

# Work Function Modification via Combined Charge-Based Through-Space Interaction and Surface Interaction

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Work function modification of electrodes is an important factor to achieve high performance in organic electronics. However, a clear explanation of the origin of work function modification has remained elusive. Here, it is investigated how the work function of electrodes is affected by the charge-based through-space interaction with the well-known surface interaction. The studies reveal that the formation of a surface dipole leads to a work function shift, even when the work function modifying layer and substrate are separated. A work function shift is also demonstrated by electrophoretic deposition of ionic polyelectrolytes while the same polyelectrolytes do not cause any work function shift when they are spin cast. More noteworthy is that a neutral (nonionic) polymer which has no specific surface-interacting functional groups can induce work function shift of its substrate by a charge-based through-space interaction when deposited by electrospaying. These results provide a more comprehensive understanding of work function modification and motivate the design and selection of a wide range of effective work function modifying layers for organic electronics.

Work function plays a key role in organic electronics since effective charge carrier injection and collection are largely dependent on the work function of the electrodes.<sup>[1–3]</sup> In literature, many different methods have been reported regarding how the work function of various electrodes including zinc oxide (ZnO),<sup>[1,4,5]</sup> indium tin oxide (ITO),<sup>[1,6–15]</sup> Au,<sup>[1,14,16,17]</sup> or Al<sup>[14,18,19]</sup> could be efficiently modified. Especially, ITO is widely used and considered to be a promising electrode for organic electronics such as

organic solar cells (OSCs) for several reasons: it is transparent in the visible region and it has not only high conductivity but also the capability to collect either electrons or holes through work function modification.<sup>[20]</sup> To illustrate, inverted OSCs, which have been extensively studied due to their superior long term ambient stability and printability relative to conventional OSCs, use ITO as a cathode by controlling its work function.<sup>[15,21,22]</sup> Thus, understanding the origin of the work function modification process is of critical importance for organic electronic devices. Currently, introducing a thin layer of interfacial materials between the electrode and the active layer is studied to modify the work function of the electrode through the formation of interfacial dipole interactions. For example, He et al. reported that the efficiency of OSCs can be raised to 9.2% by effective work function tuning

with an alcohol/water-soluble conjugated polymer.<sup>[6]</sup> Lee et al. showed that high performance OSCs with 8.32% efficiency could be fabricated using a combination of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) and nonconjugated polyelectrolytes as recombination layers that lead to effective work function reduction at the ITO electrode.<sup>[15]</sup> Additionally, both anionic and cationic polyelectrolyte interlayers have been studied to achieve a proper energy level alignment for

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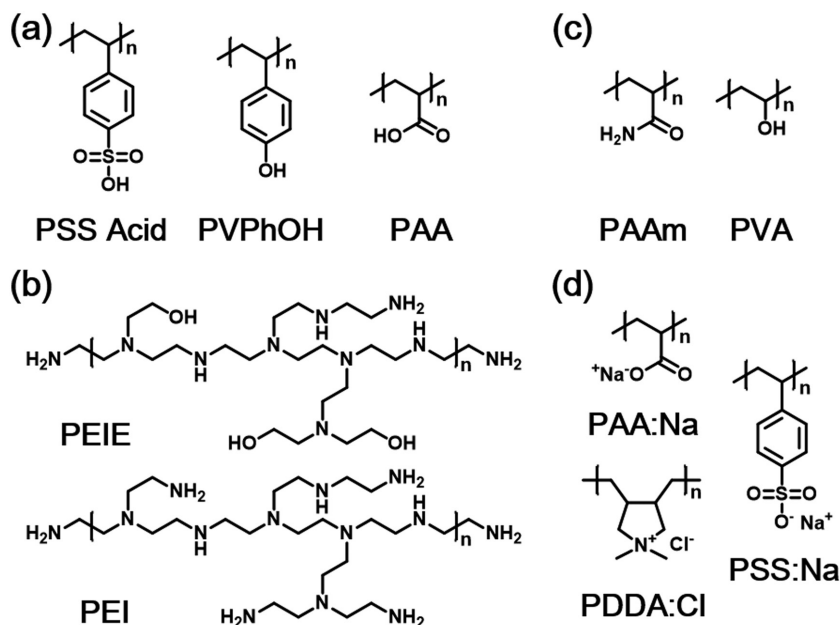
an improved power conversion efficiency by means of reoriented interfacial dipoles in the presence of an externally applied electric field.<sup>[19,23]</sup>

Organic coatings typically influence a material's work function through changes to the surface electric field; three primary mechanisms that affect work function are the push back effect, Fermi level pinning, and interfacial dipole formation.<sup>[24,25]</sup> For example, the electron repulsion (push back) between an inactive organic coating and a substrate can result in the formation of a work function reducing dipole.<sup>[26,27]</sup> Alternately, a semiconducting organic material's reduction or oxidation potential may be lower or higher, respectively, than a substrate's Fermi level; when these materials are brought into contact, charge transfers between them creating a work function modifying dipole.<sup>[24,28]</sup> This effect reaches beyond the immediate interface with the substrate, too, for the immediate monolayer can only support a certain charge density.<sup>[29,30]</sup>

We got interested in conducting a systematic study on the origin of the work function modification by means of various polyelectrolytes coating via various thin film formation methods. The importance of surface interaction through direct contact between the polyelectrolyte and its substrate in work function modification has already been suggested in many studies dedicated to the work function modification.<sup>[1,31,32]</sup> However, the origin of work function modification is still the focus of great research effort, and there are experimental results that are not consistent with the direct contact mechanism such as the thickness dependence of the work function modifying layer in work function modification.<sup>[4,21]</sup>

In the literature the through-space interaction via an electrically-driven redistribution of the charge in electrodes has also been investigated to tune the work function of ITO substrates.<sup>[33]</sup> We reveal, with a representative polyelectrolyte set, that the surface interaction is not necessary in work function modification and at the same time suggest the presence of the charge-based through-space interaction between the polyelectrolyte layer and the substrate. We also demonstrate that work function can be modified through charge-based deposition techniques such as electrophoretic deposition and electrospinning even though the same materials do not exhibit meaningful work function shift when their films were formed by spin casting without an external electric field. Our results indicate that a combination of the surface interaction and the charge-based through-space interaction plays a significant role in tuning the work function of electrodes for various electronic device applications.

In order to study the mechanism behind the work function modification, we have chosen ten different organic materials, which were not limited to specific backbones or functional groups, as shown in **Figure 1**. To compare the work function shift depending on charge-based properties, we divided our chosen materials into four groups: acid-like, base-like, neutral



**Figure 1.** The chemical structures of a representative set of a) acid-like, b) base-like, c) neutral (nonionic), and d) ionic polyelectrolytes.

(nonionic), and ionic polyelectrolytes. When spin-cast samples are prepared from base-like and acid-like materials, the work function of ITO is observed to be decreased or increased, respectively (**Table 1**). Base-like polyelectrolytes induce a negative charge on the ITO surface, forming a dipole pointing outward from the electrode resulting in a decreased work function.<sup>[33]</sup> However, acid-like compounds form opposite interfacial dipoles compared to the base-like polymers, which result in an increase of the work function. Although the work function shift has been reported in zwitterionic polymers having an overall charge neutrality,<sup>[34]</sup> almost no work function shift was observed in nonionic neutral polymer samples since the interfacial dipole is not formed.<sup>[14]</sup> Similarly, a negligible change in work function is observed with poly(sodium styrene sulfonate) (PSS:Na)<sup>[14]</sup> and the two other ionic polyelectrolytes. This may be explained by a weak charge-based through-space interaction owing to the counter ions. We additionally measured the work function shift by means of ultraviolet photoelectron spectroscopy (UPS) and Kelvin probe force microscopy (KPFM) to validate the values and trend we obtained from our custom-built Kelvin probe (**Table 1** and **Figure S1**, Supporting Information). The experimental results are in agreement with our hypothesis and with a charged layer model discussed by Schlapak et al.; charged materials create interfacial dipoles and lead to work function modification.<sup>[33]</sup>

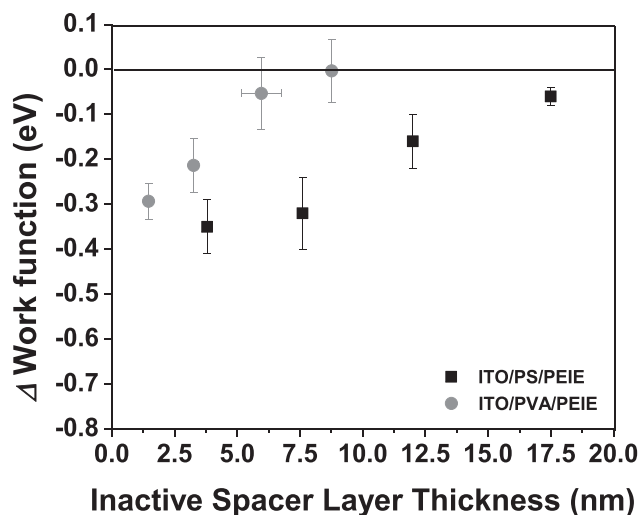
Based on our experimental data and previous study cited in this article, we questioned whether work function modification process is able to occur by the charge-based through-space interaction without direct contact between the polyelectrolyte and its substrates. To investigate the effect of the charge-based through-space interaction solely between ITO and the work function modifying layer, thin inactive spacer layers such as polystyrene (PS) or poly(vinyl alcohol) (PVA) were placed on top of the surface of ITO. Neither PS nor PVA changes the work

**Table 1.** The work function shift of polyelectrolytes, relative to clean ITO, as measured by kelvin probe spectroscopy, KPFM in air, and UPS.

Polyelectrolytes		$\Delta$ Work function relative to ITO		
		Kelvin probe	KPFM	UPS
Base-like	PEI	$-0.82 \pm 0.01$	–	–
	PEIE	$-0.72 \pm 0.03$	$-0.51 \pm 0.01$	$-1.26$
Acid-like	PAA	$0.30 \pm 0.02$	–	–
	PVPhOH	$0.27 \pm 0.05$	$0.13 \pm 0.01$	$0.59$
	PSS Acid	$0.36 \pm 0.01$	–	–
Neutral (nonionic)	PVA	$0.03 \pm 0.04$	–	$0.00$
	PAAm	$0.01 \pm 0.00$	$0.00 \pm 0.01$	–
Ionic	PDDA:Cl	$-0.04 \pm 0.01$	–	–
	PSS:Na	$0.02 \pm 0.03$	$0.01 \pm 0.01$	$-0.03$
	PAA:Na	$0.02 \pm 0.04$	–	–

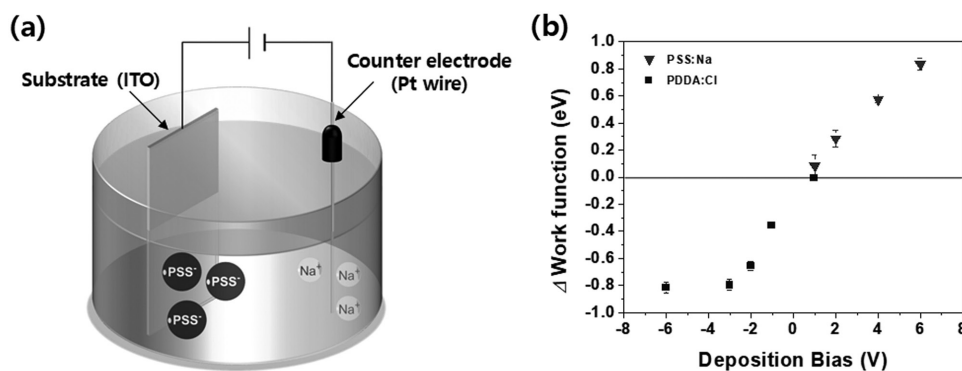
function of ITO on its own, but the thickness control afforded via spin casting and the difference in dielectric constant near 10 for PVA<sup>[35]</sup> and near 2.8 for PS,<sup>[36]</sup> will allow for varied attenuation of the expected through-space interaction between poly(ethylenimine 80% ethoxylated) (PEIE) and ITO. **Figure 2** presents the work function shift of ITO versus interlayer thickness. PEIE coated substrates having a thin, inactive, surface interaction blocking PS or PVA spacer both displayed a shifted work function of ITO, demonstrating that there is a possibility of the presence of an important factor in modifying the work function. As the thickness of the inactive spacer layer becomes larger, the degree of work function shift decreases in both the PVA and PS cases. This behavior is rationalized by our expectation that the polymer-originated electrical force decreases with increasing inactive spacer layer thickness, which in turn results in a reduction of charge redistribution on the ITO surface, a reduced dipole, and a reduced work function shift. Interestingly, we see that an interlayer with a larger dielectric constant results in a steeper attenuation,<sup>[37]</sup> consistent with the idea that a through-space electrical force drives the formation of a work function modifying dipole. We further investigated the film morphology by conductive atomic force microscopy (C-AFM) to confirm a full coverage of the ITO surface by the inactive spacer layer. Compared to a clean ITO substrate, significantly lower conductivity at the same applied bias was observed for the PS samples, which indicates that the observed work function shift is not from direct contact between PEIE and ITO (Figure S2, Supporting Information). Also, the morphology of the PS and PVA spacer layer before and after spin coating of 2-methoxy ethanol was analyzed using tapping mode AFM to see any surface disruption by sequential deposition of PEIE solution in 2-methoxy ethanol. AFM topography images of the PS (Figure S3, Supporting Information) and the PVA (Figure S4, Supporting Information) layer prepared at two different spin coating speeds do not show any noticeable morphology change.

As mentioned above ionic polyelectrolytes did not show any meaningful work function shift when they were spin coated on ITO without applying an external electric field. According



**Figure 2.** Work function shift, relative to bare ITO, of ITO/PEIE when PS (squares) or PVA (circles) is placed as a spacer layer between PEIE and ITO. The dielectric constants of PS and PVA are near 2.8 and 10, respectively.

to our proposed mechanism, if we can remove a polyelectrolyte's counter ion from the surface of ITO, the charged-based interaction between PSS<sup>-</sup> or poly(diallyl dimethylammonium) (PDDA<sup>+</sup>) and the ITO will increase and cause a work function shift. To examine this, we deposited PSS:Na or poly(diallyl dimethylammonium chloride) (PDDA:Cl) on an ITO surface using an electrophoretic deposition method from an aqueous solution. Electrophoretic deposition was performed using a CH instruments CHI600C potentiostat by immersing a clean ITO substrate into a 2 mg mL<sup>-1</sup> polyelectrolyte solution in water and applying a constant potential for 5 min, followed by drying at 100 °C for 10 min. A platinum wire was used as a counter electrode. Electrophoretic deposition consists of two processes.<sup>[38]</sup> During the first process, the applied electric field allows polyelectrolytes to move electrophoretically to the oppositely charged electrode in the solution (**Figure 3a**). The second process is the deposition of the electrophoretically attracted materials on the electrode, which yields the formation of a polymer film. The amount of material deposited per a given time is dictated by the applied bias.<sup>[39]</sup> A positive bias was applied to the working electrode for anionic PSS<sup>-</sup> and for the deposition of cationic PDDA<sup>+</sup>, a negative bias was applied.<sup>[40]</sup> As can be seen in **Figure 3b**, when PSS:Na is deposited under the positive bias and PDDA:Cl deposited under negative bias, they move the work function of ITO, which indicates that the applied bias precludes the presence of counter ions near the substrate by a repulsive interaction and enables us to use ionic polyelectrolytes as work function modifying layers. This is in contrast to the spin cast films of PSS:Na or PDDA:Cl which are expected to retain their counter ion and only display a negligible work function shift ( $<\pm 0.04$ ). The result corresponds to the explanation by the charge-based through-space interaction; when the positively (negatively) charged ion reaches the ITO surface, it results in the formation of dipoles pointing outward from (toward) the ITO surface. To further clarify the mechanism, control experiments were performed in a NaCl solution without



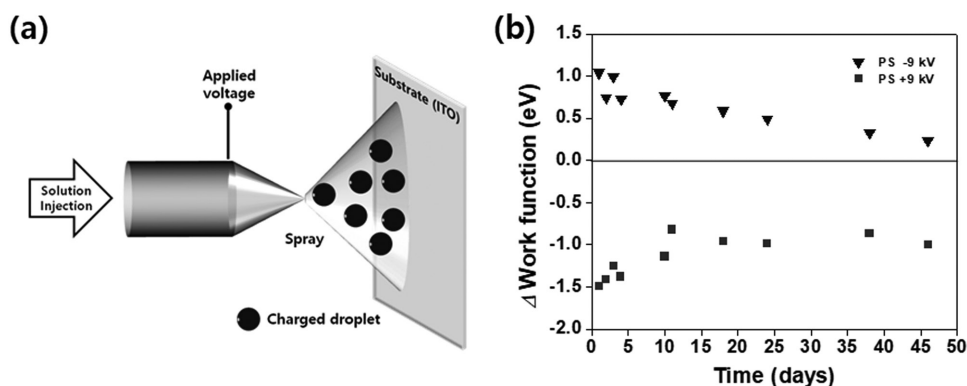
**Figure 3.** a) Schematic illustration of the electrophoretic deposition of PSS:Na under positive bias. b) Work function shift, relative to bare ITO, of ITO/PSS:Na (triangles), and ITO/PDDA:Cl (squares) which were prepared using electrophoretic deposition method.

polyelectrolytes and we did not observe any meaningful shift in work function (data not shown).

In order to further investigate the influence of a charge-based through-space interaction, samples deposited with PS using an electrospaying technique were prepared. Electrospaying was performed by injecting polystyrene from a 2 mg mL<sup>-1</sup> solution in chloroform at a rate of 0.25 mL h<sup>-1</sup> while applying a bias of 9 kV on the injecting tip relative to a backing plate. The substrate is placed in the injection path (Figure 4a). PS does not have any functional group which can easily interact with hydroxyl groups on the ITO surface nor does it have any acidic or basic moiety. The electrospaying technique allows us to achieve deposition of dissolved organic materials onto a desired substrate by forming charged droplets driven by the electric field we applied.<sup>[41]</sup> As shown in Figure 4b, when +9 kV is used during PS deposition, the positively charged PS droplets which were produced lead to a negative charge on the surface of ITO. Thus, the work function of ITO decreases by 1.5 eV due to the resulting dipole. The degree of work function shift by this electrically induced charge gradually decays for both positive and negative cases since neutral compounds such as PS cannot stabilize either positive or negative charge permanently. Remarkably, the positively charged PS shifts ITO's work function more strongly than a negatively charged (deposited at -9 kV) material, and it remains more stable over time. It is reasonable to postulate that n-type ITO has an excess of relatively

free negative charge,<sup>[42]</sup> which enables it to stabilize the positive charge of PS deposited at +9 kV. This result is consistent with our hypothesis that the work function can be modified by the charge-based through-space interaction, even though there is no direct surface interaction with the surface hydroxyl groups on ITO.

In conclusion, this study was performed to understand how polyelectrolytes modify the work function of their substrate by focusing on a combination of the surface interaction and the charge-based through-space interaction. We have shown that when acid-like or base-like polyelectrolytes were deposited on ITO substrates, they induce a work function shift by the formation of a surface dipole on ITO. The work function shift is also observed when the direct contact between the ITO substrate and polyelectrolyte is blocked by placing an inactive spacer, although the shift is not as strong as without the spacer. In addition, when an electrophoretic deposition technique was used with ionic polyelectrolytes, which has a negligible effect on the work function shift of ITO when spin cast, ITO samples showed a work function shift. Furthermore, it is interesting to find that the work function of ITO coated with PS, which is neutral, could be modified through the charge-based through-space interaction by employing an electrospaying technique. Taken together, these observations consistently suggest that while the surface interaction is the major factor affecting work function modification processes,



**Figure 4.** a) Schematic illustration of electrospaying deposition. b) Work function shift, relative to bare ITO, of ITO/PS when PS is deposited at -9 kV (triangles) or +9 kV (squares) by the electrospaying technique.

the charge-based through-space interaction has also a significant effect on modifying the work function of electrodes. These results motivate the selection and design of materials for work function modification of their electrodes in organic electronic devices.

## Experimental Section

**Materials and Characterization Techniques:** All polymers and solvents were used as received from Sigma-Aldrich. ITO coated glass (Delta Technologies CG-50IN-S107) was cleaned prior to use by sonicating in isopropanol and acetone each for 10 min, followed by a 10 min UV-ozone treatment. Polymer solutions were typically cast at 3000 rpm for 30 s from 2 mg per mL solvent: poly(vinyl alcohol) 100% hydrolyzed (PVA), poly(sodium styrene sulfonate) (PSS:Na), poly(styrenesulfonic acid) (PSS Acid), poly(acrylic acid) (PAA), poly(acrylamide) (PAAm), poly(acrylic acid) sodium salt (PAA:Na), and PDDA:Cl were cast from water; poly(ethylenimine) (PEI), PEIE (both at 0.4 wt%), and poly(vinylphenol) (PVPhOH) are cast from 2-methoxyethanol; polystyrene (PS) was cast from toluene. For comparison, the clean ITO sample was prepared and measured, and all of polymer samples were spin cast onto ITO and measured in air using a homemade Kelvin probe microscope.<sup>[43]</sup> C-AFM and KPFM measurements were performed using Asylum Research MFP-3D under ambient conditions. A Pt-Ir5-coated contact-mode AFM probe (Nanosensors, ATEC-CONTPT, spring constant 0.2 N m<sup>-1</sup>) was used for the top contact of C-AFM, and a Pt-coated Si Probe (Nanosensors, stiffness ≈0.5-1N m<sup>-1</sup>, resonant frequency ≈75 kHz) was used for KPFM measurements.<sup>[44]</sup> UPS spectra were recorded in an ultrahigh vacuum chamber using He I (21.2 eV) photons at a resolution of 0.01 eV.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

organic electronics, polyelectrolyte, work function

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