Thermodynamically Stable Pickering Emulsion Configured with Carbon-Nanotube-Bridged Nanosheet-Shaped Layered Double Hydroxide for Selective Oxidation of Benzyl Alcohol

Yuanyuan Shan, Chang Yu, Juan Yang, Qiang Dong, Xiaoming Fan, and Jieshan Qiu*

Carbon Research Laboratory, Liaoning Key Laboratory for Energy Materials and Chemical Engineering, State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, No. 2 Ling Gong Road, Dalian 116024, China

S Supporting Information

ABSTRACT: A simple strategy to configure a high thermodynamically stable Pickering emulsion with 2D sheet-shaped layered double hydroxide (LDH) coupled carbon nanotube (CNT) nanohybrid (LDH−CNT) is reported. With the benefit of a unique 2D sheet-shaped structure of the LDH, the as-made LDH−CNTs with amphiphilicity as solid emulsifiers have a good capability for assembling and stabilizing at the water−oil interface, and a superior thermostability emulsion is delivered, indicative of an increased catalytic performance for selective oxidation of benzyl alcohol to benzaldehyde. Such a unique and excellent thermodynamic stability characteristic makes high reaction interfacial areas well-kept during the reaction process, yielding high catalytic performance. The present strategy provides a simple method for configuration and design of solid nanoparticle emulsifiers with high thermodynamic stability, which will make such a material be of great potential in many important applications such as catalysis and emulsifiers.

KEYWORDS: amphiphilic nanohybrids, thermodynamic stability, LDH−CNT, benzyl alcohol, Pickering interfacial catalysis
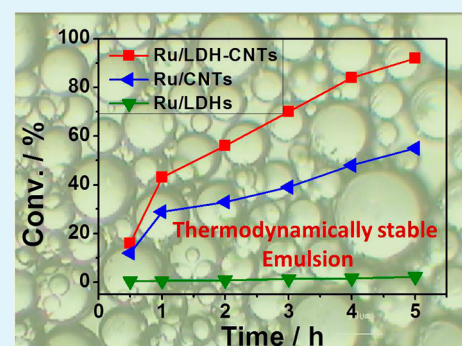
1. INTRODUCTION

Pickering interfacial catalysis (PIC) stabilized by solid nanoparticle emulsifiers at the water−oil interface has received increasing interest for fine chemicals synthesis due to the higher activity derived from enhanced interfacial areas and easier separation and recovery in comparison to the traditional surfactants after reaction.[1,2] It is not uncommonly believed that such an emulsion is a kinetically relatively stable system at room temperature to a great degree, which would not reflect the real and intrinsic characteristics of Pickering emulsion catalysis during reaction process at a special temperature.[3,4] It is well-known that the reactions available now for fine chemicals synthesis usually happen at high temperature. Moreover, mechanical stirring is also employed to ensure formation of emulsion and mitigate mass-transport resistance, thus leading to a large energy input.[5,6] With this in mind, it is very necessary and critical to keep the thermodynamic stability of emulsion during relatively harsh reaction conditions, which will also take full advantage of the intrinsic characteristics and avoid or reduce energy input to some extent. Therefore, creating novel solid nanoparticle emulsifiers with high thermostability, especially at a certain temperature, and investigating the effects of emulsion stability on their catalytic performance remain major challenges.

It was also not an uncommon fact that the stability of an emulsion is mainly affected and dominated by the solid nanoparticle emulsifiers,[7] of which the nanohybrids with amphiphilicity can more efficiently stabilize emulsion than solid nanoparticles with uniform wettability and homogeneous surface.[8] As for concerns regarding amphiphilic nanohybrids, researchers have tried to combine hydrophilic sphere-shaped metal oxides (such as SiO_2, Al_2O_3, MgO, and TiO_2) with the hydrophobic carbon nanotube (CNT) matrix, thus producing nanohybrids with amphiphilicity. It was also found that the as-formed emulsion properties and type can be tuned by controlling the hydrophilicity/lipophilicity balance (HLB),[9] which was also confirmed by Resasco et al.[10] Nevertheless, these emulsifiers available now still need to be considered to further modulate and increase their thermostability, thus being capable of bringing into play intrinsic functions at a certain temperature. Nonomura found that the particle shape and surface properties are the effective and key factors for modulating the adsorbing state of the solid nanoparticles and further affecting its stabilized emulsion properties.[11−13] It was also found that the nanosheet-shaped emulsifiers at the water−oil interface can restrict the rotation in comparison to sphere-shaped emulsifiers to a great degree, thus making the emulsion relatively more stable.[14] As we know, the active sites of the two-dimensional (2D) sheet-shaped materials are easily exposed in comparison to those of the sphere-shaped particles, thus

Scheme 1. Schematic of the Synthetic Process and Formation Mechanism for the LDH−CNT Nanohybrids
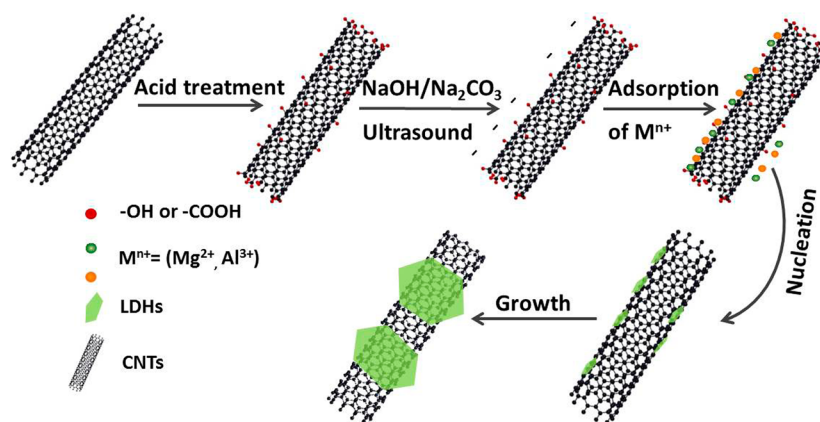
leading to the large surface areas and distinctive properties, which would be favorable for the catalysis process to some degree.[15−17]

Layered double hydroxide (LDHs) as typical 2D nanosheet-shaped materials has been conceived to be promising candidates as basic supports for the oxidation of alcohol reaction because of their tunable composition and environmental friendliness.[18−20] It was also found that the emulsion stabilized by LDHs can be produced via emulsification; nevertheless, the emulsion is unstable due to their low attachment energy.[3] As a result, the poor stability of emulsion stabilized by LDHs limits the practical application of LDHs in emulsion catalysis reactions to a certain degree. Sun et al. found that the sodium dodecyl sulfate and Span 80 modification show a positive effect on the formation and stability of the emulsion stabilized by LDHs.[3,21] Nevertheless, the separation of surfactants after reaction needs to be considered in such a system. In this regard, configuring a novel Pickering emulsion with high thermodynamic stability by amphiphilic LDH-based nanohybrid solid emulsifiers in the absence of surfactants is highly desired.

Herein, we report a simple method to configure a highly thermodynamically stable Pickering emulsion with 2D sheet-shaped LDH-coupled CNT nanohybrids (LDH−CNTs). With the benefit of the unique 2D sheet-shaped structure of LDHs, a superior thermostability emulsion is realized at the water−oil interface, which is not explored in the previous literature. Also, the selective oxidation of benzyl alcohol as a probe reaction was used to detect the catalytic activities of the Ru-based LDH−CNTs catalyst as solid emulsifiers. It is found that LDH−CNT nanohybrids can stabilize and assemble at the water−oil interface without stirring under the present reaction, and high catalytic activity and selectivity for alcohol oxidation can be achieved.

The synthetic process of LDH−CNT nanohybrids is outlined in Scheme 1. For a typical run, acid-treated CNTs was first dispersed in the mixed alkaline solutions, and then they were treated under ultrasonic conditions, yielding well-dispersed CNTs. Also, the as-obtained negatively charged CNTs were easily coated by sheet-shaped LDHs via electrostatic interaction followed by interface nucleation and crystal growth under hydrothermal conditions.

2. EXPERIMENTAL SECTION

Preparation of LDH−CNTs. Before preparation of the LDH−CNT nanohybrids, the pristine CNTs material was refluxed in a

mixture of water, HNO_3, and H_2SO_4 (volume ratio, 1:1:3) at 100 °C for 4 h, and then filtered and washed with deionized water until the filtrate was neutral. After that, it was dried at 80 °C for 12 h under vacuum, yielding acid-treated CNTs. The as-treated CNT material was dispersed in mixed solution containing NaOH (0.15 M) and Na_2CO_3 (0.1 M) with ultrasound for 1 h. The mixed salt solution containing $Mg(NO_3)_2·6H_2O$ (2.0 mmol) and $Al(NO_3)_3·9H_2O$ (1.0 mmol) was slowly added into the above sodium alkali solution containing CNTs under vigorous stirring, and the pH value of the solution was adjusted to 10.5 with the mixed sodium alkali solution. Then, the as-obtained solution was transferred to an autoclave and treated at 100 °C for 16 h. The as-obtained products were washed with deionized water for several times to remove nitrate and sodium ions, and then finally dried at 80 °C for 12 h under vacuum, yielding LDH−CNT nanohybrids.

Preparation of Ru-Based Emulsion Catalysts. Ru catalysts supported on LDH−CNTs were prepared by a wetness impregnation method.[22] For a typical run, 1 g of $RuCl_3·3H_2O$ is dissolved in 100 mL of deionized water, yielding 7.9 mg mL^{-1} of $RuCl_3$ aqueous solution. The as-made LDH−CNTs was impregnated in an aqueous solution of $RuCl_3$ (mass ratio of LDH−CNTs to $RuCl_3$ is 50:1) under ultrasonic conditions for 30 min, and then the mixture was incubated at room temperature (RT) for 24 h. The LDH−CNTs supported $RuCl_3$ samples were dried at 80 °C for 12 h under vacuum, reduced at 400 °C in flowing H_2 for 2 h, and then cooled to RT in argon. For comparison, the Ru/CNTs and Ru/LDHs catalysts were also prepared, in which the same procedures as described above were adopted.

Preparation and Characterization of Emulsions. Before measuring the emulsion properties, a certain amount of LDHs, CNTs, or LDH−CNTs was added to deionized water and toluene mixed solution with 1:2 of volume ratio, then sonicated and vibrated, forming a homogeneous emulsion between the water (bottom) and the organic (top) phases. The interfaces of the three water, emulsion, and oil phases can be clearly distinguished. The droplet size of emulsion stabilized by emulsifiers was monitored with a polarizing microscope after the emulsion was prepared for 1 h. The volume fraction of the emulsion phase was measured after the homogenized solution was suspended for 1 h.

Emulsion Type Measurement. The emulsion type was investigated by dilution method, in which the emulsion droplet is incorporated to the water phase of the water and oil mixture, meaning that the emulsion is o/w (oil in water) type; otherwise, it is the w/o (water in oil) type.[9]

Contact Angle Measurement. The three-phase contact angle (θ) of the LDH−CNTs and CNTs was measured across the water phase using the compressed disk method at 25 °C.[3] The sample powders were compressed into a circular disk with Shimadzu Press at the pressure of 400 kgf cm^{-2}. The thickness of the compressed disk was about 2 mm. The prepared disk was then placed at the bottom of an open, transparent glass vessel. The detailed process of contact angle measurement is as follows: the toluene was first poured into the vessel,

and then a drop of methyl orange aqueous solution was placed on the particle layer. The appearance of the water drop on the particle layer was immediately photographed, and the contact angle was directly measured using a protractor.

Evaluation of Emulsion Catalytic Activity. Emulsion oxidation of benzyl alcohol was carried out in a 50 mL three neck round-bottom flask without vigorous stirring; the detailed information for this process was described in our previous work.[22,23] For a typical run, 0.2 g of Ru/LDH−CNTs catalyst, 2 mmol of benzyl alcohol, 10 mL of toluene, and 5 mL of water were placed in a flask that had been flushed with flowing oxygen at atmospheric pressure, and heated at 85 °C for different time. The products were analyzed by GC (Agilent 6890N).

Materials Characterization. The field-emission scanning electron microscopy (FESEM, FEI Nova Nano SEM 450 at 3 kV) and transmission electron microscope (TEM, FEI Tecnai F30 at 300 kV) were employed to observe the morphology of the samples. Powder X-ray diffraction (XRD) patterns were recorded on a D/Max-2400 with Cu Kα radiation ($\lambda = 1.5406$ Å). The content of Ru was measured by inductively coupled plasma (ICP, Optima 2000DV, PerkinElmer). Specific surface area and pore size distribution were calculated on the basis of the nitrogen physical adsorption results (Micromeritics 3Flex).

3. RESULTS AND DISCUSSION

The typical XRD pattern of LDH−CNTs nanohybrids is shown in Figure 1a, of which the peak at 24.1° corresponding to the
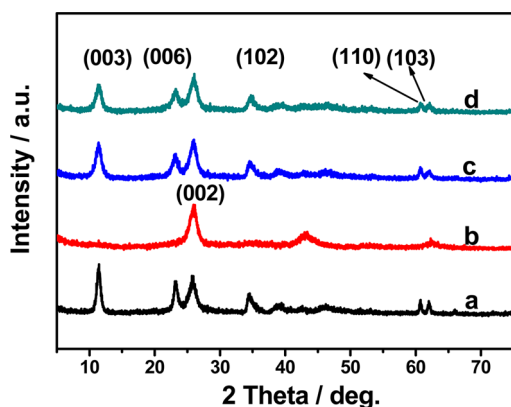
Figure 1. XRD patterns of (a) LDH−CNTs, (b) LDO−CNTs, (c) LDH−CNTs by rehydrating fresh LDO−CNTs at the toluene−water interface for 3 h, and (d) LDH−CNTs by rehydrating fresh LDO−CNT in the water phase for 24 h.

(002) diffraction of graphite layers can be clearly observed. The peaks at 11.8°, 23.1°, and 61.5° are indexed as (003), (006), and (110) characteristic diffractions of the hydrotalcite-like structure in the LDH−CNTs samples, implying that the material is a layered structure. As we know, the reduction of catalysts is a crucial step and is commonly carried out at a relatively high temperature; in this case, the layered structure of the LDH as support easily collapses, and an amorphous material will be produced,[24] which will have a negative effect on practical catalysis application. With this in mind, LDH−CNT nanohybrids after treatment at 400 °C and redispersion at the water−oil interface or in the water phase were further characterized to investigate their structure and component properties. The corresponding XRD results are also shown in Figure 1. It can be clearly seen that the characteristic diffraction peaks of LDHs disappears after thermal treatment (Figure 1b). The reason for this would be that amorphous layered double oxides (LDOs) were formed after the removal of CO_3^{2-} and OH^-, which was also in agreement with the results in the literature.[24] It is very interesting that such a structure of the

LDOs can be easily rehydrated and reconstituted either at the water−oil interface or water phase, which can also be confirmed by XRD patterns of as-made LDH−CNT nanohybirds by rehydrating fresh LDO−CNTs at the toluene−water interface for 3 h (Figure 1c) and fresh LDO−CNTs in water for 24 h (Figure 1d). In other words, the present reduction temperature has no influence on the layered structure of LDHs; thus, the intrinsic characteristics of the catalysis still corresponds to LDH catalysis instead of LDOs in the present system.

The representative SEM and TEM images of the LDH−CNTs nanohybrids are shown in Figure 2. It can be clearly seen
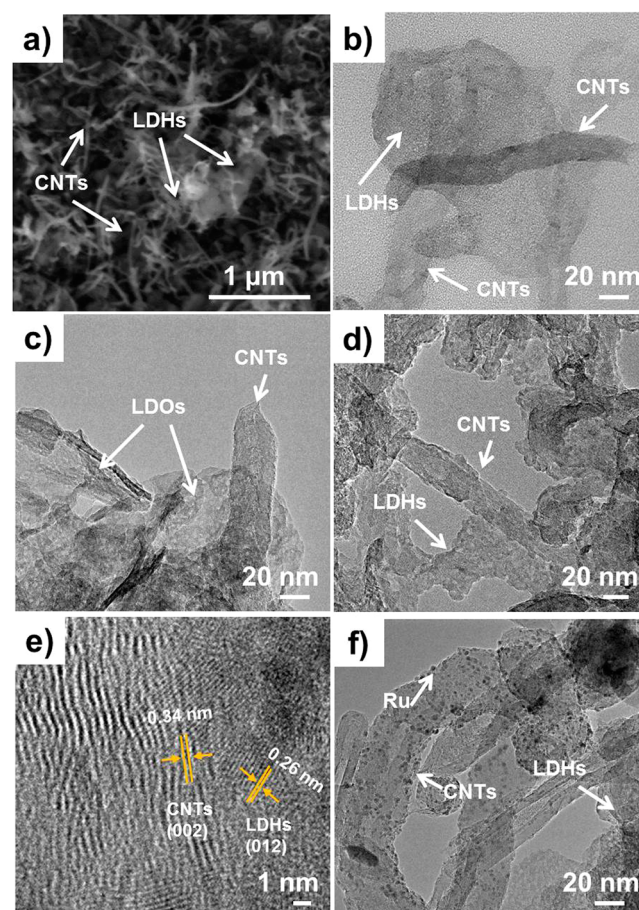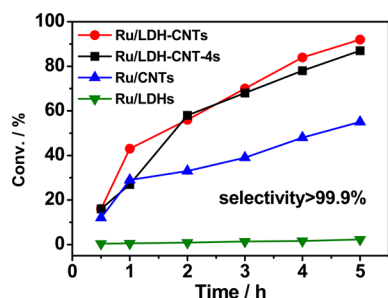

Figure 2. (a) SEM and (b) TEM images of LDH−CNTs, (c) TEM image of LDO−CNTs, (d) TEM and (e) HRTEM images of LDH−CNTs by rehydrating fresh LDO−CNTs at the toluene−water interface for 3 h, and (f) TEM of Ru/LDH−CNTs.

that CNTs can be uniformly distributed within the sheet-shaped LDHs matrix, and the size of the LDHs is in the range 50−100 nm (Supporting Information Figure S1), as indicated by arrows in Figure 2a. An additional TEM image (Figure 2b) shows that CNTs can be better bridged and incorporated into the LDHs nanosheet, which is in agreement with the results of SEM. The corresponding LDO−CNTs image (Figure 2c) shows that a layered morphology can be well-kept after removal of CO_3^{2-} and water with thermal treatment. The TEM image of rehydrated LDO−CNTs is also shown in Figure 2d, where a distinguishing interface still exists between the LDH and CNT. An interplanar distance of 0.26 nm corresponding to the (012) plan characteristic of an LDH nanosheet is also found in the rehydrated LDO−CNT nanohybrids, further confirming that

the LDHs is recovered and reconstituted in the presence of water. Such superiority of LDH−CNTs with a water memory effect can guarantee the natural characteristics based on LDHs instead of LDOs catalysis in PIC process.
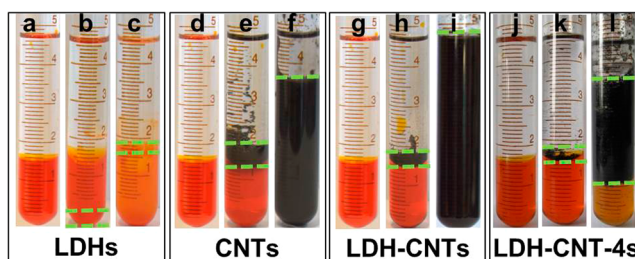
The catalytic activity of the LDH−CNT nanohybrids as the emulsion catalyst support for the selective oxidation of benzyl alcohol to benzaldehyde was evaluated and compared with those of LDHs and CNTs, of which the detailed results are shown in Figure 3. Compared with the results for Ru/CNTs


Figure 4. Digital photos of emulsions stabilized by LDHs, CNTs, LDH−CNTs, LDH−CNT-4s that were produced by changing hydrothermal time to 4 h. The green dotted line represents the interfaces of emulsion and water or toluene: (a, d, g, j) water (methyl orange in water) and toluene mixed solution without any particles, (b, e, h, k) water and toluene mixed solution in the presence of solid nanoparticles, (c, f, i, l) Pickering emulsion stabilized by different nanoparticles after ultrasound.

Figure 3. Conversions of benzyl alcohol over different supports in the aerobic oxidation of benzyl alcohol [reaction conditions: benzyl alcohol 2 mmol, deionized water 5 mL, toluene 10 mL, catalyst 200 mg (0.02 mmol Ru), $T = 85$ °C, $t = 5$ h, O_2 flow rate 25 mL min^{-1}].

and Ru/LDHs, Ru/LDH−CNTs catalyst shows a relatively high catalytic activity and selectivity with more than 99.9%. The conversions of benzyl alcohol increase with an increase of reaction time and reach 92% when reaction time is 5 h. The Ru-based catalysts are also further characterized by ICP and TEM to further reveal Ru active component effects. It is also noted that, for as-obtained catalysts, the actual loading of Ru derived from ICP analysis is almost the same (0.7 wt %, Supporting Information Table S1). Also, the sizes of Ru nanoparticles on LDHs, CNTs, and LDH−CNTs are narrowly distributed, and the Ru nanoparticles with 2−3 nm (Figure 2f and Supporting Information Figure S2) are uniformly dispersed on the surface of supports. In other words, the size effects can be neglected in the present system to some extent. It is also found that the BET specific surface area of the LDH−CNTs reaches 89 m^2 g^{-1}, which is close to that of the LDHs and CNTs (Supporting Information Table S2). Moreover, the supports themselves show no any catalytic activities for selective oxidation of benzyl alcohol to benzaldehyde (Supporting Information Table S3). Nevertheless, the results presented above clearly show that the catalytic activities for the benzyl alcohol oxidation over Ru supported LDHs, CNTs, and LDH−CNTs catalysts vary greatly with the supports. The possible reason for this is attributed to different emulsion properties stabilized by emulsifiers to a great degree,[9] which can be further confirmed by the following results.

The capacities of the CNTs, LDHs, and as-made LDH−CNT nanohybrids to stabilize water−oil emulsions composed of water and toluene were evaluated and compared, and the results are shown in Figure 4. The emulsifying capacities of CNTs, LDHs, and LDH−CNTs at water−oil emulsions are completely different under the identical experimental conditions. The emulsifying capability of LDHs is relatively weak, where several emulsion droplets with large diameters are present in the system (100−300 μm, Supporting Information Figure S3). It has also been confirmed that the hydrophilic LDHs nanosheet is unstable at the water−oil interface due to

its low attachment energy.[3] This is not the case for the CNTs; the volume fraction of the emulsion stabilized by CNTs is 77%. Nevertheless, the size of the emulsion droplet is relatively large (100−300 μm, Supporting Information Figure S3). It is interesting that the large volume fraction of 100% and the emulsion droplet with a relatively small size (30−150 μm, Supporting Information Figure S3) are produced in the system stabilized by LDH−CNT nanohybrids, resulting in an increased emulsion interfacial surface area to a great degree. The increased reaction interfacial area is favorable for the PIC process and leads to an enhanced catalytic activity, which is verified in our previous work and literature.[23,25] This is also the case for the present system. For comparison, it is noted that only 54% conversion of benzyl alcohol is obtained over Ru/LDH−CNTs with toluene as solvent (Supporting Information Table S3), which is much lower than that in the present emulsion system, suggesting that the PIC process is a determining step for high conversion.

Moreover, it is also expected that the emulsion thermostability can be kept at reaction temperature, thus yielding a well-kept interface area during reaction process. It is interesting that the emulsion stability at reaction temperature varies greatly with different supports. For the LDHs, the emulsion droplets at the water−oil interface begin to coalesce, and LDH material is gradually transferred to the aqueous phase and deposited at the bottom of the reaction vessel owing to its hydrophilicity (Supporting Information Figure S4). As we know, the benzyl alcohol is more likely to dissolve in toluene; thus, Ru/LDHs in the aqueous phase does not catalyze the reaction, where low conversion is achieved in such a system. For CNTs, it still shows the capability of dispersing at the water−oil interface (Figure 4e), and the PIC emulsion catalysis is still dominating, although the partial emulsion droplets occur to coalesce (Supporting Information Figures S4 and S5). Such a water/oil type emulsion[9] system stabilized by CNTs can also lead to an increased interface area in comparison to that of LDHs, yielding the high catalytic activity over Ru/CNTs catalyst. In the case of LDH−CNT nanohybrids, surprisingly, the o/w type emulsion (Supporting Information Figure S6) formed by LDH−CNT nanohybrids at the water−oil interface (Figure 4i) is relatively stable at reaction temperature in comparison to that of CNTs (Supporting Information Figure S4). The potential reason behind this is that the nanosheet-shaped structure can restrict the rotation of emulsifiers at the water−oil interface to a great degree, which has also been confirmed in
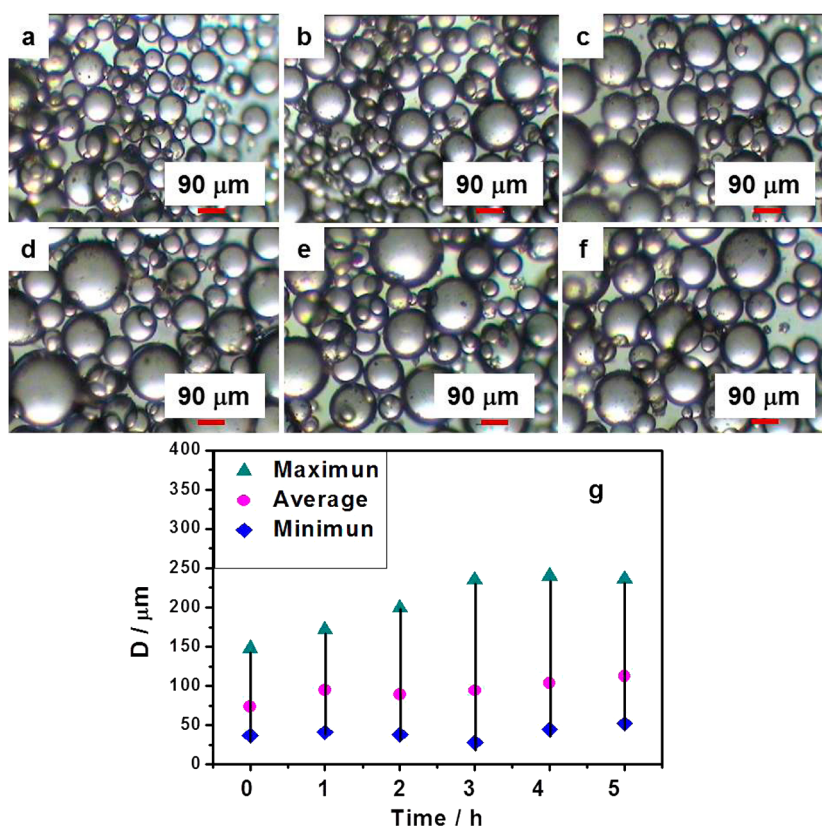
Figure 5. Optical images of toluene/water emulsion stabilized by LDH−CNT nanohybrids in 85 °C for different time: (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 5 h. (g) Droplet diameter distribution.

the literature.[14] In order to further investigate the thermostability of the emulsion stabilized by LDH−CNT nanohybrids, the optical images of toluene/water emulsion stabilized by LDH−CNT nanohybrids at 85 °C for different time are shown in Figure 5. It can clearly be seen that the diameters of emulsion droplets have a slight increase with an increase of time; nevertheless, LDH−CNTs can still assemble at the interfaces of emulsion droplets after 5 h. This further exhibits the high and superior thermodynamic stability of emulsion stabilized by LDH−CNTs. Benefiting from the high thermostability, the high emulsion interfacial surface areas that derive large emulsion volume fraction and the emulsion droplets with a relatively small size can be well-kept, thus leading to the higher conversions on Ru/LDH−CNTs.

In order to further demonstrate the positive effects of 2D LDH nanosheets for the PIC process, a comparative study was also performed by changing hydrothermal time to 4 h, yielding LDH−CNT-4s. It is also noted that the content of LDHs in LDH−CNT-4s is close to that in LDH−CNTs (Supporting Information Figure S7), indicative of a similar HLB value, even if the LDHs in LDH−CNT-4s has a relatively small size in comparison to that in LDH−CNTs (Supporting Information Figure S8). It can be clearly seen that the conversions (84%) of benzyl alcohol on Ru/LDH−CNT-4s are higher than that over Ru/CNTs (Figure 3), even though the emulsion volume formed by LDH−CNT-4s (55%, Figure 4) is lower than that of CNTs (77%). This result also further confirms the positive effects of 2D nanosheets derived from the highly thermodynamically stable emulsion (Supporting Information Figure S9) in the PIC process.

It has been reported that there are many factors affecting the stability of the Pickering emulsion, including wettability that is often expressed as a contact angle (θ) at the three-phase boundary, emulsifier shape, and so on.[26] As shown in Figure 6,
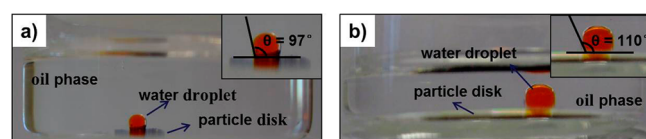
Figure 6. Schematic representation of the three-phase contact angle (θ) of (a) LDH−CNTs and (b) CNTs at the toluene−water interface.

the three-phase contact angle (θ) of LDH−CNTs at the water−oil interface is 97°, lower than that of CNTs (110°). In other words, the wettability of hydrophobic CNTs can be modulated in the presence of hydrophilic LDHs to some degree, thus producing the more stable emulsion. On the other hand, the nanosheet-shaped structure can restrict the rotation of emulsifiers at the water−oil interface to a great degree and further result in a high thermodynamic stability, which has been pointed out in the previous literature.[13,14,27]

4. CONCLUSIONS

In summary, the amphiphilic nanohybrids composed of CNT-bridged 2D nanosheet-shaped LDHs are synthesized by hydrothermal method and can assemble at the water and toluene interface very well. Also, large emulsion volume fraction and droplets with small size were easily formed, thus producing high emulsion interfacial surface areas. The emulsion stabilized by LDH−CNT nanohybrids demonstrates a high thermody-

namic stability at the toluene—water interface due to the presence of 2D sheet-shaped LDHs, which makes the high emulsion interfacial surface areas well-kept during the PIC process. With the benefit of such a unique structure and emulsion characteristics, with the LDH−CNTs as catalyst support, the Ru/LDH−CNTs catalyst shows a high catalytic conversion for selective oxidation of benzyl alcohol to benzaldehyde in the emulsion system. The present strategy will also provide a simple method for configuring a high thermodynamically stable Pickering emulsion, and such a catalytic system with less extra energy input will lead to low energy consuming. These unique characteristics make such a material have great potential in many important applications such as catalysis and emulsifiers.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

TEM images and content of Ru on different catalysts supports. Digital photos of emulsion stabilized by LDHs, CNTs, and LDH−CNTs at 85 °C. Specific surface area of LDHs, CNTs, and LDH−CNTs. Optical images of emulsion stabilized by CNTs and LDH−CNT-4s. Digital photos of emulsion type. TEM images of LDH−CNTs and LDH−CNT-4s. Conversions of benzyl alcohol over LDHs, CNTs, and LDH−CNTs. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02595.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jqiu@dlut.edu.cn. Phone: 0086-411-84986080.

Author Contributions

Y.S. and C.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Zhou, W. J.; Fang, L.; Fan, Z.; Albela, B.; Bonneviot, L.; Campo, D. F.; Titus, M. P.; Clacens, J. M. Tunable Catalysts for Solvent-Free Biphasic Systems: Pickering Interfacial Catalysts over Amphiphilic Silica Nanoparticles. *J. Am. Chem. Soc.* **2014**, *136*, 4869−4872.

(2) Drexler, S.; Faria, J.; Ruiz, M. P.; Harwell, J. H.; Resasco, D. E. Amphiphilic Nanohybrid Catalysts for Reactions at the Water/Oil Interface in Subsurface Reservoirs. *Energy Fuels* **2012**, *26*, 2231−2241.

(3) Wang, J.; Yang, F.; Tan, J. J.; Liu, G. P.; Xu, J.; Sun, D. J. Pickering Emulsions Stabilized by a Lipophilic Surfactant and Hydrophilic Platelike Particles. *Langmuir* **2009**, *26*, 5397−5404.

(4) Shen, M.; Resasco, D. E. Emulsions Stabilized by Carbon Nanotube-Silica Nanohybrids. *Langmuir* **2009**, *25*, 10843−10851.

(5) Chong, W. H.; Chin, L. K.; Tan, R. L. S.; Wang, H.; Liu, A. Q.; Chen, H. Y. Stirring in Suspension: Nanometer-Sized Magnetic Stir Bars. *Angew. Chem., Int. Ed.* **2013**, *52*, 8570−8573.

(6) Zhang, W. J.; Fu, L. M.; Yang, H. Q. Micrometer-Scale Mixing with Pickering Emulsions: Biphasic Reactions without Stirring. *ChemSusChem* **2014**, *7*, 391−396.

(7) Sacanna, S.; Kegel, W. K.; Philipse, A. P. Thermodynamically Stable Pickering Emulsions. *Phys. Rev. Lett.* **2007**, *98*, 158301−158304.

(8) Binks, B. P.; Fletcher, P. D. I. Particles Adsorbed at the Oil-Water Interface: A Theoretical Comparison between Spheres of Uniform Wettability and "Janus" Particles. *Langmuir* **2001**, *17*, 4708−4710.

(9) Yu, C.; Fan, L. M.; Yang, J.; Shan, Y. Y.; Qiu, J. S. Phase-Reversal Emulsion Catalysis with CNT-TiO₂ Nanohybrids for the Selective Oxidation of Benzyl Alcohol. *Chem.—Eur. J.* **2013**, *19*, 16192−16195.

(10) Ruiz, M. P.; Faria, J.; Shen, M.; Drexler, S.; Prasomsri, T.; Resasco, D. E. Nanostructured Carbon-Metal Oxide Hybrids as Amphiphilic Emulsion Catalysts. *ChemSusChem* **2011**, *4*, 964−974.

(11) Nonomura, Y.; Sugawara, T.; Kashimoto, A.; Fukuda, K.; Hotta, H.; Tsujii, K. Self-Assembly of Surface-Active Powder at the Interfaces of Selective Liquids. 1: Multiple Structural Polymorphism. *Langmuir* **2002**, *18*, 10163−10167.

(12) Nonomura, Y.; Fukuda, K.; Komura, S.; Tsujii, K. Self-Assembly of Surface-Active Powder at the Interfaces of Selective Liquids. 2: Behavior of an Organic-Crystalline Powder. *Langmuir* **2003**, *19*, 10152−10156.

(13) Nonomura, Y.; Komura, S.; Tsujii, K. Adsorption of Micro-structured Particles at Liquid-Liquid Interfaces. *J. Phys. Chem. B* **2006**, *110*, 13124−13129.

(14) Liang, F. X.; Shen, K.; Qu, X. Z.; Zhang, C. L.; Wang, Q.; Li, J. L.; Liu, J. G.; Yang, Z. Z. Inorganic Janus Nanosheets. *Angew. Chem., Int. Ed.* **2011**, *50*, 2379−2382.

(15) Liang, F. X.; Liu, J. G.; Zhang, C. L.; Qu, X. Z.; Li, J. L.; Yang, Z. Janus Hollow Spheres by Emulsion Interfacial Self-Assembled Sol-Gel Process. *Chem. Commun.* **2011**, *47*, 1231−1233.

(16) Yang, J.; Yu, C.; Fan, X. M.; Ling, Z.; Qiu, J. S.; Gogotsi, Y. Facile Fabrication of MWCNT-Doped NiCoAl-Layered Double Hydroxide Nanosheets with Enhanced Electrochemical Performances. *J. Mater. Chem. A* **2013**, *1*, 1963−1968.

(17) Zhang, H.; Zhang, G. Y.; Bi, X.; Chen, X. T. Facile Assembly of a Hierarchical Core@Shell Fe₃O₄@CuMgAl-LDH (Layered Double Hydroxide) Magnetic Nanocatalyst for the Hydroxylation of Phenol. *J. Mater. Chem. A* **2013**, *1*, 5934−5942.

(18) Choudary, B. M.; Kantam, M. L.; Rahman, A.; Reddy, C. V.; Rao, K. K. The First Example of Activation of Molecular Oxygen by Nickel in Ni-Al Hydrotalcite: A Novel Protocol for the Selective Oxidation of Alcohols. *Angew. Chem., Int. Ed.* **2001**, *40*, 763−766.

(19) Sachdev, D.; Naik, M. A.; Dubey, A.; Mishra, B. G. Environmentally Benign Aerial Oxidation of Benzoin over Copper Containing Hydrotalcite. *Catal. Commun.* **2010**, *11*, 684−688.

(20) Mi, F.; Chen, X. T.; Ma, Y. W.; Yin, S. T.; Yuan, F. L.; Zhang, H. Facile Synthesis of Hierarchical Core-Shell Fe₃O₄@MgAl-LDH@Au as Magnetically Recyclable Catalysts for Catalytic Oxidation of Alcohols. *Chem. Commun.* **2011**, *47*, 12804−12806.

(21) Wang, J.; Yang, F.; Li, C. F.; Liu, S. Y.; Sun, D. J. Double Phase Inversion of Emulsions Containing Layered Double Hydroxide Particles Induced by Adsorption of Sodium Dodecyl Sulfate. *Langmuir* **2008**, *24*, 10054−10061.

(22) Yang, X. M.; Wang, X. N.; Qiu, J. S. Aerobic Oxidation of Alcohols over Carbon Nanotube-Supported Ru Catalysts Assembled at the Interfaces of Emulsion Droplets. *Appl. Catal., A* **2010**, *382*, 131−137.

(23) Yang, X. M.; Wang, X. N.; Liang, C. H.; Su, W. G.; Wang, C.; Feng, Z. C.; Li, C.; Qiu, J. S. Aerobic Oxidation of Alcohols over Au/TiO₂: An Insight on the Promotion Effect of Water on the CatalyticActivity of Au/TiO₂. *Catal. Commun.* **2008**, *9*, 2278−2281.

(24) Constantino, V. R. L.; Pinnavaia, T. J. Basic Properties of Mg²⁺₁₋ₓAl³⁺ₓ Layered Double Hydroxides Intercalated by Carbonate, Hydroxide, Chloride, and Sulfate Anions. *Inorg. Chem.* **1995**, *34*, 883−892.

(25) Shi, D. C.; Faria, J.; Pham, T. N.; Resasco, D. E. Enhanced Activity and Selectivity of Fischer−Tropsch Synthesis Catalysts in Water/Oil Emulsions. *ACS Catal.* **2014**, *4*, 1944−1952.

(26) Binks, B. P.; Lumsdon, S. O. Influence of Particle Wettability on the Type and Stability of Surfactant-Free Emulsions. *Langmuir* **2000**, *16*, 8622−8631.

(27) Nonomura, Y.; Komura, S.; Tsujii, K. Adsorption of Disk-Shaped Janus Beads at Liquid-Liquid Interfaces. *Langmuir* **2004**, *20*, 11821−11823.