# Efficient fabrication of active $CeO_2$/g-$C_3N_4$ photocatalyst for $H_2$ evolution under visible light irradiation

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**Abstract:** A facile solid state impregnation method was reported to prepare $CeO_2$/g-$C_3N_4$ catalyst for photocatalytic $H_2$ evolution under visible light irradiation. The catalyst was studied and compared with the counterpart from traditional wet impregnation. All catalysts were characterized by XRD, TEM, UV-vis DRS and TG-DTA. Results showed that in comparison with wet impregnation, the solid state impregnation displayed advantages of increased interfacial $CeO_2$/g-$C_3N_4$, and enhanced interaction between $CeO_2$ and g-$C_3N_4$, which upgraded the photoactivity resultantly. As well, the reason accounting for the different properties was tentatively discussed.

**Keywords:** solid state impregnation, $CeO_2$/g-$C_3N_4$, photocatalytic $H_2$ evolution.

## 1. Introduction

With the increased global energy demands and diminishing petroleum reserves, the development of sustainable and clean energy become one of the most significant emergent research fields.[1] Hydrogen ($H_2$) energy, considered as an ideal candidate, is received much attention for its environmental friendliness, recycling possibility and high-energy capacity. Graphitic carbon nitride (g-$C_3N_4$) has been regarded as a potential visible light photocatalyst for hydrogen production, due to its advantages of the narrow band gap, excellent stability and fast charge transfer.[2,3] However, the shortcomings are obvious, such as a lack of visible light absorption ($\lambda$>460 nm), a relatively high recombination of photoinduced charge carriers, a low specific surface area, etc., which could have a negative effect on the photocatalytic performance.[4,5] Therefore, much effort has been dedicated to the development of highly efficient g-$C_3N_4$-based photocatalysts. Cerium oxide ($CeO_2$) is also an excellent photocatalyst with the feature of narrow band gap, which is able to absorb visible light, which was used to improve the g-$C_3N_4$ photocatalytic performance. Recently, a typical method featuring of solid state impregnation with good unique dispersion of active species is widely investigated. Hence, in the present study, as an alternative to wet impregnation, we extend the solid state impregnation to fabricate $CeO_2$/g-$C_3N_4$ catalysts. The main focus of the present study is to: (1) investigate the effectiveness of solid state impregnation in preparing g-$C_3N_4$ supported ceria catalysts; (2) explore the differences in the composition and structure of the catalysts made by solid state impregnation and wet impregnation, and correlate them with the photocatalytic activity of $H_2$ evolution. The characterization results reveal that both $CeO_2$ nanoparticles are well dispersed and the interaction between $CeO_2$ and g-$C_3N_4$ can be enhanced via the solid state impregnation. As a result, the obtained catalysts display superior performance in $H_2$ photocatalytic evolution, in comparison with $CeO_2$/g-$C_3N_4$ from wet impregnation.

## 2. Experimental

The g-$C_3N_4$ support was obtained by the calcination of urea in air at 550 ℃ for 4 h.

The solid state impregnation to $CeO_2$/g-$C_3N_4$ catalysts was operated as follows. A certain amount of cerium acetate was added to an agitate mortar with g-$C_3N_4$ and manually ground for 0.5 h. Then the mixed powder was transferred into a crucible, which was placed in the muffle furnace. The thermal treatment in air started at room temperature with a ramp of 1 ◦C $\text{min}^{-1}$ to 400 ◦C and maintained at that temperature for 2 h, then cooled naturally. For simplicity, the obtained samples were denoted as CeAC-SI.

The supported $CeO_2$/g-$C_3N_4$ catalyst from wet impregnation was prepared by impregnating g-$C_3N_4$ with an aqueous solution containing requisite amount of cerium acetate. After stirred for 2 h, the sample was dried at 100 ◦C in oil bath, subsequently dried at 110 ◦C in an oven overnight, and then calcined in air at 400 ◦C for 2 h. The obtained catalyst was denoted as CeAC-WI.

## 3. Results and discussion

The phase structures of as-prepared $CeO_2$/g-$C_3N_4$ (CeAc-SI and CeAc-WI) composites and g-$C_3N_4$ were characterized by XRD. In Fig. 1, the $CeO_2$/g-$C_3N_4$ composites showed the typical diffraction peaks at ~13.1 ° and 27.3 ° of g-$C_3N_4$, perfectly indexed as the (100) and (002) planes, respectively, which were ascribed to in-plane structure packing unit and the interlayer stacking.[6] In addition, there are some weak diffraction peaks at ca. 33.1 ° and 47.4 ° in CeAc-SI and CeAc-WI samples, which were attributed to the (200), and (220) crystal planes of the $CeO_2$ (JCPDS no: 04-0802), respectively. It was observed that CeAc-SI had weaker peak intensity of $CeO_2$ than that of CeAc-WI, suggesting that the solid state impregnation is more beneficial for the small $CeO_2$ nanoparticles on g-$C_3N_4$. From the enlarged XRD figure, it is found that the peak position attributed to g-$C_3N_4$ in CeAc composites was slightly shifted, indicating that there was the enhanced interfacial interaction between $CeO_2$ and g-$C_3N_4$. The morphologies of as-synthesized CeAc-SI and CeAc-WI composites were investigated by TEM. It shown that the $CeO_2$ particle sizes of CeAc-SI and CeAc-WI were 2, 10 nm, respectively. UV-vis DRS results demonstrated that $CeO_2$ was helpful for more visible light adsorption, and the solid state impregnation increased the $Ce^{3+}$ and surface oxygen vacancies. The photocatalytic $H_2$ evolution under visible light was determined, the activity was in the order: CeAc-WI> CeAc-SI>g-$C_3N_4$. The superior photocatalytic performance of CeAc-WI was resulted from the smaller $CeO_2$ nanoparticle, enhanced visible light adsorption, more $Ce^{3+}$ and surface oxygen vacancies.

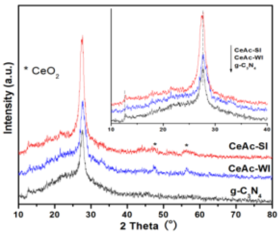

**Figure 1.** The XRD results of CeAc-SI, CeAc-WI and g-$C_3N_4$.

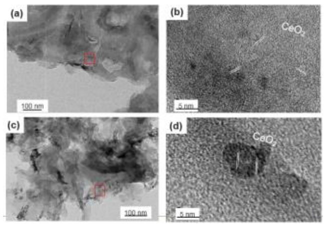

**Figure 2**. TEM results of (a) CeAc-SI (c) CeAc-WI; HRTEM results of (b) CeAc-SI (d) CeAc-WI.

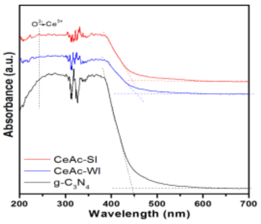

**Figure 3**.UV-vis DRS results.

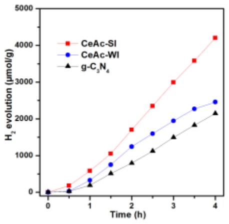

**Figure 4**. Photocatalytic $H_2$ evolution under visible light.

## 4. Conclusions

In comparison with wet impregnation, the solid state impregnation displayed advantages of increased interfacial $CeO_2$/g-$C_3N_4$. The enhanced interaction between $CeO_2$ and g-$C_3N_4$ decreased the $CeO_2$ nanoparticle size, increased visible light adsorption, more $Ce^{3+}$ and surface oxygen vacancies, and thus improved the photocatalytic $H_2$ evolution under visible light.

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