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Title Yolk-Shell-Structured CuO-ZnO- In_2O_3 trimetallic oxide mesocrystal microspheres as an efficient catalyst for trichlorosilane production

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Abstract

Trichlorosilane (TCS), the primary chemical feedstock for production of high-purity Si used in Sibased solar cells, is currently manufactured industrially via a non-catalytic hydrochlorination of metallurgical Si. This process generates a huge amount of undesirable silicon tetrachloride (STC) byproduct. Here we report the synthesis of yolk-shell-structured CuO-ZnO-In₂O₃ trimetallic oxide mesocrystal microspheres that can be employed as an efficient catalyst to produce TCS catalytically. The CuO-ZnO-In₂O₃ microspheres with multiple hetero-interfaces were prepared using a facile solvothermal reaction followed by calcination. We found that differing from a single CuO mesocrystal, the electronic density on Cu atoms in the CuO phase within CuO-ZnO and CuO-ZnO-In₂O₃ can be well-tuned via controlling the introduced composition. When used as a catalyst for Si hydrochlorination reaction to produce TCS, CuO-ZnO-In₂O₃ presents excellent catalytic performance with much high Si conversion and TCS selectivity. Under the same reaction condition, the TCS yield increased 13 times compared with the catalyst-free process. This work not only demonstrates the high possibility to realize the catalytic manufacture of TCS with less STC but also provides an approach to the facile synthesis of multi-component mesocrystal materials with a specific structure. ChemCatChem

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At present, the majority of the solar grade high-purity Si (hp-Si) is produced via the Siemens process.^[1] It involves non-catalytic hydrochlorination of metallurgical Si (m-Si) to produce trichlorosilane (SiHCl₃ or TCS) with generation of a large amount of undesired byproduct silicon tetrachloride (SiCl₄ or STC) at the temperatures above 350 °C, and the selectivity of TCS and STC in this process is around 85 and 15%, respectively. Therefore, further raising TCS selectivity or lowering reaction temperature could result in a decrease of byproduct STC output and saving energy consumption, and thus reducing TCS manufacture cost. Nowadays, the reactions of Si with CH₃Cl or ROH ($R = CH_3$, C_2H_5) (the so-called Rochow-Müller reaction) to generate organosilane monomers such as methylchloro- or alkoxysilanes is well known. These reactions can proceed with the apparent rate only in the presence of Cu-based catalysts. Previously, we investigated many Cu-based catalysts for the Rochow-Müller reaction, such as defective Cu-O-Sn nanosheet,^[2] hierarchical CuO-ZnO hollow microsphere,^[3] CuO-In₂O₃ composites with P-N junctions,^[4] heterostructured ZnO/Cu₂O with different exposed facets.^[5] These studies inspire us to explore the potential of the use of Cu-based catalysts to catalyze the production of TCS. As we know, mesocrystals are a special class of crystalline superstructures composed of highly ordered nanoparticles.^[6-8] Comparing with the conventional catalyst systems such as single crystals, polycrystals, and nanocrystals, mesocrystals have shown greatly improved properties.^[9] The unique structure enables mesocrystals new collective properties emerging from the electronic and/or magnetic coupling between their constituent nanoparticles. Recently, Bian et al.^[10] organized CuO and ZnO into a binary nanocomposite mesocrystal, which possesses a large number of interfaces between p- and n-type semiconductor nanoparticles. The efficient charge transfer at the interfaces may significantly amplify their applications in catalysis, energy conversion, and storage.^[11,12]

Here we demonstrate the facile synthesis of yolk-shell-structured CuO-ZnO-In₂O₃ trimetallic nanocomposite mesocrystals using a simple solvothermal method. The yolk-shell structure,^[13] a unique core-shell structure with a gap between the core and shell, has shown distinct advantages in

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catalytic applications: (a) the inner core can be in full contact with the reactant molecules, providing more active surface for their adsorption and activation, (b) the cavity between the core and shell is conducive to the enrichment of reactant molecules, and (c) the outer shell can provide adequate protection for the inner core. We found that, when used as the catalyst in m-Si hydrochlorination reaction to produce TCS, CuO-ZnO-In₂O₃ shows excellent catalytic property with much high Si conversion and TCS selectivity. The development of such a mesocrystal catalyst may shift the non-catalytic to catalytic production of TCS.

Yolk-shell-structured CuO-ZnO-In₂O₃ mesocrystal microspheres were prepared by using Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O and In(NO₃)₃·4.5H₂O as precursor salts, N, N dimethylformamide (DMF) as the solvent, and acetic acid (CH₃COOH) as the complexing agent. The synthesis involves a facile template-free solvothermal process and subsequent calcination (details are shown in Table S1). As shown in X-ray diffraction (XRD) pattern (Figure 1a), all of the diffraction peaks match well with the standard data for monoclinic CuO (JCPDS No. 01-089-5898), and no signals of Zn and In species are observed, probably because of their low contents or small particle sizes. By using the Scherrer equation from the {111} peak, the average crystallite size of CuO is calculated to be about 150 nm (Table S2). The scanning electron microscopy (SEM) image (Figure 1b) shows that the products exhibit a uniformly spherical morphology. These well-dispersed spheres have an average size of 17 µm, and the surface of microspheres is rough (Figure 1c). Close observation of the surface structure in Figure 1c reveals the existence of many regular stripes and boundaries (indicated by the yellow circle). A broken microsphere (Figure 1d) further explains its yolk-shell structure, and the shell thickness was estimated to be ca. 0.5 µm. Also, the porous core is self-assembled by a large number of smaller nanoparticles with a size range of 100-150 nm. This material was sliced by an ultramicrotome (detailed slicing process is shown in Figure S1). The highly porous internal structure of CuO-ZnO-In₂O₃ mesocrystal microsphere can be clearly observed by the Focus ion-beam scanning electron microscopy (FIB-SEM) image (Figure 1e and Figure S2), high-angle annular dark-field

scanning transmission electron microscopy (HAADF-STEM) image (Figure 1f) and TEM image (Figure 1g and Figure S3). Nitrogen-adsorption measurement (Figure S4) reveals that this sample has a mesoporous structure, and its surface area is about $3.9 \text{ m}^2 \text{ g}^{-1}$. These mesopores with a mean size of 20nm are formed by the assembly of small nanoparticles, as evidenced by the magnified TEM image (Figure 1h), which also shows the ordered arrangement of nanoparticles. The selected area electron diffraction (SAED) pattern (Figure 1i) reveals the quasi-single-crystalline structure of this material, indicating that the assembly of the nanoparticle building units is oriented and aligned. Furthermore, this result also suggests there is a small angle lattice mismatch between the boundaries of the nanoparticles, which is a typical feature of the mesocrystal.^[6-8] The contents of Cu, Zn, and In determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Table S2) analysis are consistent with the feeding ratios of the three precursors. These observations demonstrate the successful synthesis of the trimetallic oxide nanocomposite mesocrystal microspheres with a unique yolk-shell structure. For a comparison, yolk-shell structured CuO single metallic oxide mesocrystal microspheres (Figure S5 and S6) and yolk-shell structured CuO-ZnO bimetallic oxide mesocrystal microspheres with a Cu: Zn molar ratio of 100: 2 (Figure S7 and S8) were synthesized using the same process.



Figure 1. (a) XRD pattern and (b-d) SEM images of yolk-shell structured CuO-ZnO-In₂O₃ mesocrystal microspheres; (e) FIB-SEM image of the sliced material; (f) HAADF-STEM image and (g) TEM image obtained from the rim of the sliced material marked with the yellow square in image e; (h) high-resolution cross-sectional TEM image obtained from the rim of the sliced material marked with the yellow square in image g, and (i) the corresponding SAED pattern.

The bright-field STEM image of ultramicrotome (Figure 2a) also confirms the highly porous characteristic of internal structure. The high-magnification energy-dispersive X-ray spectroscopy (EDS) mapping analysis shows the simultaneous existence and homogeneous distribution of all the elements of O (Figure 2b), Cu (Figure 2c) Zn (Figure 2d) and In (Figure 2e). This observation is further supported by a broader-range of EDX analysis (Figure S9). A closer examination of Figure 2f reveals that the trace amount of Zn and In elements are highly dispersed in CuO. In the atomic-resolution aberration-corrected HAADF-STEM image (Figure 2g) taken at the surface region, the lattice spacings were measured to be 0.232, 0.25 and 0.248 nm, which correspond to the CuO(111), In₂O₃(101) and ZnO(400) facets, respectively, indicating highly crystallized nature of CuO, ZnO, and

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In₂O₃. It is clear that there generate intimate contact interfaces between CuO, In₂O₃, and ZnO nanoparticles in this sample. As seen from X-ray photoelectron spectroscopy (XPS) spectra (Figure 2h and Table S3), the CuO-ZnO mesocrystal has a higher binding energy of Cu 2p_{3/2} peak relative to CuO, indicating the electron deficiency of Cu atoms in it. However, for the CuO-ZnO-In₂O₃ mesocrystal, the Cu 2p_{3/2} peak is shifted to lower binding energy in comparison with that of both CuO and CuO-ZnO mesocrystals, which demonstrates that the electron density at the Cu atoms is increased in the CuO-ZnO-In₂O₃ mesocrystal. Moreover, the surface Zn species in both of the CuO-ZnO and CuO-ZnO-In₂O₃ mesocrystals are present in the form of ZnO (Figure 2i); furthermore, the binding energy of the Zn 2p_{3/2} peak in CuO-ZnO-In₂O₃ mesocrystal also shifts to lower-energy side compared with that of CuO-ZnO mesocrystals (Figure 2i). In CuO-ZnO-In₂O₃, the peak of In 3d_{5/2} at about 445.0 eV shown in Figure 2j is characteristic of In₂O₃.^[14] In the O1s XPS spectra (Figure 2k, Figure S10, and Table S3), following the order of CuO, CuO-ZnO, and CuO-ZnO-In₂O₃, the value of molar ratio between the chemisorbed oxygen (denoted as Oads) and lattice oxygen (denoted as Olatt) calculated by the peak area becomes larger gradually, indicating that introduction of ZnO and In_2O_3 enhanced the surface enrichment of adsorbed oxygen species. The Raman analysis (Figure S11) further shows that compared with those of CuO, the bands of the CuO-ZnO mesocryatal shift slightly to high wavenumber; while for the CuO-ZnO-In₂O₃ mesocrystal, instead, the bands move to low wavenumber, demonstrating that there is a different change in the Cu electronic structure when ZnO or both of ZnO and In₂O₃ were introduced into the CuO mesocrystal. This observation is consistent with the results of XPS. The surface Zn/Cu and In/Cu molar ratios measured by XPS are consistent with those in bulk determined by ICP-OES (Table S3), suggesting that the distributions of ZnO and In₂O₃ nanocrystals are homogeneous in entire CuO-ZnO-In₂O₃ mesocrystal. Taken together, the above results clearly suggest: (1) both the nanocrystals of ZnO and In₂O₃ are highly dispersed in the CuO framework, leading to the formation of multiple interfaces in CuO-ZnO-In₂O₃; and (2) the Cu

electronic states can be engineered by controlling the composition through interfacial charge transfer between different oxide nanoparticles.



Figure 2. (a) High-resolution BF-STEM image of yolk-shell structured CuO-ZnO-In₂O₃ mesocrystal microspheres and the corresponding elemental mappings of (b) O, (c) Cu, (d) Zn, (e) In and (f) the merged image. (g) HRTEM image of the edges of the sectioned material. XPS spectra of (h) Cu 2p, (i) Zn 2p, (j) In 3d and (k) O 1s.

In our synthesis strategy, the coexistence of CH₃COOH and DMF is the key to the formation of uniform mesocrystal microspheres. As shown in (Figure S12), when DMF is replaced with other solvents such as water, not the mesocrystals, but the irregular aggregates composed of nanoparticles are formed. Without CH₃COOH in the system, we also obtain only disorganized solid spheres (Figure S13). Similarly, if CH₃COOH is substituted with other reagents such as H₂SO₄, only irregular particles are harvested (Figure S14). It is worth pointing out that replacing CH₃COOH with HCl cannot result in any precipitant, indicating the importance of the presence of oxygen-containing ligand in the system. As the amount of CH₃COOH was gradually increased, the three-dimensional ordered assembled microsphere gradually formed, confirming the effect of CH₃COOH on the formation of oriented assembled structures (Figure S15). The time-dependent experiments are further carried out to reveal the formation process. After 3h of solvothermal treatment (Figure 3a), solid microspheres of ca. 3 µm size with many voids/defects on their surface are formed. A closer examination of the image shows that the microspheres are composed of small nanoparticles with a diameter of 50-80 nm (see the inset in Figure 3a). When the reaction time is increased to 4 h (Figure 3b), these microspheres assemble into larger microspheres (about 17 µm size) with quite rough surfaces. As shown in Figure 3c and Figure S16, with continuously increasing reaction time (6 h), the surface of bigger microspheres gradually become smooth and compact; nevertheless, their interior is still substantial (Figure 3c). XRD analysis reveals that the intermediate crystal after 6h of solvothermal treatment mainly consists of Cu₂O, without noticeable peaks of Zn and In species observed (Figure S17, owing to their low content). Fourier transform infrared (FTIR) spectrum (Figure S18) further shows the appearance of two distinct absorption peaks for this sample at about 2924 and 1624 cm⁻¹, which correspond to the CH₃ stretching vibrations and C-N modes, respectively, indicating it was capped with DMF. After calcination in air, the solid microspheres finally evolve into the unique yolk-shell structure (Figure 3d). Moreover, it is observed that as the reaction progressed, the mixture experienced a noticeable color change from blue to green, to red-brown, and

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finally to black (Figure S19), indicating the variation of the composition of the product. The XRD patterns of the samples prepared at different times (Figure S20) show that the sample crystallinity gradually increases with prolonging time, suggesting the simultaneous occurrence of crystallization and particle assembly. Furthermore, as shown in Table S4, the change of the lattice parameters verifies the formation of defects between nanoparticles, which can lead to different lattice strain. Based on the evolution process at various stages, the formation mechanism is proposed and illustrated in Figure 3e. First, a large number of Cu₂O, ZnO and In₂O₃ primary nanoparticles capped by DMF are generated at the initial stage due to the heterogeneous nucleation and growth via the coordination reaction of Cu²⁺, Zn²⁺, In³⁺ ions with oxygen atom in -COOH group of CH₃COOH and nitrogen atom in DMF, and followed by the reduction of Cu(CH₃COO)₂ with the capped DMF and the decomposition of Zn(CH₃COO)₂ and In(CH₃COO)₃ under solvothermal conditions. The relevant chemical reactions are shown in the following Equation 1-6:

Cu(NO ₃) ₂ +2CH ₃ COOH=Cu(CH ₃ COO) ₂ +2HNO ₃				
$HCON(CH_3)_2 + 2Cu(CH_3COO)_2 \textcircled{} Cu_2O + 2(CH_3CO)_2O + HN(CH_3)_2 + CO_2$	(2)			
Zn(NO ₃) ₂ +2CH ₃ COOH=Zn(CH ₃ COO) ₂ +2HNO ₃	(3)			
$Zn(CH_3COO)_2 \triangleq ZnO+(CH_3CO)_2O$	(4)			
In(NO ₃) ₃ +3CH ₃ COOH—In(CH ₃ COO) ₃ +3HNO ₃	(5)			
$2\ln(CH_3COO)_3 \triangleq \ln_2O_3 + 3(CH_3CO)_2O$	(6)			

Then, as the reaction time is prolonged, these nanoparticles self-assemble in an oriented attachment way into the secondary microspheres, which further attach orderly to form larger solid microsphere intermediate that contains the ligands of DMF. In general, the main driving force of the oriented attachment for the colloidal semiconductor system relies on nanoparticle interaction forces (van der Waals force, hydrogen bonding, etc.) and a decrease in system free energy.^[7,15,16] It is reported that the -COOH group can act as a crystal growth modifier to aid in the oriented growth of nanocyrstal.^[17] In our study, the following factors are believed to contribute to the oriented aggregation: 1) It seems reasonable that these small nanoparticles with high surface energies are temporarily stabilized by the

capping DMF, which can prevent their uncontrolled and random aggregation owing to the repulsive interaction; 2) both of the -COOH group and dipole-dipole interaction between the nanoparticles assist them to rotate continuously and then to orient each other and further to fuse across the interface through an Oswald ripening into a crystallographic ordered aggregate. These two factors, therefore, contribute to minimize the total system energy by decreasing the surface free energy and interface energy. Finally, by oxidation at 400 °C in air, well-developed yolk-shell-structured CuO-ZnO-In₂O₃ mesocrystal microspheres are obtained via diffusion-controlled growth due to the well-known Kirkendall effect, that is, the outward diffusion rate of Cu atoms is faster than the inward diffusion rate of O atoms, leading to a moderate increase in the size of the nanoparticle subunits because of their further attachment. In summary, in our synthetic system, DMF serves as both the solvent and the surface ligand, while CH₃COOH serves as the crystal growth modifier to promote the formation of mesocrystals. The unique property of CH₃COOH has a vital role in complexing with metal precursors and DMF to form nuclei and in assisting the oriented attachment of nanoparticles to form nanoscale heterointerfaces.





Figure 3. SEM images of the intermediate products of yolk-shell structured CuO-ZnO-In₂O₃ mesocrystal microspheres with different solvothermal times before calcination for (a) 3 h, (b) 4 h and (c) 6 h, and (d) the sample after 6 h of solvothermal treatment was further calcined at 400 °C for 3 h. Insets are the detailed inner structure of each sample. (e) Schematic illustration of the formation mechanism of yolk-shell structured CuO-ZnO-In₂O₃ mesocrystal microspheres.

Table 1 summarizes the catalytic properties of various catalysts to produce TCS using metallurgical Si powder reacted with gas HCl at 300 °C and 0.1 MPa for 6h in a fixed bed. The reaction equation is shown in Scheme S1. For comparative purposes, some reference samples were also prepared, including: (1) commercial CuO (denoted as C-CuO); (2) a physical mixture of yolk-shell structured

CuO mesocrystal microspheres, ZnO and In₂O₃ at the molar ratio of 100: 2: 1 (denoted as P-CuO- $ZnO-In_2O_3$; (3) a composite of CuO, ZnO and In_2O_3 nanocrystals with the molar ratio of 100: 2: 1 (denoted as NCs-CuO-ZnO-In₂O₃, SEM image shown in Figure S21); (4) solid CuO-ZnO-In₂O₃ microspheres (SEM image shown in Figure S22); (5) yolk-shelled-structured CuO-ZnO-In₂O₃ mesocrystal microspheres with different CuO: ZnO: In₂O₃ ratios (SEM image shown in Figure S23-S26); and (6) yolk-shelled-structured CuO-ZnO-In₂O₃ mesocrystal microspheres with lower amount of CH₃COOH (0.3 g and 0.5 g, respectively, SEM image shown in Figure S7). As shown in Table 1, in the absence of catalyst, the m-Si conversion and TCS selectivity is only 5.4% and 84.5%, respectively (entry 1). Both the samples of ZnO (entry 2, SEM image in Figure S28) and In₂O₃ (entry 3, SEM image in Figure S29) appear to be inert. C-CuO gives m-Si conversion of 10.8% and TCS selectivity of 88.8% (entry 4), suggesting that CuO is essentially active for this reaction. When using yolk-shell-structured CuO mesocrystal microspheres as a catalyst, both values are respectively improved to 20.5% and 90.5% (entry 5), confirming the advantage of this assembled structure. Dramatically, yolk-shell-structured CuO-ZnO mesocrystal microspheres exhibit improved catalytic properties: m-Si conversion is greatly increased to 41.2% with TCS selectivity of 91.5% (entry 6). For the yolk-shell-structured CuO-ZnO-In₂O₃ mesocrystal microspheres with the optimal CuO: ZnO: In₂O₃ molar ratio of 100: 2: 1, the m-Si conversion and TCS selectivity are further enhanced, reaching 66.1% and 92.8% (entry 7 and Table S5), respectively, which are much higher than those of P-CuO-ZnO-In₂O₃ (entry 8), NCs-CuO-ZnO-In₂O₃ (entry 9) and solid CuO-ZnO-In₂O₃ mesocrystal microspheres (entry 10). It is also observed that all the yolk-shell-structured CuO-ZnO-In₂O₃ mesocrystal microspheres show similar catalytic performances, further demonstrating the importance of the assembled and the unique yolk-shell structure. More importantly, compared with that of the current non-catalytic process, TCS yield on the CuO-ZnO-In₂O₃ mesocrystal microspheres achieves more than a 13-fold increment. Furthermore, it exhibits superior long-term stability (Figure S30). These results suggest that the selectivity and yield of TCS are remarkably boosted via the catalytic

process using the yolk-shell structured CuO-ZnO- In_2O_3 mesocrystal microsphere as the catalyst. Such dramatic activity enhancement is closely related to the assembled and the unique yolk-shell structure, as well as the formed nanoscale interfaces in CuO-ZnO- In_2O_3 .

Entry	Catalyst	$C_{ m Si}$ (%) ^a	$S_{\mathrm{TCS}} (\%)^b$	$S_{ m STC}$ (%) ^c	Y_{TCS} (%) ^d
1	No catalyst	5.4	84.5	15.5	4.6
2	ZnO	5.8	84.9	15.1	4.9
3	In ₂ O ₃	5.6	84.7	15.3	4.7
4	C-CuO	10.8	88.8	11.2	9.6
5	CuO mesocrystal	20.5	90.5	9.5	18.6
6	CuO-ZnO mesocrystal	41.2	91.5	8.5	37.7
7	CuO-ZnO-In ₂ O ₃ mesocrystal	66.1	92.8	7.2	61.2
8	P-CuO-ZnO-In ₂ O ₃	32.2	89.9	10.1	28.9
9	NCs-CuO-ZnO-In ₂ O ₃	35.7	86.4	13.6	30.8
10	CuO-ZnO-In2O3 microsphere	45.1	88.8	11.2	40.0

Table 1. The catalytic properties of various catalysts.

Reaction conditions: temperature, 300 °C; time, 6 h; catalyst loading, 0.15 g; Si, 10 g; HCl gas flow rate, 25 mL min⁻¹. ^{*a*} conversion of Si; ^{*b*} selectivity of TCS; ^{*c*} selectivity of STC; ^{*d*} yield of TCS.

Previous studies have demonstrated that the Cu_xSi alloyed species formed during the reaction process are the active catalytic phase in Si-involved Rochow reaction.^[2-5, 18-21] In our work, the measured XRD patterns (Figure S31) of the spent contact mass (unreacted residue) after a 10h reaction show the formation of alloyed Cu_xSi species during the reaction. Among all the catalysts investigated, the peak intensity of Cu_xSi is the strongest in the case of the CuO-ZnO-In₂O₃ mesocrystal, indicating its best ability to generate Cu_xSi with Si than the other samples. More importantly, we found that both Si conversion and TCS selectivity increase continuously with increasing Cu_xSi content (Figure S32). Moreover, increasing the reaction time can also enhance the formation of Cu_xSi species and thus improve the TCS yield. These observations support that Cu_xSi

species generated under the reaction conditions are the real active phases, and the amounts of Cu_xSi significantly affect the TCS selectivity and yield.

The structural evolution of the Si surface observed by SEM images indicate the occurrence of Si etching during the catalytic process (Figure S34). While for the CuO-ZnO-In₂O₃ mesocrystal, it almost remains the intact structure after the reaction (Figure S35). Overall, the greatly enhanced catalytic performance of the CuO-ZnO-In₂O₃ mesocrystal microspheres can be attributed to the following factors: (1) the tuned electronic structure of Cu atoms in the CuO phase through controlling the introduced component. As confirmed by the XPS and Raman analysis, in the CuO-ZnO-In₂O₃ mesocrystal microspheres, efficient charge transfer can take place via multiple intimate interfaces, which makes electron density of the Cu atoms higher, thereby promoting the adsorption of gaseous HCl molecules; (2) the previous report^[2] has revealed that relative to O_{latt}, O_{ads} is more conducive to the adsorption of Cl-containing species. In our work, a higher ratio of O_{ads} in CuO-ZnO-In₂O₃ than that of the CuO and CuO-ZnO mesocrystal microspheres was observed, which should enhance the adsorption of HCl; and (3) the unique yolk-shell structure not only provides more contact surface for adsorption of gaseous HCl molecules but also affords sufficient cavities to enrich gaseous HCl molecules. All the factors can increase the *in situ* formation of Cu atom and accelerate the diffusion of the formed Cu atoms to the Si surface, leading to the generation of more Cu_xSi active species and thus high catalytic activity and selectivity. Moreover, the hierarchically oriented assembled structure endows the microspheres with high structural stability, improving catalytic stability, although a more detailed reaction mechanism needs further investigation. As we know, the solar Si is obtained from TCS that is industrially manufactured via the non-catalytic process. Our work demonstrates that the use of the catalytic process can lead to the tremendous increase of the TCS selectivity and yield as well as less by-product of STC, thereby significantly reduce the cost of solar Si.

In summary, we have successfully synthesized the CuO-ZnO-In₂O₃ trimetallic oxide mesocrystal microspheres with the yolk-shell structure and uniform size using a facile solvothermal method

followed by calcination. This type of the microspheres is formed mainly based on the ordered assembly driven by the employed CH₃COOH molecule and the intrinsic dipole field. This strategy can generate well-defined nanoscale hetero-interfaces between different metal oxides that can effectively facilitate the charge transfer. Furthermore, the change of electronic density (increase or decrease) on Cu atoms in the CuO phase can be achieved by controlling the introduced component. With these structural features, the CuO-ZnO-In₂O₃ mesocrystal microspheres exhibit excellent catalytic performance in the production of TCS through hydrochlorination of Si. Also, this strategy can apply to the synthesis of more complex mesocrystals as new catalysts.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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This communication reports the synthesis of yolk-shell-structured CuO-ZnO-In₂O₃ trimetallic oxide mesocrystal microspheres by a simple solvothermal reaction. The formation mechanism was well investigated by tracking different stages of crystallization. The synthesized CuO-ZnO-In₂O₃ mesocrystal with nanoscale hetero-interfaces and tuned Cu electronic density in the CuO phase exhibited excellent catalytic property for silicon hydrochlorination to produce trichlorosilane.

Keyword: trimetallic oxide mesocrystals, yolk-shell structure, interfacial charge transfer, superstructure, catalytic production of trichlorosilane

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Title: Yolk-Shell-Structured CuO-ZnO- In_2O_3 trimetallic oxide mesocrystal microspheres as an efficient catalyst for trichlorosilane production



TOC Figure