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COMMUNICATION

Pure Carbon Nanodot for Excellent Photocatalytic Hydrogen Generation

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Pure carbon nanodots(CNDs) without any modification and co-catalyst can drive photocatalytic hydrogen generation. The hydrogen generation rate of CNDs highly reaches 3615.3 $\mu\text{mol g}^{-1}\text{h}^{-1}$ when methanol was used as the sacrificial donor, which is 34.8 times higher than that of commercial Degussa P25 photocatalyst at same condition. Moreover, the CNDs show good stability, the hydrogen generation rate has negligible changes even after four cycles testing.

Over the past decades, light-driven H_2 production has attracted increasing attention because of its capability to harvest solar energy and converting it into chemical energy. To date, a number of photocatalysts, including Ti-based, Ta-based, Zr-based, Nb-based, Ge-based, Ga-based, S-based and Z-scheme photocatalysts, have been developed.¹ However, only a few photocatalysts show high photocatalytic activity and stability.^{1,2} Generally, co-catalysts such as noble metal Pt, are often needed to improve photocatalytic performance.³ However, the high cost and low storage of noble metal limit its practical application. Therefore, developing cheap but efficient photocatalyst is still urgent.

In recent years, Carbon nanodots (CNDs) have attracted much interest because of their non-toxic, stable, abundant, and inexpensive nature.^{4, 5} CNDs have exhibited potential application in sensing, optoelectronic, and energy conversion. Specifically, CNDs as photocatalyst have also been explored.⁶⁻⁸ Hu reported that CNDs have high photocatalytic activity and decomposes methylene blue

under visible light irradiation.^{9, 10} Sun and his coworkers have observed that surface-functionalized CNDs, with Au or Pt, can be employed as photocatalyst for CO_2 reduction and hydrogen production.^{11, 12} Very recently, Teng has found that nitrogen-doped graphene oxide quantum dots achieved overall water splitting in acid aqueous solution (pH = 3) under visible light irradiation.¹³

Although some progress has been achieved, the study of CNDs as photocatalyst is still in its infant stage. In addition, the modification of noble metals on CNDs and the acidic environment of water-splitting reaction limit its practical application and also influence the basic understand of CNDs intrinsic photocatalytic properties. To our knowledge, no research reports that pure CNDs without any modification can drive water-splitting reaction. Here, CNDs were prepared via the ultrasonic-hydrothermal process, and their intrinsic photocatalytic activity was studied. Results show that the pure CNDs show high hydrogen production in pure water under UV light irradiation, even without any modification and co-catalyst. The hydrogen evolution rate of CNDs is up to $423.7 \mu\text{mol g}^{-1}\text{h}^{-1}$ in pure water. The hydrogen evolution rate of CNDs was further improved to $3615.3 \mu\text{mol g}^{-1}\text{h}^{-1}$ when methanol was used as the sacrificial reagent, which is 34.8 times higher than that of commercial Degussa P25 photocatalyst at same condition. Moreover, the CNDs photocatalyst show good stability.

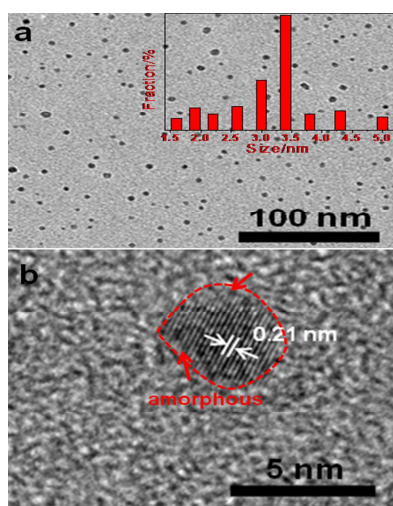


Fig 1 (a) TEM (Inset is the size distribution of the CNDs) and (b) HRTEM images of the CNDs

The transmission electron microscopy (TEM) images of the CNDs, as shown in Fig 1a, which shows that the CNDs are spherical particles with diameters distributed in the range of 1.5 nm to 5 nm. The average diameter was about 3.4 nm, which was obtained through a statistical analysis of 200 nanoparticles (shown in the inset of Fig 1a). High-resolution TEM (HRTEM) images (Fig 1b) show that their lattice spacing is 0.21 nm, which corresponds to the (0 to 110) facet of graphite.¹⁴ In addition, it is clearly seen that there exists partial amorphous structure on the edge of CNDs. HRTEM image indicates that the co-existence of sp^2 and sp^3 hybridized carbon in the CNDs.

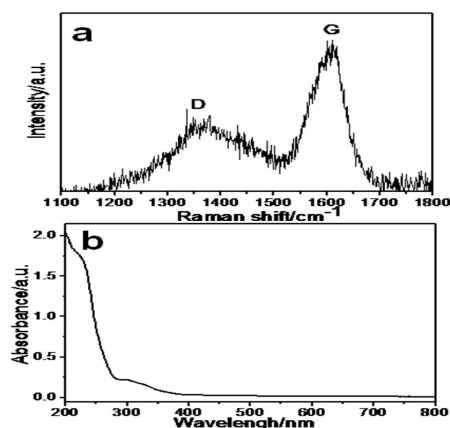


Fig 2 (a) Raman and (b) UV-vis adsorption spectrum of the CNDs

Raman spectrum of the CNDs (Fig 2a) shows that the D, G bands of the CNDs are all visible. The G and D bands are attributed to the in-plane vibrations of sp^2 carbon atoms and disordered amorphous carbon atoms, respectively.¹⁵ The relative intensity of the G to D band (I_D/I_G) in CNDs was used to characterize the level of disorder in graphitic carbons, and the calculated relative intensity for the prepared CNDs was 0.47, which is smaller than previous literature.¹⁶ These results confirmed the well-crystallized sp^2 core and the partial amorphous edge nature of CNDs, which was consistent with the HRTEM characterizations. A typical UV-visible absorption spectrum of CNDs is shown in Fig 2b. Its common feature is the spectral line that has two main absorption regions. The adsorption region from 200 nm to 270 nm is attributed to the $\pi-\pi^*$ transitions of aromatic sp^2 domains in CNDs, whereas the shoulder peak above 270 nm is due to the $n-\pi^*$ transitions of C=O in the sp^3 hybrid regions.¹⁸ The photoluminescence (PL) emission spectra of CNDs are shown in Fig S1. The main PL emission peaks were located at about 450 nm, and the intensity of PL emission depended on the excitation wavelengths, which was similar to previous reports.¹⁹⁻²¹ The PL quantum yield of CNDs (excitation at 320 nm) using Rhodamine B as a reference is 2.42%, comparable with those of the reported luminescent CNDs.^{22, 23}

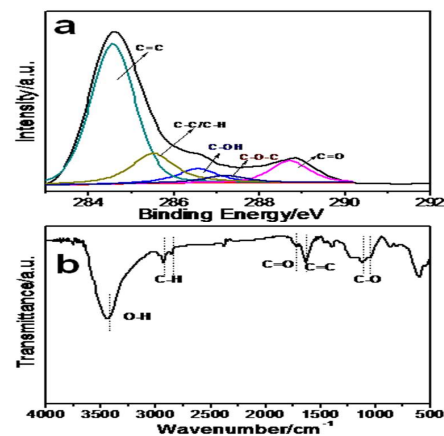


Fig 3 (a) C1s XPS and (b) FTIR spectrum of the CNDs

The structure and component of the CNDs were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Two dominant peaks at 284.8 and 532.2 eV

of the XPS survey spectrum depicted in Fig S2, were attributed to C1s, and O1s, suggesting the existence of carbon and oxygen elements.²⁴ The C1s XPS peak can be deconvoluted into five Gaussian components centered at 284.5, 285.5, 286.6, 287.2 and 288.6 eV (Fig 3a), which can be assigned to C=C, C-C/C-H, C-OH, C-O-C and C=O species, respectively.²⁵ The high-resolution O1s spectrum (Fig S3) reveals the presence of three peaks corresponding to C=O groups (531 eV), C-OH and/or C-O-C groups (532.2 eV) and carboxyl groups (533.8 eV).^{24,26} The FTIR spectra can be used to determine the functional groups present on the surfaces of CNDs. As shown in Fig 3b, the peak at 1638 cm^{-1} is attributed to C=C vibration, and the peak at 1720 cm^{-1} is attributed to C=O vibration. A broad absorption peak associated with OH vibration is observed within 3000 cm^{-1} to 3600 cm^{-1} , and the peaks within 1000 cm^{-1} to 300 cm^{-1} are attributed to the C-OH stretching and O-H bending vibrations.²⁷ The XPS and FTIR results indicate that the CNDs contain a lot of oxygen-containing groups, which help CNDs to be well dispersed in water.

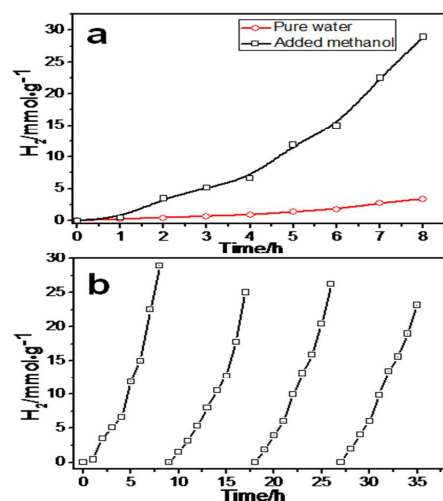


Fig 4(a) Photocatalytic hydrogen evolution of the CNDs in pure water and in methanol aqueous solution (20 vol%), (b) Stability of photocatalytic hydrogen evolution of the CNDs

Photocatalytic water-splitting reactions were performed in pure water without any other sacrificial agent (Fig 4a). It is clear to see that the amount of hydrogen (red line) increased with reaction duration time. Gas chromatography (GC) is a useful analytical tool to investigate H_2 production. Fig S4 gives the gas chromatography spectrum of gaseous product, which confirms H_2 evolution. The hydrogen production rate of the CNDs reached $423.7 \mu\text{mol g}^{-1}\text{h}^{-1}$ in pure water. To further improve the hydrogen evolution ability, methanol was employed as the holes sacrificial donor. The rate of hydrogen evolution (black line) significantly increased, reaching $3615.3 \mu\text{mol g}^{-1}\text{h}^{-1}$. Photocatalytic water-splitting reactions were also studied without CNDs or light irradiation at same condition. Data show that no hydrogen was detected, which indicates that hydrogen comes from photocatalytic process. The stability of the CNDs was also tested (Fig 4b). The hydrogen evolution rate had negligible changes even after four cycles of testing, confirming good photostability. The photocatalytic water-splitting reaction was also carried out under visible light irradiation, but hydrogen was not detected, which is different from previous reports.^{11, 13} From the UV-vis adsorption spectrum of CNDs, the intensity in visible light region is weak, which is likely responsible for the obtained results. For the carbon nanomaterials, it is also widely approved that the size of carbon-based materials can determine their energy gap.²⁸ Some theoretical calculations and experiments have proven that the energy gap of small sp^2 cluster came from the quantum-sized graphite fragment.²⁸⁻³¹ As the size of the cluster decreases, the gap increases gradually.³⁰ In the present work, HRTEM image shows that CNDs contain small sp^2 clusters. Therefore, it would be rational to speculate that the photocatalytic activity of CNDs comes from quantum size effect. Linear potential scans were conducted to determine and analyze the conduction band (CB) of CNDs.³² Fig S5 shows that the CB of CNDs is -0.906 eV (versus NHE), which

satisfies the thermodynamic potentials for hydrogen evolution, consistent with experimental results. We plotted the square and square root of the absorption energy against the photon energy to determine the energies of the direct and indirect gaps, respectively.³³ It is clearly that the energy gap (E_g) value of CNDs is 4.88 eV for direct transition, whereas the E_g value of CNDs is 2.97 eV for indirect transition (Fig S6 and S7). However, indirect bandgap transition is inconsistent with experimental results, which suggest the CNDs is direct bandgap transition. Therefore the valance band (VB) value is 3.974 eV ($4.88 - 0.906 = 3.974$ eV). In addition, we also investigated the photocurrent generation of CNDs (Fig S8) at different bias voltages. The CNDs are indeed able to generate significant photocurrents under UV irradiation, consistent with photocatalytic results. At same time, the photocatalytic performance of commercial Degussa P25 without noble metal modification was also studied at same condition (Fig S9). Results show that the hydrogen generation rate of commercial Degussa P25 without co-catalyst is $16.25 \mu\text{molg}^{-1}\text{h}^{-1}$ in pure water. When methanol was added as the holes sacrificial donor, the hydrogen generation rate only reached $103.7 \mu\text{molg}^{-1}\text{h}^{-1}$. It is clearly that the hydrogen generation rate of CNDs surpasses that of P25 by more 34.8 times in methanol aqueous solution. We also prepared CNDs/P25 composite photocatalyst by simple physical adsorption. Result shows that the hydrogen evolution rate of CNDs/P25 is up to $242.72 \mu\text{molg}^{-1}\text{h}^{-1}$ in methanol aqueous solution (Fig S9). Compared with CNDs, the activity of CNDs/P25 is relatively low, which may be attributed to low adsorption amount. When Pt cocatalyst was loaded on CNDs, the photocatalytic activity was further improved. The hydrogen evolution rate of Pt/CNDs reaches $14.2 \text{mmolg}^{-1}\text{h}^{-1}$, whereas the hydrogen evolution rate of Pt/P25 is $7.46 \text{mmolg}^{-1}\text{h}^{-1}$ in methanol aqueous solution (Fig S10). Fig S11 shows the UV-visible adsorption spectrum of P25. The adsorption edge is about 400 nm,

consistent with other reports.³⁴ Previous studies confirmed the CB and VB positions of P25 are about -0.19 eV and 2.81 eV, respectively.³⁴ It is clearly that the CB position of CNDs is more negative than that of P25, suggesting high reduction ability of CNDs.³⁵ The VB position of CNDs is relatively positive, which indicates strong oxidation potential. Therefore, the excellent photocatalytic activity of CNDs may be due to big band gap, strong reduction and oxidation potential.³⁵ It is widely accepted that the lower the PL intensity of photocatalysts, indicates that the lower the recombination rate of photo-induced electron-hole pairs, and the higher the photocatalytic activity.³⁶ In our study, the PL quantum yield of CNDs is very low (2.42%), which suggest photo-generated electrons in CNDs mostly participated in the channel of photocatalysis. Therefore, the CNDs show high photocatalytic activity.

Conclusions

In summary, the photocatalytic activity of pure CNDs was studied. The results show that pure CNDs alone achieve water splitting and have good stability. The hydrogen generation rate of pure CNDs highly reaches $3615.3 \mu\text{molg}^{-1}\text{h}^{-1}$. Despite its preliminary character, this study can clearly indicate that pure CNDs without co-catalyst and any modification can be an excellent photocatalyst to drive hydrogen generation. This finding provides that sustainable pure carbon materials can be as versatile materials used in the modern field of renewable energy.

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Notes and references

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