

## Controlling the Coffee Ring Effect on Graphene and Polymer by Cations \*

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Recently, there are great efforts that have been taken to suppressing/controlling the coffee ring effect, but it is of challenge to achieve inexpensive and efficient control with less disturbance, suitable for scalable production and highly enhancing the printing/dyeing color fastness. By only adding trace amounts of salt into the suspensions, here we experimentally achieve the facile and highly efficient control of the coffee ring effect of suspended matter on substrates of graphene, natural graphite, and polyethylene terephthalate surfaces. Notably, friction force measurements show that ion-controlled uniform patterns also greatly enhance color fastness. Molecular dynamics simulations reveal that, due to strong hydrated cation- $\pi$  interactions between hydrated cations and aromatic rings in the substrate surface, the suspended matters are adsorbed on the surfaces mediated by cations so that the suspended matters are uniformly distributed. These findings will open new avenues for fabricating functional patterns on graphene substrates and will benefit practical applications including printing, coating, and dyeing.

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The coffee ring effect,<sup>[1,2]</sup> the formation of a ring that occurs when the solvent evaporates from a drop of solution that contains non-volatile solutes in a volatile solvent, has been a large obstacle in many fundamental and daily applications ranging from printing, coating, dyeing, complex assembly, to micro-/nano-fabrication.<sup>[3-10]</sup> For example, it leads to non-uniform printing and dyeing on polymers and textiles, which greatly affects appearance and product applications. There have been great efforts to suppressing or controlling the effect,<sup>[4,5,11-18]</sup> such as particle shape variation,<sup>[4]</sup> addition of surfactants,<sup>[11,18-20]</sup> polymers,<sup>[16]</sup> sol-gel inducers,<sup>[12]</sup> co-solvents,<sup>[13,21]</sup> or proteins,<sup>[14]</sup> as well as using external optical or electric fields.<sup>[15]</sup> These strategies have usually relied on additives,<sup>[11-14,16]</sup> temperature,<sup>[17,22]</sup> external optical or electronic fields,<sup>[15,18,23]</sup> or even making the suspension particle asymmetry.<sup>[4,24,25]</sup> However, the challenge still remains for inexpensive efficient control, with less disturbance, for scalable production and enhanced color fastness, which are the key to those fundamental and daily applications in a given system.

Fabricating functional patterns on graphene sub-

strates would have great potential applications in many graphene-based fields, such as graphene-based field effect transistors, complex catalysts, nanodevices, and biomolecule detectors.<sup>[26-33]</sup> Uniform printings/coatings should be an effective pathway for fabricating these functional patterns.<sup>[34]</sup> Clearly, the ubiquitous nature of the coffee ring effect has made these processes difficult, resulting in inhomogeneous functional patterns.

In this Letter, we experimentally achieve facile and highly efficient control of the coffee ring effect on graphene and polymer surfaces, as well as on other aromatic-ring substrates, simply by adding trace amounts of salt (i.e., NaCl, LiCl, KCl, CaCl<sub>2</sub> or MgCl<sub>2</sub>) to the suspended solute solution. We obtain enhanced color fastness of dye molecules (over 100% for acid red 1). Molecular dynamics (MD) simulations attribute the control to hydrated cation- $\pi$  interactions between the solute and aromatic rings in the graphene and polymer substrates, promoting adsorption of suspended matters onto the substrates bearing aromatic rings.

In experiment, we used aqueous suspensions of

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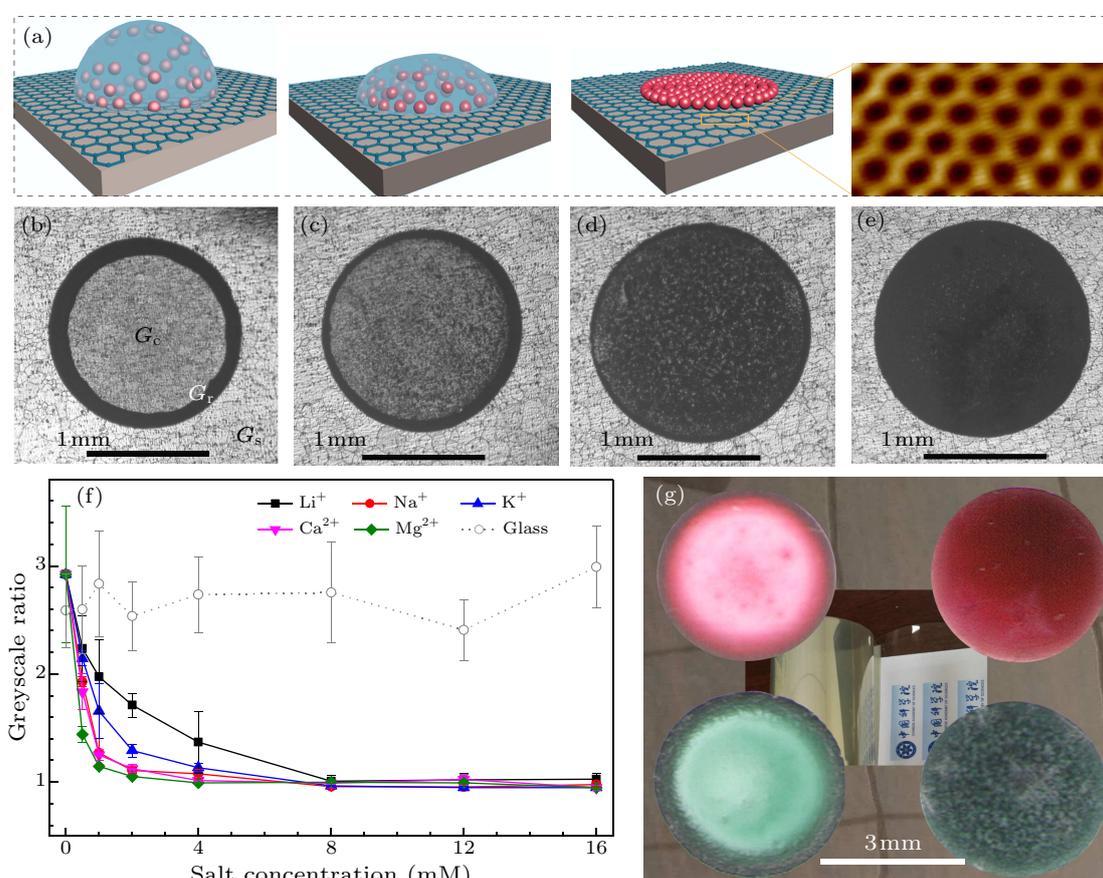
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polystyrene microspheres, as reported previously.<sup>[1,4]</sup> Some suspensions were thoroughly mixed with solutions of NaCl to obtain mixtures of different NaCl concentrations. Drops of these mixtures and the aqueous suspensions without NaCl were then placed separately on a chemical vapor deposition (CVD) grown graphene substrate on copper (Fig. 1(a)). After drop evaporation at  $10.0 \pm 3.2^\circ\text{C}$ , the morphologies of the dried patterns left on the substrates were recorded by optical microscopy, followed by a greyscale analysis. Figure 1(b) shows the patterns for the suspension without NaCl. We can see a ring-like pattern with a dark rim and a light grey center on graphene, which displays a clear coffee ring effect. Remarkably, as shown in Figs. 1(c)–1(e), the image contrast be-

tween the rim and center of the pattern was gradually reduced for mixtures with increasing NaCl concentration (2.0–8.0 mM). In fact, at the concentration of 8.0-mM NaCl, the pattern in Fig. 1(e) appears to be uniform. Other salts such as LiCl, KCl,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$ , were also effective (Figs. S4–S7).

Notably, the ionic control behavior was also observed on other substrates such as the most common thermoplastic polymer resin of polyethylene terephthalate (PET) and natural graphite surfaces (Figs. S8–S11). As shown in Fig. 1(g), the ring-like feature on a PET film disappeared at the NaCl concentration of 16 mM. In the depicted studies, we used aqueous soluble acid red 1 and acid blue 25 dye molecules, respectively.



**Fig. 1.** Control of the deposition patterns of suspended matters by cations. (a) A schematic of how cations in a drop (blue hemisphere) determine the deposition of polystyrene microspheres (red beads). The inset shows an atomically resolved scanning tunneling microscopy (STM) image of a graphene lattice. (b)–(e) Optical microscopy images of particle patterns on graphene after evaporation of drops of suspension or mixture with different salt concentrations (0 mM, 2.0 mM, 4.0 mM, and 8.0 mM, respectively). (f) Greyscale ratios ( $GR = \frac{G_c - G_s}{G_r - G_s}$ ) of patterns of the deposited matters on graphene (solid lines) and glass (dotted line) substrate. (g) Photographs of patterns on a PET film after evaporation of drops of mixtures of acid red 1 (upper) and acid blue 25 (lower) solutions with 0 mM (left) and 16.0 mM (right) NaCl, respectively.

To quantitatively characterize the uniformity of the deposited polystyrene microspheres, we computed the greyscale ratio, denoted by GR,  $GR = (G_c - G_s)/(G_r - G_s)$ , where  $G_c$ ,  $G_r$ , and  $G_s$  are the average greyscales at the pattern center, the pattern rim,

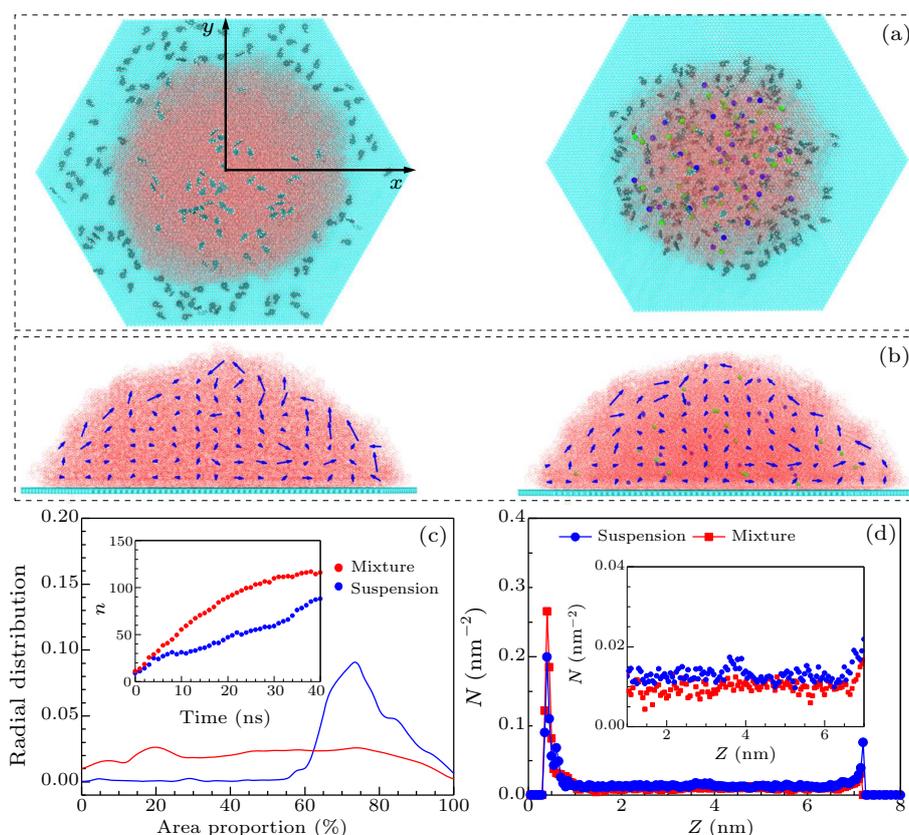
and the substrate, respectively. As shown in Fig. 1(f), the greyscale ratio greatly decreases from  $2.90 \pm 0.72$  for the suspension without NaCl to  $1.00 \pm 0.05$  for the mixture with 8.0 mM NaCl solution. It is clear that  $GR = 1.00$  corresponds to uniform deposition. Thus,

the pattern was essentially uniform at the salt concentration equal to and greater than 8.0 mM. These results clearly indicate that the ring-like pattern can be well controlled by the concentration of NaCl in the mixture.

Values of GR using other salts (i.e., LiCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>) showed that patterns approached uniformity at 8.0 mM and 4.0 mM for monovalent and divalent cations, respectively, although their decreasing ratios of GR values differed (Fig. 1(f)). In particular, the GR ratio decreased more slowly for drops mixed with monovalent cations than that with diva-

lent cations.

The ion-controlled uniform patterns clearly enhanced the color fastness of the dye molecules. This was demonstrated via contact atomic force microscopy (AFM, Figs. S12–S14). Specifically, we measured friction forces while scanning four dye patterns formed after evaporation. As shown in Fig. S14, the friction forces of coral red and dark cyan dye patterns reach  $220.0 \pm 67.0$  nN and  $79.6 \pm 14.8$  nN, respectively, at the NaCl concentration of 16.0 mM. These values were factors of 2.14 and 1.24 greater, respectively, than those measured for patterns produced without NaCl.



**Fig. 2.** Molecular dynamic simulations of the styrene molecules in drops of suspension or mixture on graphene sheets. (a) Top views of the drops of suspension and mixture on graphene during evaporation. The cyan, red, blue, green, and white spheres represent C, O, Na, Cl, H atoms, respectively. (b) Flow rate distributions in drop suspensions (without NaCl, left) or mixtures (with NaCl, right). (c) Radial distribution for the first layer ( $<1$  nm) of styrene molecules from the center of the drops. The inset plots the number  $n$  of styrene molecules adsorbed on the surface ( $n$ ) with time. (d) Density distribution of styrene molecules per square ( $N$ ) along the  $Z$  direction in the drops of suspension (blue) or mixture (red).

We performed MD simulations to exploit the underlying physics. We used styrene molecules as the suspensions and a graphene sheet with aromatic rings as the solid surface since the polystyrene microspheres were too large to perform MD simulations. In the system without salt, most of the styrene molecules formed a ring-like pattern on the graphene surface around the drop of the aqueous suspension as the water evaporated. In contrast, most of the styrene molecules with 0.1 M NaCl spread out on the graphene

surface as the water evaporated (Fig. 2(a)). The inset of Fig. 2(c) shows that most of the styrene molecules are adsorbed on the surface after 40 ns simulation in both systems, and the height of these adsorbed styrene molecules is below 1 nm (Fig. 2(d)). The radial distribution of these adsorbed styrene molecules is shown in Fig. 2(c). It was flat in the presence of NaCl, and displayed a peak near the edge of the drop in its absence, which is consistent with our experimental observations. We also computed the distribution of flow

rates in the drop (Fig. 2(b)). The liquid flow displayed loops. For suspensions without cations, the flow loop pushed the styrene molecules to the drop boundary. Thus, sedimentation was greater at the boundary. In contrast, for mixtures with cations, due to the strong hydrated cation- $\pi$  interactions between the hydrated cations and aromatic rings structures in the surfaces, the styrene molecules were adsorbed onto the graphene by the cations. The adsorbed styrene molecules were not further disturbed by the flow loops toward the drop boundary, consistent with the lattice Boltzmann simulation and the *in situ* experiments (Figs. S15 and S16).

To further investigate the importance of hydrated cation- $\pi$  interactions between the salt and the substrate in the suppression of coffee rings, we have performed experiments at the same NaCl concentration and only replaced the substrate with a glass slide that does not contain any aromatic rings. Considering that there are no hydrated cation- $\pi$  interactions between the salt and the substrate, we expected that the ring-like morphology would still exist. This was borne out in the experiments (Fig. 1(f) and Fig. S17).

In summary, we have experimentally achieved facile and precise control of deposition patterns of suspended particles and molecules on graphene and other substrates bearing aromatic rings by adding trace amounts of salt to the suspensions. The ion-controlled uniform patterns greatly enhanced color fastness as well, i.e., over 100% for acid red 1. The physics underlying this process may be mainly attributed to the strong hydrated cation- $\pi$  interactions between the hydrated cations and the aromatic rings on the substrates surface. The suspended matter is uniformly adsorbed on the surfaces mediated by cations and are not further perturbed by flow loops to the drop boundary. In addition to  $\text{Na}^+$ , other metal ions could be used to control the particle deposition on substrate surfaces with aromatic rings where cation- $\pi$  interactions occur.<sup>[35–40]</sup> Overall, our findings represent a step towards a wide range of applications involving evaporation and fabrication of functional patterns on graphene as well as on other aromatic-ring-containing substrates. Examples include packaging, high-temperature fuel cells, thin-film solar cells, displays, textiles, electronics, and military applications.

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