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Mussel-inspired green synthesis of silver nanoparticles on graphene oxide nanosheets for enhanced catalytic applications<sup>†</sup>

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We report a facile green approach to the synthesis of silver nanoparticles (Ag NPs) on the surface of graphene oxide nanosheets functionalized with mussel-inspired dopamine (GO-Dopa) without additional reductants or stabilizers at room temperature. The resulting hybrid Ag/GO-Dopa exhibits good dispersity and excellent catalytic activity in the reduction of nitroarenes.

Graphene, a two-dimensional aromatic carbon monolayer, has recently received significant attention in various fields of science and engineering on account of its unique electrical, optical, thermal and mechanical properties.1-5 Among various types of graphene and related structures, solution processable graphene oxide (GO) typically prepared by chemical exfoliation possesses unique advantages for many applications owing to its facile synthetic nature in a controlled, scalable, and reproducible manner.<sup>6-9</sup> The abundant surface functional groups provide GO with excellent aqueous dispersity and also offer opportunities for further chemical modifications. Taking full advantage of the surface functional groups, as well as its large specific surface area and stability, GO nanosheets are emerging as promising supports for graphene-based hybrid nanomaterials for a variety of applications, including sensors, optical and electronic devices, energy conversion and storage, and catalysts. Toward this end, recent studies have endeavored to anchor metal, metal oxide, semiconducting, and magnetic nanoparticles (NPs) on the surface of GO either by hosting preformed NPs on graphene or by growing NPs in situ with the metal precursor in the presence of graphene nanosheets. However, many of these approaches still require additional reducing agents and/or stabilizers with proper thermal treatment.<sup>10-14</sup>

Inspired by the adhesive properties of 3,4-dihydroxy-Lphenylalanine (dopamine), which is found abundantly in marine mussel foot proteins, dopamine and its polymer, polydopamine, have been widely exploited in various fields ranging from versatile surface modifications, biomineralization, and even to Li-ion battery. In particular, its redox-active catechol group can undergo spontaneous oxidation to quinone under mild solution conditions, thus serving as a reducing agent to reduce the metal precursor to NPs, as suggested in previous reports. For example, Lee and co-workers demonstrated that Cu and Ag can form spontaneously on the dopamine and polydopamine-coated surfaces.<sup>15</sup>

In this communication, we report a facile synthetic approach to integrating the mussel-inspired chemical motif of dopamine (Dopa) to the surface of GO to afford GO-Dopa with the aim of inducing the spontaneous formation of NPs on the surface of GO at room temperature without the use of any additional reducing agents or stabilizers. As a representative example, we demonstrate the synthesis of Ag NPs on the surface of graphene nanosheets. Furthermore, we exploit the excellent catalytic activity of the resulting hybrid Ag/GO-Dopa toward the reduction of a series of model nitroarenes.

To functionalize the dopamine molecules on the surface of GO, we initially prepared GO according to the modified Hummers method.<sup>16,17</sup> The catechol group in dopamine was selectively protected with an acetonide group (Dopa\*) to prevent undesirable side reactions such as the self-polymerization of dopamine that might hinder the attachment of catechol on the GO.<sup>18,19</sup> After the preparation of Dopa\*, the free amine group of Dopa\* reacted with the carboxylic acid and/or epoxide groups on the surface of GO through an *N*-ethyl-*N'*-(3-dimethyl aminopropyl)carbodiimide methiodide (EDC)-mediated reaction, followed by the subsequent deprotection using trifluoroacetic acid (TFA) to afford the GO-Dopa with free catechol groups (Fig. 1).

FT-IR spectroscopy clearly indicates the successful surface functionalization of GO to GO-Dopa (Fig. 2a). For example, GO shows a broad peak at 3300 cm<sup>-1</sup> arising from the abundant O–H stretching vibrations. Moreover, the peaks due to C=O stretching, and conjugated C=C are visible at 1730 and 1630 cm<sup>-1</sup>, respectively.<sup>20</sup> After the reaction of GO with Dopa\*, a peak appeared at 2900 cm<sup>-1</sup>, which corresponds to C-H stretching of the alkyl group of dopamine, while the intensity of the peak at 1730 cm<sup>-1</sup> decreased and shifted because of the

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**Fig. 1** (a) Synthetic route to acetonide-protected dopamine (Dopa\*). (i) *N*-carbethoxy-phthalimide, TEA, MeOH. (ii) p-TSA, benzene. (iii) Hydrazine hydrate, DCM, MeOH. (b) Schematic representation of the preparation of GO-Dopa and Ag/GO-Dopa.



**Fig. 2** (a) FT-IR and (b) UV/vis spectra of GO (black), GO-Dopa\* (red), GO-Dopa (blue) and Ag/GO-Dopa (green).

formation of the amide bond (*i.e.*–CONH–) on the surface of GO. Because of their structural similarities, the spectra of GO-Dopa and GO-Dopa<sup>\*</sup> are very similar, however, more pronounced O–H stretching vibration is observed upon the regeneration of the catechol groups using TFA. Further characterization by UV/vis spectroscopy was performed to analyze the surface functionalization of GO (Fig. 2b). Interestingly, the absorbance maxima ( $\lambda_{max}$ ) of functionalized GO blue-shifted from that of GO ( $\lambda_{max} = 230$  nm). The conjugation of aromatic dopamine contributed to the shift of the  $\lambda_{max}$  of GO-Dopa<sup>\*</sup> and GO-Dopa, confirming the successful surface functionalization of GO.

Atomic force microscopy (AFM) images support the functionalization of the surfaces of the GO sheets. The GO-Dopa sheets are thicker than the GO sheets owing to the surface functionalization of dopamine. It is also interesting to note that the GO-Dopa sheets were stacked due to the presence of the surface anchoring catechol groups, increasing the adhesion of each graphene sheet. Once the stable GO-Dopa suspension was prepared, Ag NPs were easily formed *in situ* by simple mixing with aqueous AgNO<sub>3</sub> solution at room temperature for 3 h. Individual Ag NPs with a height of 3.30 nm were deposited on the functionalized GO sheets (Fig. 3c).

As suggested in previous reports, the catechol groups of dopamine oxidize to quinone, which offers the electrons to reduce Ag ions to form Ag NPs on the surface of GO-Dopa. Moreover, the GO-Dopa nanosheet also plays a role as a stabilizer for anchored Ag NPs, preventing the reaggregation of the resulting Ag NPs. We observed that the resulting Ag/GO-Dopa exhibits fairly good aqueous dispersity and stability for several months. As a control experiment, pristine GO was also subjected to the identical reaction conditions in order to form Ag NPs on the graphene sheet. Although Ag NPs did form on the



Fig. 3 Representative AFM and TEM images of Ag/GO-Dopa: (a) GO, (b) GO-Dopa, (c–e) Ag/GO-Dopa, with an inset image of the Ag NPs. (f) Size distribution histogram of the Ag NPs. Scale bar in AFM images is 2.5  $\mu$ m.

graphene sheets possibly due to the nucleation sites such as carboxylic acid groups coordinating with  $Ag^+$  ions, the Ag NPs generally featured a wide size distribution, low crystallinity, and poor colloidal stability; this clearly indicates the importance of the controlled growth mediated by the dopamine motif (Fig. S1 in ESI<sup>+</sup>).

According to transmission electron microscopy (TEM) images, we confirmed that Ag NPs with an average particle size of 7.71  $\pm$  1.34 nm are well dispersed on the GO-Dopa sheets (Fig. 3d and e). We also found no free Ag NPs formed outside the graphene sheet. The Ag NPs are crystalline with lattice spacings of 1.20 and 2.36 Å, which correspond to the (311) and (111) peaks, respectively. The edges and basal planes of the graphene sheets are all decorated with Ag NPs, although there is relatively higher density at the edges; this observation can be attributed to the higher distribution of surface functional groups such as carboxylic acid groups at the edges that are functionalized with dopamine. In addition, XRD analysis supports the successful formation of Ag NPs with a broad peak corresponding to the GO nanosheet at around 20° (Fig. S2 in ESI<sup>†</sup>). ICP/MS measurement confirmed that approximately 2.4% of the Ag/GO-Dopa is composed of Ag NPs. Furthermore, we also demonstrated that the distribution and sizes of the Ag NPs could be controlled by changing the reaction time, solution pH, or concentration of the Ag precursor (Fig. S3 in ESI<sup>+</sup>).

After careful characterization of the hybrid Ag/GO-Dopa, it was employed for the catalytic reduction of a series of nitroarenes in the presence of NaBH<sub>4</sub> because of the well-known catalytic activity of Ag NPs in this reaction. First, we studied the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) to evaluate the catalytic activity of hybrid Ag/GO-Dopa. The successful conversion of the reaction was monitored via UV/vis spectroscopy; specifically, the absorption peak of 4-NP at 400 nm decreases concomitantly with the increase in a new absorption peak at 300 nm, which indicates the formation of the reduced product, 4-AP. From the UV/vis spectra, the pseudo-first-order reaction kinetics were applied to determine the reaction rate constant. From the linear relation of  $\ln(C_t/C_0)$  with t, we determined that the rate constant, k, for this reaction is  $0.364 \text{ min}^{-1}$  and the turnover frequency (TOF) is 14.6 min<sup>-1</sup>, which is significantly higher than those reported earlier (typically  $10^{-1}$  to  $10^{-3}$ ) under similar reaction conditions (Fig. 4b).<sup>21,22</sup>



**Fig. 4** (a) Time-dependent UV/vis absorption spectra for the reduction of 4-NP over Ag/GO-Dopa catalyst in aqueous media at 298 K. (b) Plot of  $\ln(C_t/C_0)$  versus time for the reduction of 4-NP. Reaction conditions: 1.0 mol% catalyst and 800 equiv. NaBH<sub>4</sub>. (c) Plot of  $\ln(C_t/C_0)$  versus time for the reduction of 4-NP with three different catalysts. (d) Plot of  $\ln(C_t/C_0)$  versus time for the reduction of 4-NP at three different temperatures.

To elucidate the catalytic activity of Ag/GO-Dopa, we performed control experiments using GO and GO-Dopa. The GO and GO-Dopa showed a negligible catalytic activity with a rate constant of 0.004 and 0.003 min<sup>-1</sup>, respectively (Fig. 4c). Although the catalytic activity of GO is noticeable, it is still significantly less reactive than the hybrid Ag/GO-Dopa. We also found that the catalytic activity of Ag/GO-Dopa is affected by the temperature of the reaction (Fig. 4d). The rate constants obtained at various temperatures were plotted to provide the activation energy of the reaction; the Arrhenius plot revealed the activation energy of approximately 40.0 kJ mol<sup>-1</sup>. This value is considerably smaller than that of the Au/GO system for the same reaction (85.9 kJ mol<sup>-1</sup>).<sup>23</sup>

We further investigated the catalytic activity of the Ag/GO-Dopa composite towards the reduction of other nitroarenes. We found that hybrid Ag/GO-Dopa retains excellent catalytic activity in the reduction of a series of nitroarenes regardless of the types and positions of the substituents (Fig. S4 in ESI<sup>†</sup>). We propose that the high catalytic activity of Ag/GO-Dopa originates from three factors: (1) the high surface area and enhanced adsorption of aromatic compounds onto the surface of graphene sheets, (2) the enhanced reaction kinetics with free electrons on the surface of the graphene, and (3) the high catalytic activity of Ag NPs with superior dispersion and stability due to the chemically stable graphene sheet support.

Finally, in order to demonstrate the versatility of this bioinspired approach, we synthesized NPs of other metals such as Cu and Au on the surface of graphene nanosheets based on the protocol described for Ag/GO-Dopa (Fig. S5 in ESI<sup>†</sup>). As characterized by TEM and XRD, highly water-dispersible Cu/GO-Dopa and Au/GO-Dopa were successfully prepared at room temperature without using external reducing agents. This result further highlights the potential of our bio-inspired approach to be a facile and general means of producing metal/graphene nanostructures with different functionalities for various applications, which is the subject of our ongoing endeavour.

We synthesized hybrid Ag/GO-Dopa catalysts using an Ag precursor and the GO sheets functionalized with a musselinspired biological motif, *i.e.* dopamine. The dopaminefunctionalized GO sheets acted as both the reducing agents and stabilizers for the reduction of Ag ions at room temperature. The GO-Dopa sheets were covered with Ag nanoparticles that possess good dispersity and stability in aqueous solution. Hybrid Ag/GO-Dopa exhibits superior catalytic activity toward the reduction of a series of nitroarenes because of the interplay between the high surface area of the graphene nanosheets and the catalytic activity of the Ag nanoparticles. We anticipate that the approach presented in this study will provide a facile means of preparing nanoparticles on graphene nanosheets for advanced electronic, energy, and sensor applications.

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