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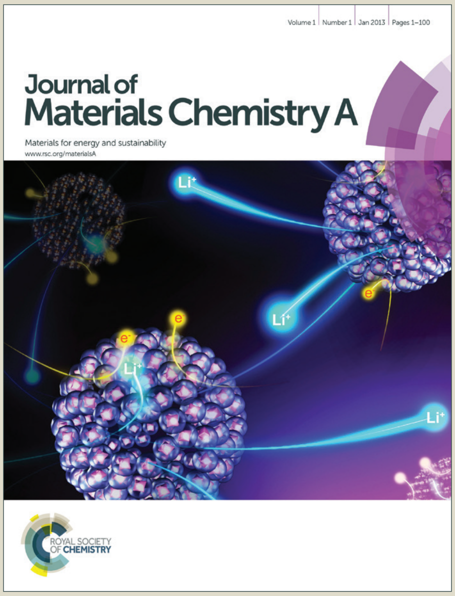

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Light-induced synthesis of photoluminescent carbon nanoparticles for Fe^{3+} sensing and photocatalytic hydrogen evolution

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We report a new method to prepare photoluminescent carbon nanoparticles (CNPs) by light-induced process. The obtained CNPs are sensitive for specific detection of Fe^{3+} with a detection limit of 0.55 ppm. CNPs also show excellent photocatalytic hydrogen production under xenon lamp irradiation. The hydrogen evolution rate is up to 4.89 μmol h^{-1} over 2.1 mg CNPs.

Carbon nanomaterials have attracted much attention owing to their unique properties and potential applications, including catalysis, adsorption, separation, and electrode materials, among others.[1, 2] Recently, carbon nanomaterials with photoluminescent properties have been found and attracted much interest.[3-5] Compared to traditional semiconductor quantum dots and organic dyes, photoluminescent carbon nanomaterials (PCNs) are superior in high aqueous solubility, robust chemical inertness, easy functionalization, good photo-stability, low toxicity and excellent biocompatibility.[6] PCNs have exhibited potential applications in biological labeling, bioimaging, disease detection, drug delivery, sensor and energy-related applications.[6-9]

To date, numerous approaches have been developed to prepare these versatile materials, including electrochemical synthesis, combustion, hydrothermal, acidic oxidation, microwave, ultrasonic, solution chemistry, arc discharge, laser ablation, plasma treatment and so on.[6, 10] However, almost all of these techniques usually require high temperature and relative complicated process.

Here we report a new and simple method for the synthesis of photoluminescent CNPs with glucose as raw materials by light-induced processes under room temperature and ambient pressure. Data show that the obtained CNPs are sensitive for specific detection of Fe^{3+}. A detection limit as low as 0.55 ppm for Fe^{3+} was obtained, which is promising for biological applications. It is worth to note that CNPs also show excellent photocatalytic hydrogen evolution. The hydrogen evolution rate of CNPs alone reaches at 2.11 μmol h^{-1}. The hydrogen evolution rate was further improved to 4.89 μmol h^{-1} when noble metal Pt was used as co-catalyst.

Transmission electron microscopy (TEM) image (Fig 1a) shows that the obtained CNPs are well-dispersed onion-like nanospheres with nearly homogeneous sizes. The average diameter of the CNPs is about 40 nm. Dynamic light scattering (DLS) was also used to measure the size distribution of CNPs, which however exhibited the larger sizes of aggregated CNPs (Fig S1) owing to the inherent principles of this method.[11, 12] High-resolution TEM (HRTEM) image (Fig 1b) shows that the short-range ordered structure of onion-like nanocarbons with concentric graphitic layers, whose interlayer spacing are around 0.38 nm. The value is slightly larger than ideal graphite (0.334 nm), consistent with X-ray diffraction(XRD) result (Fig S2).[13, 14]

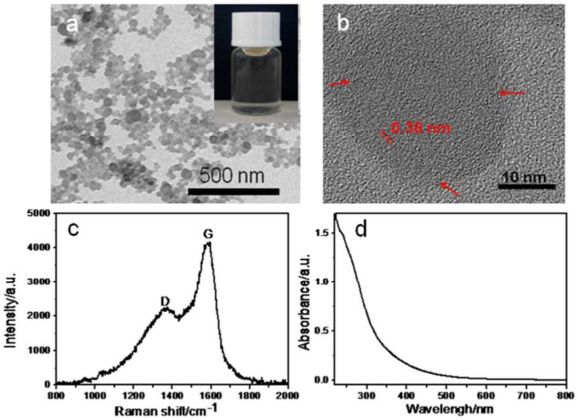

Fig 1. (a) TEM(Inset is an optical image of the CNPs) and (b) HRTEM image, (c) Raman spectrum and (d) UV-visible adsorption spectrum of the CNPs

Raman spectrum provided compelling evidence for the different types of ordered and disordered bonding environments of the sp^2 and sp^3 hybridized carbon.[15] Fig 1c shows that the peak at 1588 cm^{-1} is the G band corresponding to the E2g mode of the graphite and is related to the vibration of sp^2-bonded carbon atoms, whereas the D band located at 1378 cm^{-1} is disordered because of the scattering at the sp^3-bonded carbon edges.[15] The co-existence of the two structures is confirmed, which is consistent with the HRTEM characterizations. Fig 1d depicts the typical UV-visible absorption spectrum of CNPs. A typical absorption peak at 230 nm was observed, which is assigned to the π–π* transition of aromatic sp^2 domains. In addition, a shoulder at around 320 nm is ascribed to the n–π* transition of C=O bond, agreed with previous reports.[16]

X-ray photoelectron spectroscopy (XPS) measurement shows the existence of two elements, C and O (Fig 2a). Fig 2b shows the deconvolution of the C1s spectrum of CNPs, five types of carbon bonds: 284.5, 285.5, 287.2 and 288.6 eV, which correspond to the C=C, C-C and C-H, C-O-C, and C=O species, respectively.[17] Fourier transform infrared spectroscopy (FTIR) spectrum was recorded to gain further structural insights about CNPs. As depicted in Fig 2c, which confirmed the presence of various functional groups including OH (3430 cm^{-1}), C=O (1760 cm^{-1}) C=C (1620 cm^{-1}), C-OH (1190 cm^{-1}), C-O-C (1098 cm^{-1}), C-H (1411 cm^{-1}), which agree well with XPS results.[18-20] Elemental analysis of CNPs shows that carbon, hydrogen and oxygen composition was 61.32 wt%, 5.595 wt % and 33.085 wt% respectively. Fig 2d shows the photoluminescence (PL) spectral of CNPs. A unique phenomenon of excitation dependent photoluminescence was observed, similar to previous reports. [21-25] Zeta potential of CNPs in aqueous solution is -9.21 mV, owing to the carboxylic groups on the surface, which indicates that CNPs are highly dispersed and stable in aqueous systems (Fig S3).[26]

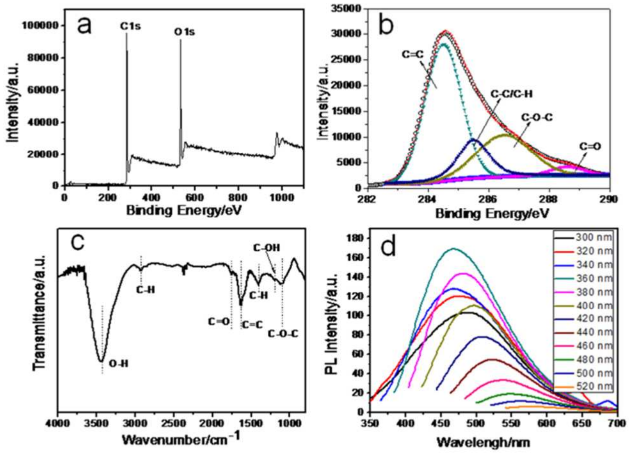

Fig 2.(a) Full range XPS spectrum,(b) XPS high resolution scan of the C1s, (c) FTIR and (d) PL spectrum of the CNPs

Taking into account the special coordinate interaction between Fe^{3+} ions and phenolic hydroxyl, we speculate that CNPs may be employed to optically detect Fe^{3+} ions.[27] Fig 3a shows the PL change of CNPs with and without addition of Fe^{3+} ions. The PL intensity almost was quenched when 137.5 ppm Fe^{3+} ions was added. Fig S4 shows dependence of $(I_0\text{-}I) / I_0$ on the concentrations of Fe^{3+} ions, where I_0 and I are CNPs fluorescence intensities at 468 nm in the absence and presence of Fe^{3+} ions, respectively. It can be seen that the detection limit for Fe^{3+} ions reaches 0.55 ppm. Selectivity is a very important parameter to evaluate the performance of the sensing system. Therefore, We investigated the effect of representative metal ions (Mg^{2+}, Ag^{+}, Cd^{2+},Cr^{3+}, Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{+} and Cu^{2+}) on the CNPs fluorescence quenching under 10 ppm concentration. As shown in Fig 3b, most of those metal ions did not induce obvious fluorescence quenching, whereas the PL intensity of CNPs resulted in the strongest quenching effect in the presence of Fe^{3+}. The selectivity diversity of different metals may be attributed to the difference of interaction between CNPs and metal irons.[28, 29]

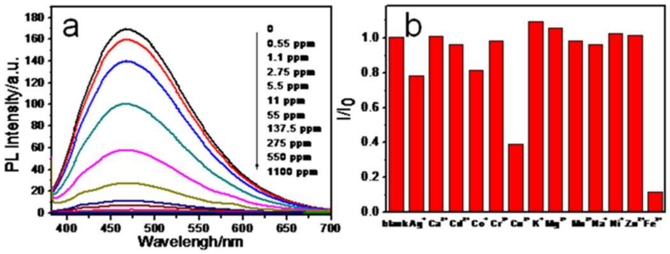

Fig 3.(a) Fluorescence quenching of the CNPs in the presence of Fe^{3+} ions, (b) Fluorescence quenching of the CNPs after addition of different metal ions

Recently, some reports have confirmed that photoluminescent CNPs show excellent photocatalytic activity for hydrogen evolution.[30, 31] Fig 4a shows the photocatalytic hydrogen evolution on the CNPs and Pt/CNPs. The hydrogen evolution rate reached at 2.11 μmol h^{-1} over single CNPs under 300 W Xenon lamp, without any modification and co-catalyst. When noble metal Pt was employed as co-catalyst, the hydrogen evolution rate was further increased. The highest hydrogen evolution rate of 4.89 μmol h^{-1} was achieved when 7 wt% Pt was employed as co-catalyst. To further increase the amount of noble metal Pt, the photocatalytic activity becomes low, which suggest the existence of an optimal value of co-catalyst (Fig S5). Stability is another key parameter to evaluate photocatalytic performance of photocatalysts. In our case, 7 wt% Pt/CNPs was employed to study its stability. As shown in Fig 4b, the photocatalytic hydrogen evolution rates of the 7 wt% Pt/CNPs had negligible change even after four cycles of testing, showing the good photo-stability of CNPs.

To uncover the formation mechanism of CNPs, we performed a blank experiment without light irradiation. TEM results show that no CNPs were obtained. Previous reports have proven that carbohydrates can be decomposed into other compounds by radical process after UV irradiation and carbon radicals were detected using EPR spectral.[32, 33] Phillips reported that photodecomposition of glucose directly due to adsorption of the light itself.[34] Fig S6 shows the UV-visible adsorption spectrum of glucose aqueous solution. It can be seen that glucose molecules have obvious adsorption in ultraviolet region. Based on preliminary data, the possible formation mechanism of CNPs might be that glucose molecules are decomposed into carbon-related radical after UV irradiation. Then, these carbon-related radical building blocks formed CNPs by C-C coupling polymerization (as shown in Fig 4c).

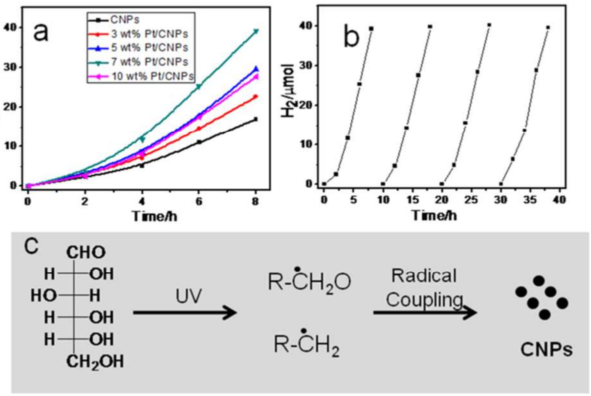

Fig 4.(a) Photocatalytic hydrogen evolution over the CNPs and Pt/CNPs in methanol aqueous solution, (b) Stability of photocatalytic hydrogen evolution over the 7wt% Pt/CNPs,(c) Possible formation mechanism of the CNPs by light-induced process.

Conclusions

In summary, we develop a new and simple method to prepare CNPs by light-induced process. Results show that the obtained CNPs are sensitive for detection of Fe^{3+} ions with 0.55 ppm detection limit. It was found that the obtained CNPs can be used as an excellent photocatalyst. The photocatalytic hydrogen evolution rate of CNPs highly reaches at 4.89 μmol h^{-1} under Xenon lamp irradiation. This finding will provide a new possibility to prepare CNPs by photo-polymerization of photo-active organic molecular under light irradiation.

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Notes and references

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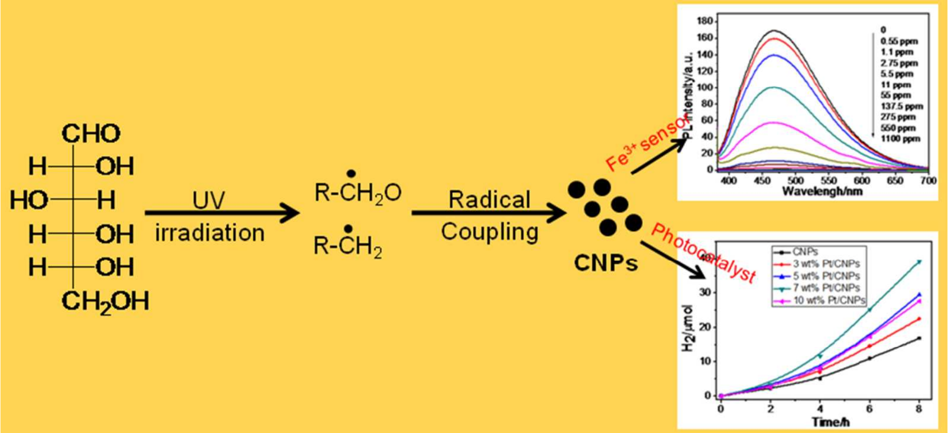

A new method to produce multifunctional CNPs was developed by light-induced process.