

SiO₂-Surface-Assisted Controllable Synthesis of TaON and Ta₃N₅ Nanoparticles for Alkene Epoxidation**

Qingsheng Gao,* Sinong Wang, Yuchun Ma, Yi Tang, Cristina Giordano, and Markus Antonietti

Metal nitrides are promising materials because of their prominent properties originating from metal–nitrogen bonds and noble-metal-like electron features, such as thermal stability, mechanical hardness, superconductivity, and high catalytic performance in hydrocarbon conversion.^[1] More importantly, their bulk and surface properties are significantly associated with the nitridation levels, which can be adjusted as such. Taking tantalum (oxy)nitrides as the current example, introducing N atoms into Ta₂O₅ brings a remarkably narrowed and tunable band-gap energy, thus enabling novel visible-light photocatalysts.^[2] Meanwhile, the catalytic properties of Ta in tantalum (oxy)nitrides for nonphotocatalytic reactions are also expected to be improved because of the tailored nitridation and easier electron transfer from N (vs. O) to Ta centers. However, there are still no reports on these effects to the best of our knowledge. Significantly, such modulation of material properties by controlled nitridation provides a new strategy for designing novel catalysts.^[2a,3]

The controllable synthesis of TaON and Ta₃N₅ nanoparticles (NPs) with tailored chemical composition is therefore an attractive goal,^[2c,3a] which is, however, difficult to achieve by current strategies because of easy overreactions of nitridation.^[4] For example, by-products of Ta₃N₅, Ta₄N₅, and even TaN will be easily generated from further nitridation of TaON during calcination. The traditional method using NH₃ is limited for the danger associated with using NH₃ at high temperature and the complexity related to the rigid control of gas composition, flow rate, and pressure.^[4,5] Moreover, although urea and cyanamide have been reported as safe nitrogen sources for preparing tantalum nitrides, only impure and deeply reduced TaN could be obtained, as an effective control on reactions is absent.^[6]

Recently, we discovered that the controlled release of N source from urea is significant to control metal nitridation.^[7] As a further controlled version of urea pyrolysis, we present

herein a new SiO₂-surface-assisted strategy for the controlled fabrication of TaON and Ta₃N₅ NPs, which successfully avoids the disadvantage mentioned above. Assisted by SiO₂, the production of TaON over Ta₃N₅ NPs with tailored composition was achieved through calcination of Ta–urea (TaU) gels with suitable urea/Ta ratios ($R_{U/Ta}$). A mechanism is proposed that urea is converted into carbon–nitride (CN_x) species on SiO₂-surface at mild temperature,^[8] which further acts as a slow release N source for controlled nitridation. The electronic properties of Ta are tuned by the different nitridation levels in TaON and Ta₃N₅ NPs, which significantly improves the activity for alkene epoxidation, as compared to Ta₂O₅ NPs. This is the first time to discover that introducing N into Ta₂O₅ can remarkably improve epoxidation activity because of the easier electron transfer from N (vs. O) to Ta. Furthermore, the controlled nitridation endows catalysts with tunable surface basicity, noticeably influencing epoxidation selectivity. Owing to the facile synthesis and prominent catalytic behavior associated with tailored nitridation, we believe that our effort will pave the way for designing nanostructured catalysts of metal–nitrides.

As the key assisting agent, SiO₂ NPs (5–15 nm, S_{BET} = 527.3 m² g^{−1}) were added into TaU precursor, resulting in a homogenous gel denoted as TaU/SN. After calcination under N₂ flow and following treatment with NaOH solution, highly crystalline TaON and Ta₃N₅ NPs were obtained at $R_{U/Ta}$ values of 1.5 and 3.0, respectively. These products were confirmed as γ -TaON (ICDD: 01-076-3258) and Ta₃N₅ (ICDD: 04-004-4564) by their X-ray diffraction (XRD) patterns (Figure 1 a). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 1 b–e) show that the products are NPs with size of 20–25 nm, which can be easily dispersed in EtOH or water by ultrasonic agitation. The size nicely fits with the calculated results from XRD analysis, which reveal values of approximately 20.6 nm for TaON and 18.9 nm for Ta₃N₅. γ -TaON can be well identified in high-resolution TEM images (Figure 1 c) by the clear lattice fringes of (110) and (001), while for Ta₃N₅ the planes of (200) and (110) are well observed (Figure 1 e).

The colors of samples give further clear evidence about their structures, as yellow TaON and red Ta₃N₅ NPs show absorption bands around 500 and 600 nm, respectively, in UV/Vis spectra (Figure S1 in the Supporting Information). This result proves the narrowing of the band gap compared with Ta₂O₅ as a result of nitridation. Moreover, NPs composed of tunable TaON and Ta₃N₅ phases are easily obtained (Figure S2) by switching the $R_{U/Ta}$ value from 1.5 to 3.0, further indicating the potential for their controlled synthesis.

Several control experiments were carried out to examine the mechanism underlying the controllable synthesis of TaON

[*] Dr. Q. S. Gao, Dr. C. Giordano, Prof. M. Antonietti
Department of Colloid Chemistry
Max Planck Institute of Colloids and Interfaces
Research Campus Golm, 14424 Potsdam (Germany)
E-mail: qingsheng.gao@mpikg.mpg.de

S. N. Wang, Dr. Y. C. Ma, Prof. Y. Tang
Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials
Fudan University, Shanghai 200433 (P.R. China)

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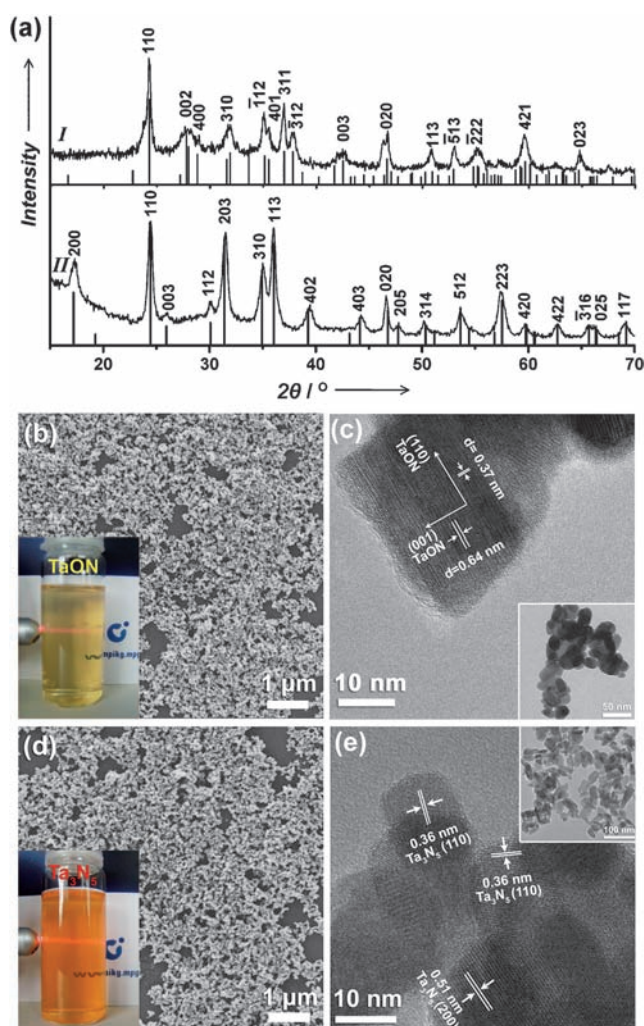
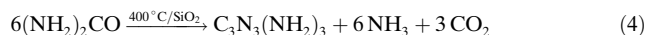
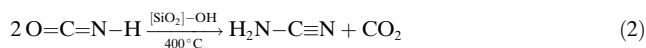
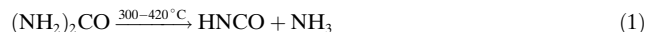


Figure 1. a) XRD patterns of I) TaON and II) Ta₃N₅ NPs obtained by the SiO₂-surface-assisted urea method with $R_{U/Ta}$ values of 1.5 and 3.0. The simulated patterns for γ -TaON and Ta₃N₅ are also shown. b) SEM and c) TEM images of TaON NPs, and d) SEM and e) TEM images of Ta₃N₅ NPs. Insets of (b) and (d) shows photos of TaON and Ta₃N₅ NPs dispersed in EtOH.

and Ta₃N₅ NPs in the presence of SiO₂. It was found that SiO₂ is indispensable. Without SiO₂, only bulky mixtures of TaON, Ta₃N₅, and even Ta₄N₅ were obtained, indicating that the controlled nitridation and nucleation relies on the large-surface SiO₂ template (Figure S3). Because of the easy overreactions during nitridation, mixtures of TaON and Ta₃N₅ were obtained with $R_{U/Ta}$ values ranging from 1.5 to 4.0 in the absence of silica. Ta₃N₅ becomes predominant when the $R_{U/Ta}$ value is increased to 6.0, but unfortunately it is accompanied by TaON and Ta₄N₅ as by-products. Further experiments reveal that the specific surface area of SiO₂ is significant to its function to avoid overreactions. When bulky SiO₂ (ca. 500 nm) with a small surface area of $S_{BET} = 5.6 \text{ m}^2 \text{ g}^{-1}$ was used, the overreactions could not be avoided, and only the mixture of TaON and Ta₃N₅ was received at $R_{U/Ta}$ values of 1.5 and 3.0, respectively (Figure S4). Therefore, the interactions and reactions between the SiO₂ surface and urea should

be taken into account for the controlled generation of TaON and Ta₃N₅ NPs.

It is well known that upon fast heating from 300 to 420 °C, urea decomposes to ammonia and isocyanic acid [Eq. (1)].^[8] Catalyzed by OH groups on silica, isocyanic acid is converted into cyanamide, which can trimerize to form melamine [Eqs. (2) and (3)].^[8] The overall reaction is given in Equation (4).



With further thermal treatment, as-formed melamine polycondenses to CN_x species with yellow melon and even *s*-triazines.^[9] The formation of CN_x species from urea during our calcination can be well confirmed by FTIR investigation. After treating TaU/SN precursor at 500 °C, the FTIR spectrum (Figure 2a) clearly displays the characteristic bands associated with the vibrations of C≡N (2053 cm⁻¹), C-N(-C)-C (1363 cm⁻¹) and *s*-triazine (1624 and 1556 cm⁻¹).^[8a,10] Similar observations for the process without SiO₂ suggest that the conversion from urea to CN_x can be also achieved by Ta-OH. However, the above absorption bands in the presence of SiO₂ are blue-shifted relative to those without SiO₂, which implies that the interaction between the SiO₂ surface and CN_x stabilizes the CN_x species.^[11] Moreover, the large surface area of SiO₂ NPs remarkably enhances such function. Because CN_x is available for metal nitridation through decomposition to active N species,^[12] its delayed decomposition on SiO₂ surface is significant for controlled nitridation. The different CN_x decompositions against heating with and without SiO₂ can be well reflected by the evolution of N content in TaU/SN and TaU ($R_{U/Ta} = 3.0$) treated from 500 to 700 °C (Figure 2b). CN_x decomposition slows down with the assistance of SiO₂. The content of N is kept at the same level around 8.0 wt % under 650 °C, and remarkably decreases to 6.97 wt % at 700 °C, indicating major decomposition around 700 °C. However, without SiO₂, the N content is drastically and continuously decreased from 500 to 700 °C. The mole ratios of N/Ta also present the consistent evolution. It should be pointed out that the easier CN_x decomposition in TaU will induce inhomogeneous N species atmosphere and consequent overreactions.^[4] Thus, the formation and stabilization of CN_x on large SiO₂ surface is important for TaON and Ta₃N₅ controlled synthesis because of the suppression of N source release (Figure 2c).

In this mechanism, the surface area of silica is the key factor. If the same amount of mesoporous SBA-15 with larger surface ($S_{BET} = 675.4 \text{ m}^2 \text{ g}^{-1}$) than SiO₂ NPs is employed, pure TaON NPs are obtained at a lower $R_{U/Ta}$ value of 1.0 (Figure S6), which suggests that more CN_x can be stored on the larger surface of SBA-15. When the $R_{U/Ta}$ ratio is increased to 4.0 and 5.0, the deep nitridation product, Ta₄N₅, is generated as a result of excessive CN_x within SBA-15, compared with pure Ta₃N₅ NPs obtained at the same ratios using SiO₂ NPs (see Figure S2). This result further validates

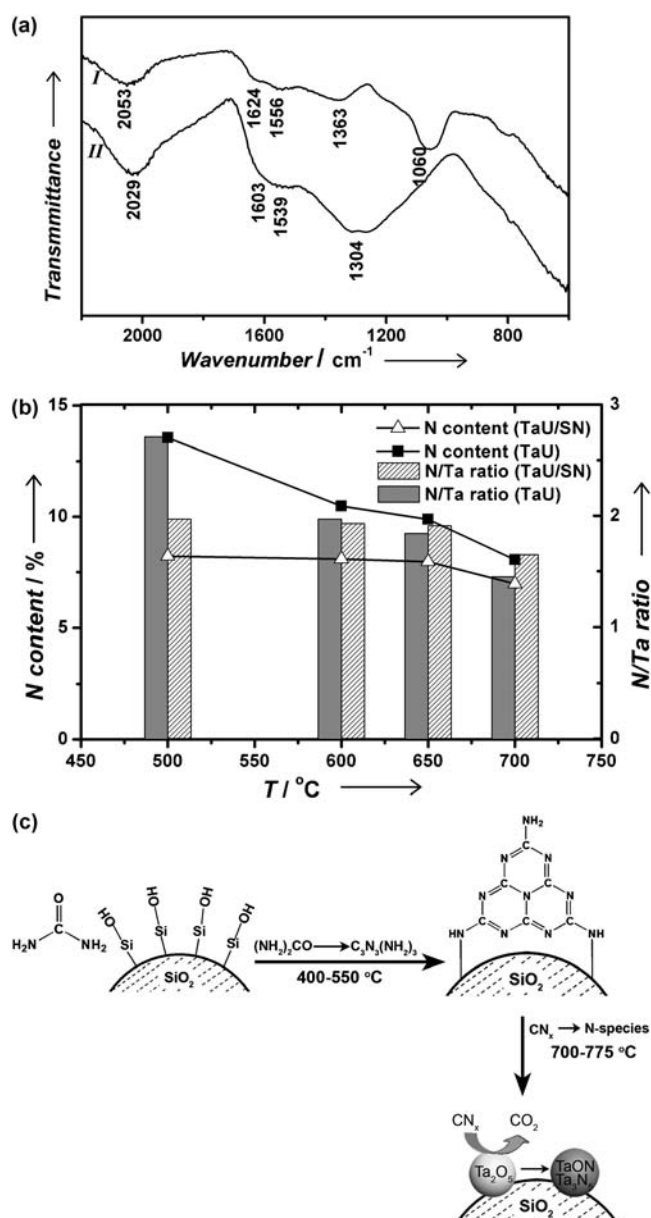


Figure 2. a) FTIR spectra of products obtained after treating I) TaU/SN and II) TaU at 500 °C. b) N content and N/Ta mole ratio evolutions of TaU/SN and TaU with increasing temperatures. c) Illustration of SiO₂-surface-assisted mechanism for controllable synthesis of TaON and Ta₃N₅ NPs through CN_x-intermediate process catalyzed by SiO₂.

the mechanism of the SiO₂ surface for achieving controlled nitridation. Additionally, such a mechanism was also found to be general for other metals such as Zr, in which Zr₂N₂O NPs are well obtained and overreaction ZrN is suppressed by SiO₂ (Figure S7). We believe this will open up opportunities to design various nanostructures of functional metal–nitrides.

Changing the nitridation level of tantalum (oxy)nitrides provides a new approach to tune the electronic properties of Ta atom, because of the lower electronegativity of N atoms than O atoms. This situation is already indicated by X-ray photoelectron spectroscopy (XPS, Figure 3). In Ta₂O₅ NPs, the Ta 4f_{7/2} and 4f_{5/2} peaks appear at 26.5 and 28.3 eV (Figure 3a), which correspond to Ta⁵⁺ in Ta₂O₅.^[13] With the

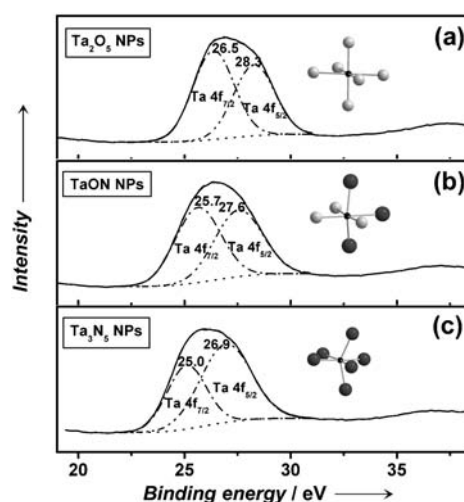
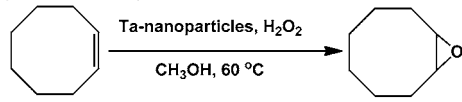


Figure 3. Ta 4f XPS spectra of a) Ta₂O₅, b) TaON, and c) Ta₃N₅ NPs. The Ta 4f peaks are shifted to lower energies and have increased N/O ratio in TaON and Ta₃N₅ NPs relative to those of Ta₂O₅. The structures in the insets of (a–c) present the octahedral coordination environment of a) Ta₂O₅, b) TaON, and c) Ta₃N₅. Ta small black ball, O gray ball, N large black ball.

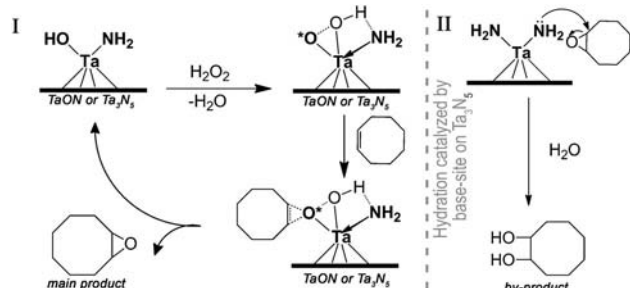
introduction of N, these peaks are shifted to lower binding energies of 25.7 and 27.6 eV in TaON, and 25.0 and 26.9 eV in Ta₃N₅, respectively (Figure 3b,c). The noticeable red shifts of about 0.8 and 1.5 eV in respective TaON and Ta₃N₅ are believed to be due to the easier electron transfer from N than O.^[3a] Remarkably, the increased electron density around Ta will endow such nanoparticles with improved catalytic properties.

The oxides of group V are promising alkene oxidation catalysts,^[14] and available Ta catalysts for epoxidation have recently attracted much attention because epoxides are important intermediates in fine chemical production and polymer synthesis.^[15] Herein, we employed cyclooctene epoxidation as a probe reaction for our TaON and Ta₃N₅ NPs, as well as Ta₂O₅ NPs (Table 1). All of these NPs possess similar sizes (ca. 20 nm) and surface areas (ca. 20 m² g⁻¹, Table S1). Ta₂O₅ NPs exhibit a low conversion of 57.1 %, whereas, improved activity with higher conversion of 96.0 % and 96.5 % was presented on TaON and Ta₃N₅ NPs, respectively (Table 1, entries 1–3). In view of their similar surface area, the improved activity of Ta in TaON and Ta₃N₅ should be ascribed to the increased electron density around Ta resulting from N introduction, as ascertained by XPS results in Figure 3. As reported, the epoxidation activity of Ta is associated with the step of [Ta–O*] reacting with alkene to epoxides, and can be improved by effective electron-donor ligands around Ta.^[15c,d] In TaON and Ta₃N₅ NPs, the N atom can serve as an electron donor and promotes the O* transfer from [Ta–O*] to cyclooctene, consequently improving the activity (Step I in Scheme 1). According to XPS results, Ta₃N₅ NPs with lower Ta 4f binding energies than TaON is expected to be more active, and, correspondingly, its conversion of 65.4 % is observed to be higher than that on the latter (59.1 %) when reaction time is shortened (Table 1, entries 4 and 5). Furthermore, the epoxidation selectivity is also

Table 1: Epoxidation of cyclooctene over Ta₂O₅, TaON, and Ta₃N₅ NPs^[a].

			
Entry	Catalyst	Conversion [%]	Selectivity [%]
1	Ta ₂ O ₅ ^[b]	57.1	95.9
2	TaON ^[c]	96.0	95.6
3	Ta ₃ N ₅ ^[c]	96.5	78.4
4	TaON ^[d]	59.1	97.9
5	Ta ₃ N ₅ ^[d]	65.4	79.8
6	Ta ₃ N ₅ -H ^[e]	96.9	85.8
7	Ta ₂ O ₅ -H ^[e]	57.9	97.9
8	Ta ₂ O ₅ -OH ^[f]	54.9	99.3
9	TaON ^[g]	96.8	96.1
10	Ta ₃ N ₅ ^[g]	99.0	85.4
11	Ta ₃ N ₅ -OH ^[h]	97.5	74.9
12	blank	12.8	99.0

[a] Typical reaction conditions: 0.92 mL of cyclooctene, 0.04 g of catalyst, 4.0 mL CH₃OH, and 3.0 mL H₂O₂ (50 wt %), 60 °C for 18 h. [b] Ta₂O₅ NPs were obtained through traditional reverse homogeneous precipitation (Figure S8). [c] TaON and Ta₃N₅ NPs were obtained by the SiO₂-surface assisted method. [d] The reaction time was decreased to 10 h. [e] Catalysts were used after treating with 1 M HCl for 1 day. [f] Catalyst was used after treating with 1 M NH₃·H₂O for 1 day. [g] TaON and Ta₃N₅ NPs were obtained by Ca-assisted urea method. [h] Ta₃N₅ NPs obtained through Ca-assisted urea method were used after treating with 1 M NH₃·H₂O for 1 day.



Scheme 1. I) Epoxidation of cyclooctene by TaON and Ta₃N₅ NPs, and II) overreaction of hydration to diol products catalyzed by the basic site on Ta₃N₅.

significantly influenced by N introduction. Ta₂O₅ and TaON NPs present the selectivity as high as 95.9% and 95.6%, respectively, whereas only a lower selectivity of 78.4% is found on Ta₃N₅ (Table 1, entries 1–3). In the GC–MS results of products catalyzed by Ta₃N₅ NPs, considerable amounts (ca. 21.3%) of cyclooctane–(di)ol are detected (Figure S9), indicating the hydration of epoxide to (di)ol products as overreactions.^[16] As enough N is introduced, a strong basic site will be generated on the catalysts,^[17] such as Ta₃N₅, which is validated by their temperature programmed desorption (TPD) curves of CO₂ (Figure S10). Thus, catalyzed by base sites on Ta₃N₅ NPs, the as-formed epoxide is hydrated with water from H₂O₂ solution, resulting in decreased epoxide selectivity (Step II in Scheme 1). Moreover, such basicity originating from N is tunable by acid or base treatment because of reversible protonation, generating an altered

selectivity. For example, the Ta₃N₅ NPs treated by 1 M HCl show the increased selectivity of up to 85.8% (Table 1, entry 6). Conversely, the selectivity on Ta₂O₅ NPs cannot be obviously varied by acid or base treatment (Table 1, entries 7 and 8), supporting again the surface base character derived from N atom.

The consistent performances of TaON and Ta₃N₅ NPs obtained by another Ca-assisted urea method^[7] (Table 1, entries 9–11) further confirm the improved activity and tunable selectivity significantly associated with their tailored nitridation level. It should be noted that Ta₃N₅ NPs from Ca-assisted processes are received after HCl washing to remove Ca species, and they deliver epoxide selectivity of as high as 85.4%, which can be decreased to 74.9% after treating with 1 M NH₃·H₂O (Table 1, entry 11). From the above results, it can be concluded that introducing N significantly promotes the Ta activity for epoxidation, and also generates tunable basicity important to tailor the epoxide selectivity. Controlled nitridation plays a key role in epoxidation, and, herein, TaON NPs with suitable nitridation degree present high activity and selectivity.

In summary, a novel SiO₂-surface-assisted urea method was introduced for the controlled synthesis of TaON and Ta₃N₅ NPs. By varying the urea/Ta ratio in the precursor gel, both TaON and Ta₃N₅ NPs with defined structure and size can be achieved. Moreover, a novel mechanism employing SiO₂ surfaces is proposed whereby silica catalyzes and stabilizes CN_x formation to achieve a slow release N source for controlled nitridation. The as-synthesized TaON and Ta₃N₅ NPs show improved activity and tunable selectivity for cyclooctene epoxidation. This behavior is explained by the increased electron density around Ta and surface basicity based upon the controlled introduction of N atom. The nitridation level is important to achieve highly active and selective metal catalysts for epoxidation, and our method is believed to be broadly applicable to the design of novel nanostructured catalysts.

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