be more robust, recyclable, and stable up to 10 catalytic cycles under the harsh oxidative reaction conditions in a wider range of more eco-friendly solvents. We have also been able to utilize the photoclick protocol of the maleimide anchoring group to precisely deposit the Ni complexes on specific regions. Our study thus forms the basis for future discoveries on using light to deposit functional molecular catalysts on inert or semiconducting

scaffolds to create hybrid (photo)catalysts that can synergize the benefits of both homogeneous and heterogeneous catalysts. Moreover, we believe that this spatially and temporally controlled photoclick reaction to deposit functional molecules can be applied in other fields, including biosensing, renewable energy, and optoelectronic devices, for example.

EXPERIMENTAL SECTION

Synthesis of dendritic SiO₂ nanoparticles

Cetyltrimethylammonium chloride (CTAC) solution (25 wt%, 24 mL) and triethanolamine (TEOA, 0.16 mL, 0.18g, 1.21 mmol) were added in a 100 mL round bottom flask filled with de-ionized water (36 mL) and the mixture was stirred gently at 60 °C for 1 h. Subsequently, tetraethyl orthosilicate (4 mL, 18.0 mmol) in cyclohexane (16 mL) was carefully added to the surfactant solution in an oil bath at 60 °C, with a stirring at a rate of about 150 rpm. The reaction flask was then kept at 60 °C with stirring for 12 h to obtain the white powder product (0.53g, 49%). The product was collected by centrifugation and washed three times with ethanol. The product was extracted once with a 0.6 wt % ammonium nitrate in ethanol solution at 60 °C for 6 h, followed by calcination at 550 °C for 5 h at a ramping rate of 1 °C min⁻¹ to remove the surfactant completely.

Processing of TiO₂ P25 nanoparticles

Prior to use in the anchoring reaction, the commercially purchased TiO₂ P25 nanoparticles (Sigma-Aldrich) were treated with piranha solution to remove any surface organic impurities and hydroxylate the surface to facilitate anchoring. In a typical procedure, TiO₂ P25 nanoparticles (40 mg, 0.50 mmol) were soaked in freshly prepared piranha solution (conc. H₂SO₄: H₂O₂ = 3:1)

for 2 h. Subsequently, it was washed thoroughly with de-ionized water and dried in a furnace at 300 °C for 3 h to remove traces of H₂SO₄. It was then dried at 120 °C for 5 h under vacuum to remove any remaining surface moisture.

Ni-1@TiO₂

A degassed, anhydrous DCM (5 mL) solution of Ni-1 (10 mg, 0.013 mmol) was added to an oven dried quartz glass Schlenk tube. Pre-processed TiO₂ P25 nanoparticles (21 mg, 0.26 mmol) was then added. The Schlenk tube was sonicated for 5 min before the solvent was removed under vacuum. The solid mixture was stirred under UV irradiation (254 nm, 125 watt) for 8 h. After the reaction, the nanoparticles were collected and washed several times by DCM to remove any excess and unbound **Ni-1** present.

Ni-1@SiO₂

Ni-1@SiO₂ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, dendritic SiO₂ nanoparticles (30 mg, 0.50 mmol) were used.

Ni-1@CeO₂

Ni-1@CeO₂ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, CeO₂ nanoparticles (43 mg, 0.25 mmol) were used.

Ni-1@WO₃

Ni-1@WO₃ was prepared using the same method as for **Ni-1@TiO₂**. Instead of TiO₂, WO₃ nanoparticles (58 mg, 0.25 mmol) were used.

General procedure for alkene epoxidation with Ni-1 homogeneous catalyst

To a solution of alkene (0.50 mmol) in 2.0 mL dichloromethane (DCM) was added **Ni-1** (18.7 mg, 0.025 mmol), *n*-decane (97.5 μ L, 0.500 mmol) and tetra-*n*-butylammonium bromide (8.0 mg, 0.025 mmol). Finally, 1.8 mL of 0.70 M sodium hypochlorite solution was added to the mixture and stirred vigorously at room temperature. After the reaction, 100 μ L of organic layer was withdrawn using a syringe, diluted with DCM in a 10 mL volumetric flask, and subjected to gas chromatography mass spectrometry (GC-MS) measurements.

Alkene epoxidation using heterogeneous Ni-1@TiO₂ catalyst

To a solution of alkene (0.10 mmol) in 2 mL DCM, was added **Ni-1@TiO₂** (23.5 mg), *n*-decane (19.5 μ L, 0.100 mmol), tetra-*n*-butylammonium bromide (2.0 mg, 6.0 μ mol), and aqueous sodium hypochlorite (0.36 mL, 0.70 M). The mixture was stirred vigorously at room temperature. After the reaction was complete, the reaction mixture was carefully transferred to a centrifuge tube and the catalyst was recovered by centrifugation and washed with water, ethanol, and DCM. Finally, it was dried under vacuum before being re-used for subsequent cycles. To prepare the GC-MS sample, 500 μ L of the organic layer was withdrawn using a syringe and diluted with DCM in a 10 mL volumetric flask.

Alkene epoxidation using heterogeneous Ni-1@SiO₂ catalyst

The alkene epoxidation was conducted following the same procedure as for **Ni-1@TiO₂**, but **Ni-1@SiO₂** (25.5 mg) was used instead of **Ni-1@TiO₂**.

Gas chromatography (GC) analysis of alkene epoxidation

DCM was used as the solvent for GC analyses of the samples. The measurements were performed using a Thermo Fisher Scientific Trace GC Ultra DSQ-II GC-MS machine. Compound *n*-decane was used as the internal standard.

UV-visible diffuse reflectance spectroscopy (DRS) measurements

DRS was measured with a Shimadzu 3600 UV-vis-NIR spectrophotometer with BaSO₄ as an internal standard.

Fourier transform infrared (FT-IR) spectroscopy measurements

FT-IR spectroscopy measurements were carried out with a Bruker Vertex 80v FT-IR spectrometer. In a typical experiment, about 1.5 mg of the sample was mixed with about 30.0 mg of potassium bromide (KBr) to make a pellet. The pellets were made with a Specac Atlas manual hydraulic press 15T at 10 ton pressure. The FT-IR experiments were conducted in transmission mode with data collected from 400 to 4000 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) experiments

The XPS samples were prepared by coating the solid, powdered samples on SPI double-sided adhesive carbon tape. The XPS data obtained was processed using the CasaXPS software. The spectra were calibrated internally by setting the C 1s signal at 284.6 eV.

High-Resolution Transmission Electron Microscopy (HRTEM) imaging

The sample preparation involved sonication of an aliquot of the powder in analytical grade ethanol for 10 min. A single drop of the colloidal solution was deposited on a thin-film carbon

coated copper TEM grid and dried in air. HRTEM images were taken using a JEOL JEM 2100 microscope operated at 200 kV.

X-ray absorption spectroscopy (XAS)

X-ray absorption fine structure (XAFS) characterization at the Ni K-edge was carried out at the XAFCA beamline of the Singapore Synchrotron Light Source (SSLS).⁴⁰ All XAS measurements were collected with a ring energy of 0.7 GeV and a ring current of ca. 200 mA. A Si(111) crystal monochromator was used and the data were collected in transmission mode at ambient temperatures. The X-ray energy was calibrated at the inflection point of the absorption edge of a nickel foil. Data analysis was carried out with the programs Athena and Artemis included in the Demeter package (version 0.9.25). Each of the powder samples was prepared as a pellet using a pelletizer of diameter 10 mm and mounted on the sample holder for the XAS measurement. ARTEMIS fittings were carried out with k -weight = 1,2,3; k range = 3 – 12.69, and R range = 1 – 3 Å.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements

The samples were measured using a Thermo Scientific iCAP 7000 series ICP-OES spectrometer. Standard solutions were prepared by dissolving appropriate amounts of Ni standards (Inorganic Ventures) in 3 % (v/v) nitric acid (HNO₃). All samples were prepared using 4.5 mL ICP grade HNO₃ (70 %, Inorganic Ventures) and diluted into a 100 mL volumetric flask using ultrapure water. For the catalyst loading experiment, **Ni-1@TiO₂** (23.5 mg) and **Ni-1@SiO₂** (25.5 mg) samples were treated with 4.5 mL ICP grade nitric acid in a 15 mL centrifuge tube for 1 h before adding 5 mL ultrapure water. The undissolved parts were removed by

repeated centrifugation and washing with ultrapure water (5 mL X 5). All the dissolved parts were collected together in a 100 mL volumetric flask and filled up to the 100 mL mark using ultrapure water. For the catalyst leaching study, the heterogeneous reaction mixture was centrifuged to remove the solids and 0.5 mL of the aliquot was collected and treated with 4.5 mL HNO₃ for 1 h before diluting to 100 mL using ultrapure water.

The Ni content for **Ni-1@TiO₂** was found to be 0.212 mmol/g of the catalyst, whereas for **Ni-1@SiO₂** it was found to be 0.197 mmol/g of the catalyst. For the catalyst leaching experiment the Ni content of the sample was found to be below the detection limit of the equipment.

Static contact angle measurements

The samples were measured using a Theta Life tensiometer equipped with a Fireware digital camera. The measurements were done using sessile drop method with 4 µL drop volume. The samples were prepared by spin-coating a dispersion of 10 mg of the sample in 0.5 mL of methanol at 300 rpm on glass substrates. To minimize errors, multiple samples were prepared and measurements were performed at different positions of the substrate.

Dynamic light scattering (DLS) measurements of homogeneous Ni-1 reaction mixture

To check the presence of any particles in the biphasic reaction mixture, the aqueous and DCM phases were separated and checked separately during catalysis. In the DCM phase, particles were not observed. However, in the aqueous phase, micron-sized large particles were detected, which could be aggregates of the insoluble **Ni-1** complex particles in the aqueous phase. Nonetheless, at the end of the reaction, both phases showed no particles again, suggesting that the **Ni-1** aggregates redissolve into DCM.

Spatially controlled deposition of Ni complexes on nanoparticle-coated FTO

The photoclick experiments were performed in a Schlenk flask made of quartz under an argon atmosphere using a 254 nm UV source (125 watt). The paper masks were attached to the SiO₂- and TiO₂-coated FTO plates with Teflon tape and placed in the Schlenk flask. In each experiment, a DCM solution (10 mL) of **Ni-3** (23 mg, 0.026 mmol) was added. The solution was bubbled with argon for 10 min before being sealed and irradiated with UV for 10 h. After the irradiation, the plates were removed and rinsed with DCM to remove any unanchored complex, and then dried in air.

ASSOCIATED CONTENT

Supporting Information Available: Synthetic details of the ligands and Ni complexes, spectroscopic characterization, and essential crystallographic data. This information is available free of charge *via* the Internet at <http://pubs.acs.org>.

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Funding Sources

NTU start-up grant (M4081012), Nanyang Assistant Professorship (M4081154), MOE Tier 1 grants (M4011611 and M4011791), Agency for Science, Technology and Research (A*STAR), AME IRG grants A1783c0002 and A1783c0003.

ACKNOWLEDGMENT

H.S.S. is supported by an NTU start-up grant (M4081012), the Nanyang Assistant Professorship (M4081154), and MOE Tier 1 grants (M4011611 and M4011791). The authors acknowledge the support from the Solar Fuels Laboratory at NTU. The authors also gratefully acknowledge the Agency for Science, Technology and Research (A*STAR), AME IRG grants A1783c0002 and A1783c0003, for funding this research. D.G. thanks Dr. Yongxin Li for his help in the X-ray crystal structure analysis and Mr. Ya-Chuan Kao and Prof. Xing Yi Ling for their guidance in static contact angle measurements.

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