



Communication

A nano-engineered graphene/carbon nitride hybrid for photocatalytic hydrogen evolution

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ABSTRACT

A metal-free photocatalytic hydrogen evolution system was successfully fabricated using heteroatom doped graphene materials as electron-transfer co-catalysts and carbon nitride as a semiconductor. The catalytic role of graphene is significantly dependent on the heteroatom dopant of the graphene, such as O, S, B, N doped/undoped graphene co-catalysts, and N-graphene shows the best catalytic hydrogen evolution rate.

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Hydrogen, obtained from photocatalytic water-splitting, could be an abundant and sustainable energy vector, as water is both fuel precursor and combustion product. An attractive route towards the development of the necessary photocatalytic system is the combination of a semiconductor with both light-harvesting and electron/hole generation functions, and co-catalysts which provide the reaction sites for the water splitting reactions [1]. The likely scale of future applications suggests that avoiding the use of expensive elements in the preparation of such systems is undoubtedly highly desirable. However, most of the photocatalytic systems reported involve the use of rare-earth and/or transition metal elements. We have shown previously that a graphene (GR)/carbon nitride (CN) nanocomposite is an effective electrochemical hydrogen evolution catalyst [2]. Here, we demonstrate that this nanostructured combination of a metal-free carbon nitride as a photocatalyst and doped graphene as co-catalyst [3] is also effective as a system for the photocatalytic evolution of hydrogen. The carbon nitride described in this paper is composed predominantly of parallel chains of tris-s-triazine (cyamelurine) units [4]. This material does not have the stoichiometric ratio C_3N_4 as it contains a small amount of hydrogen (~2 wt%), which is consistent with the composition sometimes referred to as Liebig's melon [5]. However,

consistent with literature practice, we refer to this material as carbon nitride. In our system the reactivity of the graphene co-catalyst can be further altered by hetero-atom doping, with N-graphene showing the best catalytic hydrogen evolution rate among the O, S, B and N doped/undoped GR co-catalysts. These results yield a proof-of-principle for the underlying concept and shed light on the development of metal-free photocatalytic water splitting systems.

Nanosheet-structured carbon nitride was selected to build a layer-to-layer contact with the graphene materials. This approach should maximize the contact areas and any electronic coupling between graphene and carbon nitride materials, promoting electron transfer between them [2,6]. High temperature treatment of bulk carbon nitride in air results in the formation of a nanosheet morphology consisting of nanorod structures [7] as shown in Fig. 1(a). The hydrophobic GR materials were easily dispersed into the dried ionic liquid, 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][OTF]), via ultrasonication. (N/B/O/S)-GR/CN hybrids were prepared in [Bmim][OTF] at 300 °C under N_2 for 2 h (ESI). The composite CN/GR materials are 20:1 (w/w) CN:GR (ESI).

The presence of layer-to-layer contact between the graphene and CN materials is consistent with the transmission electron microscopy (TEM) images (Fig. 1), where the stacking between a graphene layer and a CN layer was clearly observed. In all cases, the Fourier Transform Infra-Red (FTIR) spectra of the graphene/CN samples (Fig. S1) exhibit the full range of characteristic FTIR absorptions associated with the CN framework, indicating that the

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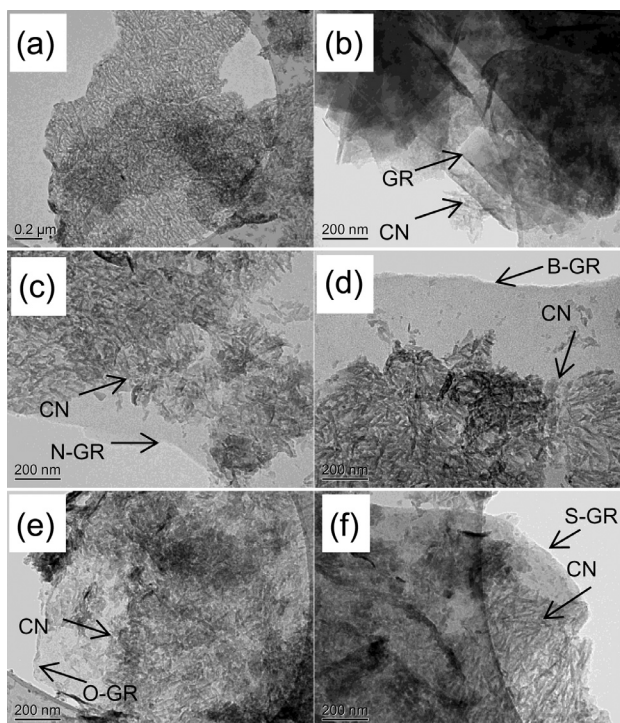


Fig. 1. TEM images of hybrid photocatalysts (a) CN, (b) GR/CN, (c) N-GR/CN, (d) B-GR/CN, (e) O-GR/CN and (f) S-GR/CN.

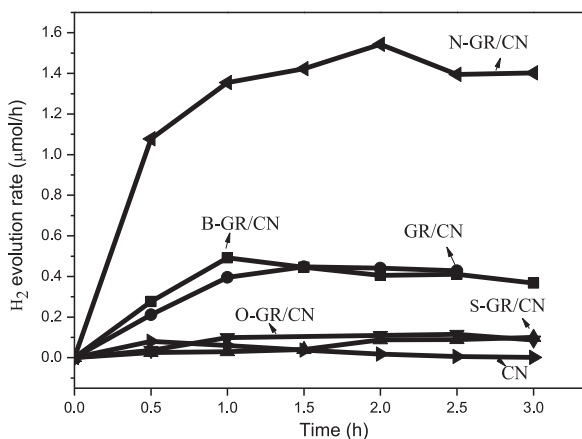


Fig. 2. Time courses of photocatalytic H₂ evolution rates in the presence of 1 mg composite catalysts, 10 vol% triethanolamine (TEOA) in H₂O (20 mL) and irradiation at $\lambda > 395$ nm.

preparation process did not change the framework of the CN [8]. The vibrational absorptions of graphene materials are not observed, which is consistent with them obscured by the CN spectrum, due to their low relative intensity. Electronic (UV–vis) spectra (Fig. S2) of graphene/CN hybrid samples show band-to-band transitions similar to those of CN, indicating that the graphene materials have no effect on the band structure of CN. Additional UV–vis absorptions at longer wavelengths are observed from the hybrid samples due to the absorption by the graphene materials. Fig. 2 shows the time-dependent plot of the H₂ evolution rate upon photo-irradiation ($\lambda > 395$ nm) of 1 mg of the composite catalysts without other co-catalysts. In the absence of either the light, the sacrificial agents or CN, no hydrogen evolution activity was observed. The unmodified CN catalyst shows an average H₂ evolution rate of 0.03 $\mu\text{mol H}_2/\text{h}$ over 3 h.

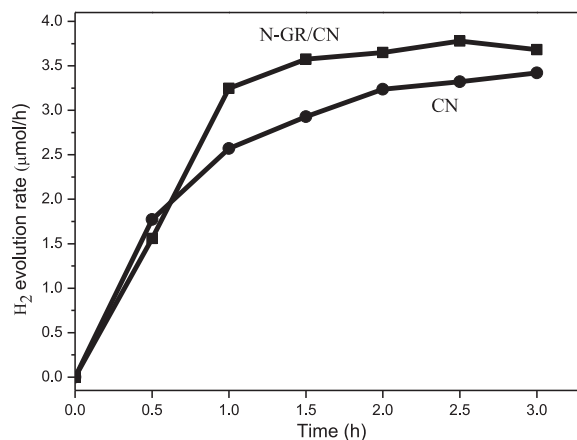


Fig. 3. Time courses of photocatalytic H₂ evolution rates in the presence of 1 mg g-CN, 3 wt% photodeposited Pt, 10 vol% TEOA in H₂O (20 mL) and irradiation at $\lambda > 395$ nm.

An obviously decreasing trend in the H₂ evolution rate for the unmodified CN sample is observed from 0.08 $\mu\text{mol/h}$ at 0.5 h to 0.001 $\mu\text{mol/h}$ at 3 h, indicating that the CN itself is not stable under the photoirradiation conditions. The O-GR/CN and S-GR/CN catalysts show a comparable initial H₂ evolution rate to that of the unmodified CN catalyst suggesting that the O-GR and S-GR materials are not effective electron-transfer catalysts for the CN photocatalyst. However, they do appear to stabilize the CN in the composite. Thus, in contrast to the gradual decrease of the H₂ evolution rate over 3 h, stable and enhanced average H₂ evolution rates are observed on GR/CN (0.38 $\mu\text{mol/h}$) and B-GR/CN (0.40 $\mu\text{mol/h}$), whereas much lower H₂ evolution rates are observed for the O-GR/CN and S-GR/CN catalysts, with average rates of 0.09 $\mu\text{mol/h}$ and 0.06 $\mu\text{mol/h}$, respectively. The N-GR/CN material shows the highest activity among the samples tested with an average H₂ evolution rate of 1.38 $\mu\text{mol/h}$. This significantly improved activity, some 46 times higher than that of the unmodified CN catalyst, indicates the obvious catalytic role of N-graphene. To test whether the N-GR had any detectable effect on the intrinsic properties of the CN in the N-GR/CN composite, the hydrogen evolution abilities of CN and the composite were tested with Pt metal as a common co-catalyst. The photocatalytic H₂ evolution performance of Pt-doped CN and Pt-doped N-GR/CN is shown in Fig. 3.

The Pt-doped N-GR/CN composite shows an average H₂ evolution rate of 3.24 $\mu\text{mol/h}$, which is only moderately higher than that of the Pt-doped CN catalyst, which has an average H₂ evolution rate of 2.87 $\mu\text{mol/h}$. This indicates that the semiconductor carbon nitride, in both the nanostructured CN and N-GR/CN samples, is similarly effective when coupled to the highly efficient co-catalyst Pt, although the additional presence of N-GR does have an overall beneficial effect. Therefore, the significant difference of the H₂ evolution rate between the CN and N-GR/CN catalysts in the absence of Pt is then mainly due to the catalytic role of N-GR. Notably, the H₂ evolution activity is dependent on the doped heteroatom of the graphene. Among the samples tested, the average H₂ evolution rates follow the order CN < S-GR/CN < O-GR/CN < GR/CN \approx B-GR/CN < N-GR/CN, where the N-GR/CN shows the highest activity. The excellent photocatalytic H₂ evolution rate of N-GR/CN compared to other hybrid catalysts would be consistent with either one or both of the following. Firstly, the presence of the intrinsic chemical and electronic coupling effect between N-graphene and carbon nitride as revealed by Qiao on the electrocatalytic H₂ evolution reaction may also be present and play a significant role in this photocatalytic system. This electronic coupling facilitates the electron transfer between the carbon nitride and

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