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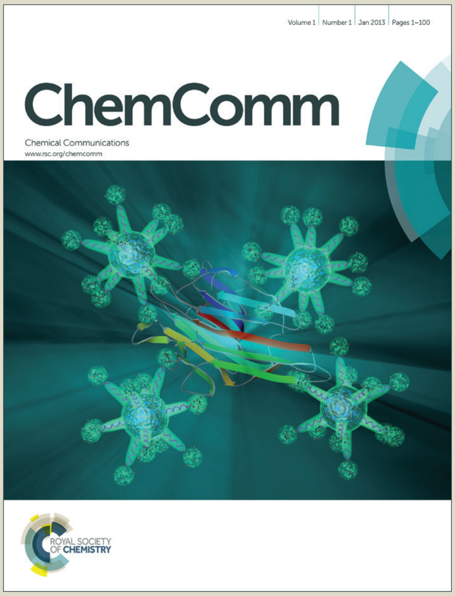

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Hydroxyl-rich C-dots Synthesized with One-pot Method and Its Application in the Preparation of Nobel Metal Nanoparticles

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Hydroxyl-rich C-dots were used as both the reducing and stabilizing agent in the preparation of noble metal nanoparticles (AuNPs, AgNPs and Au@AgNPs) for the detection of glucose.

Carbon quantum dots (C-dots) is a new kind of fluorescent carbon nanomaterial consisting of a graphite structure or amorphous carbon core and carbonaceous surfaces with rich oxygen-containing groups. They have attracted considerable attention in recent years.[1] Due to the quantum confinement effect and surface energy traps, C-dots possess excellent fluorescence properties. Compared with semiconductor quantum dots (QDs) usually were composed of heavy metals, C-dots have the advantages of chemical inertness, low toxicity, resistance to photobleaching and good biocompatibility for bioimaging and biomedical applications. For example, Sun's group reported the potential of C-dots for in vitro and in vivo bioimaging.[2, 3] C-dots were also used as fluorescent signal source for the designing of fluorescence sensors for DNA,[4] glucose[5] and metal ions.[6] In particular, the C-dots shows enhanced visible light photocatalytic activity of its complexes due to the red shift of the absorption edge, enhanced absorptivity in the visible range and help for the transfer of photogenerated electrons reduce the recombination rate of electron-hole of C-dots.[7, 8] For example, based on the above properties， Liu et al prepared a C-dots/TiO_2 nanosheets nanocomposites with superior photocatalytic activity than pure TiO_2 nanosheets under visible light irradiation.[8] Therefore, C-dots have inspired extensive study on them due to their promising applications for bioimaging, sensors, optoelectronic devices and catalysis.

In addition to excellent opticals and fluorescence properties, C-dots can also act as the excellent electron acceptor and electron donor which have promising potential to be an oxidizing or reducing agent.[9] For example, Zheng *et al* synthesized C-dots with acidic oxidation methods and then they reduced the carbonyl and epoxy groups on the surface of C-dots into hydroxyl groups with $NaBH_4$. The hydroxyl-rich C-dots were used to reduce $HAuCl_4$ at 60 ^oC for 12 h to synthesize AuNPs.[10] Sun et al prepared C-dots by laser ablation methods, the C-dots have the ability of harvesting photons after surface-functionalized with PEG and were used to reduce $HAuCl_4$ to AuNPs under photoirradiation condition.[11] These above reports imply that the functional groups play an important role in the reduction performance of C-dots. However, additional energy (photoirradiation or heating) and/or pre- functionalizing are needed for the application of C-dots as reduction agent in these reported methods.

Herein, we successfully synthesized hydroxyl-rich C-dots with the method of one-pot electrochemically carbonization of ethylene glycol. The synthesized C-dots do not need further processing or surface functionalization and have excellent reducibility. It can act as the reductant for directly synthesis of AuNPs by simply mixing C-dots with metal salt at room temperature within 30 s. This method is simple, fast and without any additional reductant, stabilizing agent and any external energy. Meanwhile, the synthesized AuNPs are stable for more than four months in aqueous solutions and show excellent peroxidase-like activity and can catalyze H_2O_2 to oxidize 3,3,5,5-tetramethylbenzidine (TMB) for colorimetric detection of H_2O_2 and glucose. Moreover, as-synthesized C-dots also show general reducibility to synthesize noble metal nanoparticles, such as silver nanoparticles (AgNPs) and Au-core/Ag-shell composite nanoparticles (Au@AgNPs).

C-dots with abundant surface functional groups were electrochemically synthesized using ethylene glycol as precursor based on our previous work with a few modifications[12] (see detailed synthesis in the Electronic Supplementary Information, ESI). The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (Fig. 1A) images show that the C-dots were of low multiple dispersity with the diameters ranging from 2 to 4 nm. HRTEM image of one nanoparticle shows a crystalline structure with lattice spacing of 0.20 nm which may be attributable to the (102) diffraction planes of graphitic (sp2) carbon (JCPDS 26-1076). The surface functional groups of the C-dots were characterized by Fourier transform infrared spectrum (FT-IR). The result was shown in Fig. S1. The obvious peaks at 3406 cm^{-1}, 1075 cm^{-1} and 1257 cm^{-1} should be assigned to the hydroxyl groups of C-dots.[13, 14] The rich hydroxyl groups may originate from the hydroxyl groups of ethylene glycol. The UV-vis spectra, fluorescence (FL) excitation and emission spectra of the C-dots were shown in Fig. S2. The as-synthesized C-dots have a strong absorption peak at 258 nm which is typically attributable to the π-π* transition.[15] The maximum FL emission peak centered at 460 nm when excited at 363 nm, like most other fluorescence C-dots, these as-synthesized C-dots show an excitation-dependent FL behavior.[16, 17]

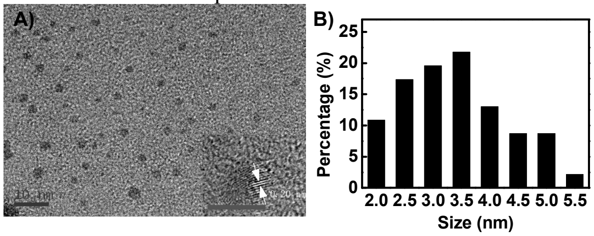

Fig. 1 (A) Typical TEM image of as-synthesized C-dots, inset: HRTEM image of single C-dots. (B) Size distribution histograms of C-dots.

The synthesis of AuNPs using C-dots as the reductant was selected as model system to explore the feasibility of synthesis of noble metal nanoparticles. When $HAuCl_4$ was added into C-dots solution, the color of mixture solution changed from yellow to red immediately (within 30 s) at room temperature. An absorption peak at 526 nm (Fig. 2A) in its UV-vis absorption spectrum of the mixture solution was observed, which matches well with the typical Plasmon resonance absorption peak of AuNPs.[18] UV-vis spectra recorded at different incubating time (Fig. 2B) shows that the absorption of AuNPs appeared within 30 s and the absorption peak appeared gradually red-shifts and the adsorption intensity increased with the increase in incubation time. The full width at half maximum and maximum absorption wavelength did not obvious changed after 20 min, suggests that the reaction could finish within 20 min. In addition, no color change and aggregation were observed after storage for more than four months. It indicates that C-dots can act as excellent reductant and stabilizer for reducing gold ions and stabilize the nanoparticles. This stability may due to the interaction of the residual hydroxyl groups of C-dots with AuNPs through hydrogen bonding to protect AuNPs from aggregating.[19]

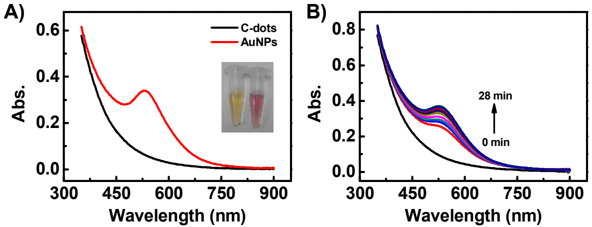

Fig. 2 (A) UV-vis spectra of C-dots and as-synthesized AuNPs. Inset: photograph of C-dots (left) and AuNPs (right). (B) Temporal evolution UV-vis spectra of C-dots and C-dots mixed with $HAuCl_4$ under room temperature.

Transmission electron microscopy (TEM) was used to characterize the morphology and size of as-synthesized AuNPs. As shown in Fig. 3A, the as-synthesized AuNPs are nearly spherical with diameters ranging from 12 to 14 nm (Fig S3). The clear lattice spacing of 0.24 nm on HRTEM image displays the message corresponding to the (111) lattice space of metallic Au (JCPDS 04-0784). However, the C-dots could be hardly found in the TEM picture, which may be due to the low contrast on the substrate used.[20] The scanning transmission electron microscopic (STEM) imaging has been performed to further investigate the structure of as-synthesized AuNPs. As shown in Fig. 3C-E the elemental mapping distributions of a single nanoparticle indicates that the AuNPs contain some carbon elements. The carbon element should be came from C-dots, and the C-dots may be attached to the AuNPs surface through hydrogen bonding to protect AuNPs from aggregating.[19] The significantly increased signal of cross-sectional compositional line profiles reflect that C-dots have been attached to the AuNPs surfaces (Fig. S4).

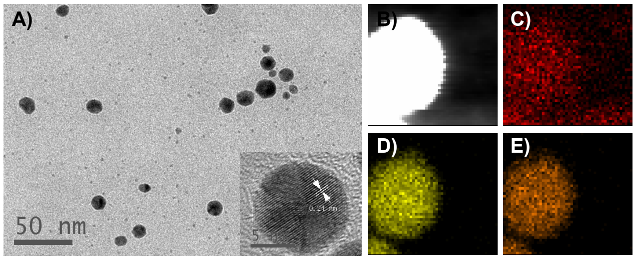

Fig. 3 (A) Typical TEM image of as-synthesized AuNPs, inset: HRTEM image of single AuNPs. (B) STEM image of one AuNPs. (C-D) Elemental maps for C-K, Au-L and Au-M, respectively.

We speculated that the remarkable reduction property of C-dots maybe come from the nature of its surface functional groups. A comparative study of the functional groups on C-dots surface before and after reaction with $HAuCl_4$ was performed with Fourier transform infrared spectrum (FT-IR) and X-ray photoelectron spectroscopy (XPS). As shown in Fig. S5A, the obvious peaks at 3406 cm^{-1}, 1075 cm^{-1} and 1257 cm^{-1} which assigned to the hydroxyl groups of C-dots were observed.[13, 14] Compared with the original C-dots, the relative intensity of hydroxyl groups (3406 cm^{-1}) decreased and the intensity of carbonyl groups (1715 cm^{-1}) significantly increased after reaction with $HAuCl_4$, indicating that hydroxyl groups on the surface of C-dots can reduce $HAuCl_4$ to form AuNPs and turn to carbonyl groups after reaction. XPS spectrum was shown in Fig. S5B and summarized in Tab. S1. The intensity of the hydroxyl group binding energy decreased (from 0.28 to 0.23) and the intensity of the carbonyl groups binding energy increased (from 0.05 to 0.08) after reaction, which was in agreement with FTIR characterization. These results reflect that hydroxyl groups were involved in the reduction of metal salt to form metal nanoparticles and the hydroxyl groups transformed into the carbonyl groups or carboxyl groups finally. The observation is consistent with other reports.[21-24]

To investigate the properties of the as-synthesized AuNPs, the catalytic oxidation of the peroxidase substrate TMB was tested in the presence of H_2O_2. Fig. S6 shows the UV-vis absorption spectra for the different test solutions. As shown in Fig. S6, the absorbance intensity of TMB-AuNPs-H_2O_2 system was much higher than that of the TMB-AuNPs and TMB-H_2O_2 systems. Additionally, the absorbance at 652 nm increased with increasing in H_2O_2 concentration (Fig. 4A). And the color variation of TMB oxidation catalyzed by as-synthesized AuNPs was H_2O_2 concentration-dependent. This indicates that the absorbance change can be used for the detection of H_2O_2. As shown in Fig. 4B, the absorbance at 652 nm was proportional to H_2O_2 concentration from 0.01-0.2 mM (R^2 = 0.99) with a detection limit of 3.0 μM (S/N=3) and the color variation was obvious on visual observation (Fig. 4B). Based on these results, AuNPs was used for glucose detection successfully (Figure 4C and D). The

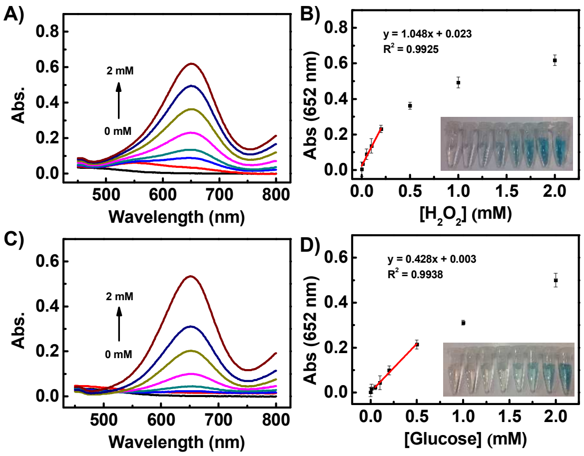

Fig. 4 The UV-vis spectra of (A) TMB+AuNPs+H_2O_2 and (C) TMB+AuNPs+GOx+glucose system with analyte of different concentration. Response curves of (B) H_2O_2 and (D) glucose, respectively. Inset: images of production of colored products for different concentrations of H_2O_2 and glucose.

linear detection range of glucose was 0.05-0.5 mM (R^2 = 0.99) and the detection limit was estimated to 14 μM (S/N=3). The color variation for glucose response was also obvious.

For confirming the universality of the C-dots as both reductant and stabilizer in the synthesis of noble metal nanomaterials, the synthesis of silver nanoparticles (AgNPs) and Au-core/Ag-shell composite nanoparticles (Au@AgNPs) using C-dots as reductant at room temperature were investigated. AgNPs were synthesized by using the same method as AuNPs and Au@AgNPs were synthesized by seeding growth method using as-synthesized AuNPs as seed (see detailed synthesis in the ESI). Fig. 5A and C show UV-vis absorbance spectra of as-synthesized AgNPs and Au@AgNPs. The as-synthesized AgNPs exhibit an absorption peak at 400 nm, which is the typical surface Plasmon resonance absorption of AgNPs, indicating the formation of AgNPs (the reaction could finish within 22 min, Fig. S7). The AuNPs seed only exhibit a Plasmon resonance band at 526 nm. When the molar ratio of Au/Ag is around 1, two SPR bands located at 400 nm and 496 nm can be observed, which indicates the surface of AuNPs was covered by AgNPs partially or formed independent particles.[25] However, with the increase of the concentration of Ag^+, only a Plasmon resonance band of AgNPs was found. It can be inferred that the reduction of Ag^+ alone occurs on the preformed Au core surface rather than forming more nucleation sites, and the core-shell structure of Au-Ag composite nanoparticles were formed.[25, 26] As shown in Fig. 5B and D, the as-synthesized AgNPs and Au@AgNPs are spherical and have diameters ranging from 6-8 nm and 13-16 nm (Fig. S8 and S9), respectively. The HRTEM image of AgNPs reveals clear lattice spacing of 0.24 nm corresponding to the (111) lattice space of metallic Ag (JCPDS 04-0783). The TEM image of Au@AgNPs shows each composite nanoparticle has a high-contrast interior core and is surrounded by a low-contrast shell, which is a solid evidence for the formation of Au@AgNPs.

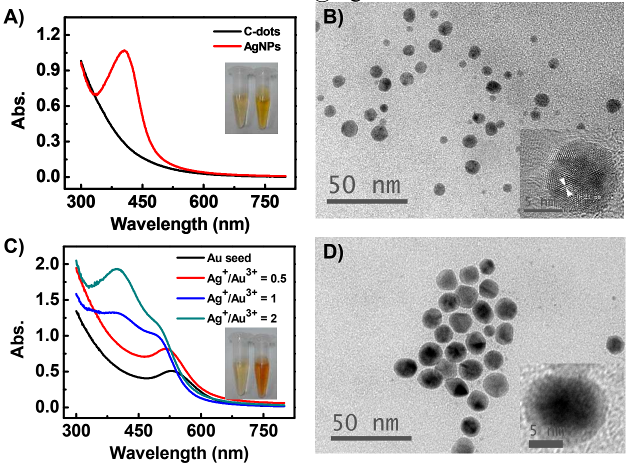

Fig. 5 (A) UV-vis spectra and (B) TEM image of as-synthesized AgNPs, inset: photograph of C-dots (left) and AgNPs (right), and HRTEM image of single AgNPs, respectively. (C) UV-vis spectra and (D) TEM image of as-synthesized Au@AgNPs, inset: photograph of C-dots (left) and Au@AgNPs (right), and HRTEM image of single Au@AgNPs, respectively.

In summary, electrochemical carbonization of ethylene glycol has been successfully used to synthesize hydroxyl-rich C-dots. The hydroxyl-rich C-dots can be used as an efficient reductant and stabilizing agent for fast synthesis of noble metal nanomaterials. This method is simple, facile and did not require any additional energy. Furthermore, as-synthesized AuNPs was used to detect H_2O_2 and glucose successfully. Our present study has opened a facile and fast synthesis way for synthesis of noble metal nanoparticles.

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Notes and references

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