Mesoporous Au/TiO_2 Nanospheres for Green Solvent-Free Visible-Light-Driven Oxidative Coupling Reactions of Amines

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Abstract: Design of "green" oxidation catalysts to drive the direct oxidation of amines to imines have attracted great attention. Herein, we designed a catalyst of ordered mesoporous Au/M-TiO_2 nanoparticles using a template-based approach. The as-prepared Au/M-TiO_2 nanoarrays of anatase crystalline structure show high specific surface area (234 m^2/g), and exhibit particularly high visible light activity for photocatalytic selective aerobic oxidation of benzylamine to N-benzylidene benzylamine in a green approach by utilizing dioxygen as an oxidant in solvent-free conditions. The yield of N-benzylidene benzylamine in Au/M-TiO_2 is obviously higher than that of the Au/P25 and Au/Acros anatase photocatalysts.

Keywords: Au/TiO_2, solvent-free, plasmonic photocatalysis.

1. Introduction

Catalytic oxidation of amine to imine is of intense interest since imines are important versatile intermediates for fine chemicals and pharmaceuticals.[1, 2] Moreover, the development of green catalytic systems for effective conversion of amines into its corresponding imines in solvent free and mild conditions is highly desirable, but remains a significant challenge.[3, 4] To overcome this issue, we developed an ordered mesoporous Au/M-TiO_2 plasmonic photocatalyst with high surface area (234 m^2/g) using a template-based method. The Au/M-TiO_2 exhibits particularly high visible light activity for selective aerobic oxidation of amines to imines, using a green chemistry approach with dioxygen as the benign oxidant in solvent-free conditions. Furthermore, we can also achieve high yield and selectivity of imine in air atmosphere. This work opens the possibility to develop mesoporous TiO_2 for efficient and green organic synthesis.

2. Experimental

The mesoporous M-TiO_2 nanoparticles was template from the mesoporous silica nanoparticles (MSN) by using titanium chloride as titanium precursor. Subsequently, the as-prepared M-TiO_2 was added into $HAuCl_4$ aqueous solution, with an introduction of $NaBH_4$ solution as reductant. Then, the nanocomposites were rinsed with water and vacuum-dried. The as-prepared sample was labeled as Au/M-TiO_2.

3. Results and discussion

The high-magnification micrographs in Figure 1a1-2 demonstrate that the ordered mesoporous structure of Au/M-TiO_2, and the Au NPs are highly dispersed on M-TiO_2 supports, the corresponding SAED pattern in Fig.1a1 confirmed the anatase structure of M-TiO_2 in Au/M-TiO_2. Figure 1a3 reveals that both Au NPs and M-TiO_2 are crystallized as evidenced from the well-resolved Au (111) (d = 0.230 nm) and TiO_2 (013) (d = 0.243 nm) crystalline lattices.

In the drive towards achieving green catalysis, we conducted the solvent-free strategy for plasmonic photocatalysis of benzylamine to N-benzylidene benzylamine under visible light irradiation ($\lambda > 420$ nm). With 1 atm of O_2 as the oxidant, the photocatalyst Au/M-TiO_2 exhibited very high selectivity (99%) and an extermly high yield (1.73 mmol, 0.19 mol/mol•h cat) for the oxidation of benzylamine to N-benzylidene benzylamine. The yield ratio in Au/M-TiO_2 is 1.5, 1.6, and 3.7 times higher than that of Au/P25 (yield = 1.16 mmol, yield ratio = 0.13 mol/mol•h cat, selectivity = 98%), Au/Acroc anatase (yield = 1.05 mmol, yield ratio = 0.12 mol/mol•h cat, selectivity = 80%), and bare M-TiO_2 (yield = 0.47 mmol, yield ratio = 0.05 mol/mol•h cat, selectivity = 99%) under the same conditions, respectively. Meanwhile, the yield of N-benzylidene benzylamine can still reach 1.30 mmol with a yield ratio of 0.14 mol/mol•h cat, under air atmosphere. Furthermore, we identified the active radical species involved in the photocatalytic process by the ESR spin-trap technique with DMPO as the spin trapping compound (Figure 2a). The obviously characteristic peaks of DMPO-$\bullet O_2^-$ were observed for Au/M-TiO_2 under visible light irradiation, confirming the generation of $\bullet O_2^-$ radicals. Interestingly, the results demonstrate Au/M-TiO_2 can generate more $\bullet O_2^-$ radicals than Au/P25 and Au/Acros anatase under visible light irradiation. Consequently, the proposed reaction mechanisms are shown in Figure 2b, the plasmonic photocatalysis act as a main reaction pathway, while photosensitization processes coexist during reactions.

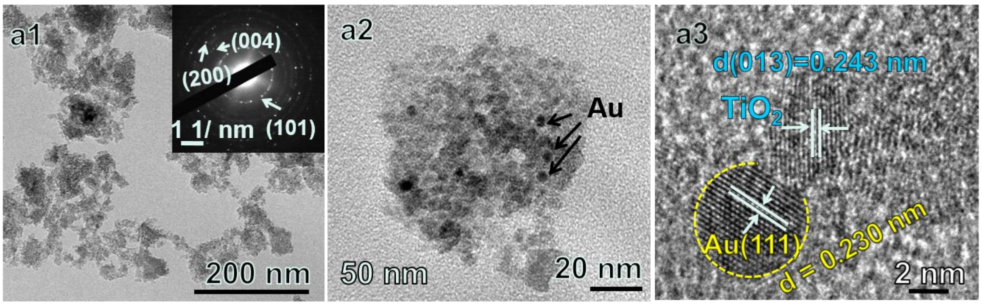

Figure 1. (a1, a2) TEM images, corresponding SAED pattern, and (a3) high-magnification TEM images of Au/M-TiO_2.

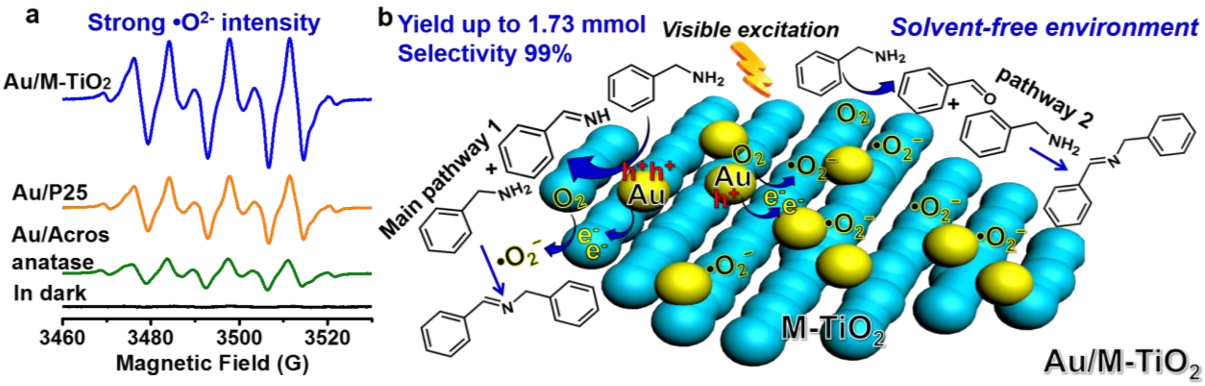

Figure 2. (a) DMPO spin-trapping ESR spectra of Au/M-TiO_2, Au/P25 and Au/Acros anatase in methanol dispersion under visible light irradiation at ambient temperature and Au/M-TiO_2 in the absense of light, respectively. (b) Scheme of the proposed mechanism for selective aerobic oxidation of benzylamine to N-benzylidene benzylamine over Au/M-TiO_2 under visible light irradiation.

4. Conclusions

In summary, the ordered mesoporous Au/M-TiO_2 nanoparticles with anatase crystalline and a large specific surface area (234 m^2/g) has been successfully designed and synthesized by a facile hard-templating method. The mesoporous Au/M-TiO_2 exhibited superior visible light photocatalytic performance in the selective oxidative coupling reactions of various amines in a green approach by utilizing dioxygen as an oxidant in a solvent-free environment at ambient temperature. The Au/M-TiO_2 can achieved higher yield than that of Au/P25 and Au/Acros anatase in the oxidation of benzylamine to N-benzylidene benzylamine. This report contributes to the use of visible light responsive TiO_2-based photocatalyst with high specific surface area to achieve green and high efficient organic synthesis.

References

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