Constructing robust all-inorganic contacts enable stable perovskite solar cells with efficiencies over 20%

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Developing photovoltaic (PV) cells for harvesting renewable and clean solar energy is a promising strategy to meet the growing energy demand. Perovskite solar cells (PSCs), as a new player in the photovoltaic field, exhibit rapid development with an original power conversion efficiency (PCE) of 3.81% in 2009, a promising PCE of over 20% in 2014 and a record PCE of 22.1% in 2017 [1,2]. The explosive developments and achievements in photovoltaic effect of organometal halide perovskite shed light on the exploitation of low-cost and highly efficient photovoltaic technique. Staged PCEs over 20% have been frequently obtained with the innovations in tailoring of perovskite absorber formation, composition and defect, charge transporting layers as well as interfacial engineering [2–4]. Currently, PCE is not a critical factor that limits its real commercial application. In addition to the potential PCE loss in up-scaling fabrication, the long-term stability is the main obstacle of pushing such kind of PSCs from laboratory to market.

For the state-of-the-art PSCs, the PCE drop may originate from the degradation of different components in a device, such as perovskite itself or the charge transporting layers. Due to the low formation energy of perovskites, they are highly susceptible to degradation in ambient. Therefore, it is essential to prohibit the perovskite photoactive layer from exposing to such environments. Such drawback can be overcome *via* functionalization of perovskite and rigorous encapsulation [5,6]. Additionally, the most efficient PSCs (>20%) so far are mainly fabricated by using p-type organic semiconductors as hole transporting layers (HTLs), such as 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spiro-bifluorene (spiro-OMeTAD) and polytriarylamine (PTAA). However, their relatively high cost and poor stability? compared to the n-type inorganic semiconductors (TiO₂,

ZnO) are undesirable for the large-scale commercialization of PSCs. Further, these devices based on organic HTLs only can reach their peak performance in the presence of organic lithium salt and 4-*tert*-butylpyridine. These additives can cross into the perovskite layer and accelerate device degradation.

Constructing low-cost and robust all-inorganic contacts is a promising strategy to eliminate these unstable organic HTLs in nature. Pioneer work was conducted by Prashant and co-workers [7], employing TiO₂ and CuI as n-type and p-type contacts, respectively. Subsequently, several all-inorganic contacts have been demonstrated including TiO₂-CuSCN, NiO_x-ZnO (SnO₂), Li_{0.05}Mg_{0.15}Ni_{0.8}O-Ti(Nb)O_x and TiO₂-CuGaO₂ [8–11]. Although these all-inorganic contacts yield obvious improvements in long-term stability of PSCs, proving the validity of this concept, the stabilized PCE is still away from the top class (>20%).

Recently, Grätzel and co-workers pushed the concept of all-inorganic contacts to target stabilized PCE exceeding 20% with TiO₂ and CuSCN as the electron and hole transporting layers (Fig. 1a) [12]. In this work, a fast solvent removal method enables the creation of compact, highly conformal CuSCN layers that facilitate efficient carrier extraction and collection. Instead of traditional spin-coating in previous researches, CuSCN solution of diethyl sulfide (DES) is drop-cast quickly while the substrate is spinning at high speed. Such dynamic deposition approach preserves the quality of perovskite layer, minimizing the damage induced by DES, which is a main barrier in CuSCN-based PSCs. CuSCN displays a higher hole mobility than commonly used spiro-OMeTAD by about three orders of magnitude, which enables it as an effective HTL even in its doping-free state.

Although successful establishment of TiO₂-CuSCN all-

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Figure 1 (a) Cross-sectional scanning electron microscopy (SEM) image of the device with all-inorganic contacts. (b) Maximum power point tracking for 60 s, yielding stabilized PCEs of 20.5% and 20.2%, respectively, for spiro-OMeTAD-based and CuSCN-based devices. (c) Operational stability of an unencapsulated CuSCN-based device with and without a thin layer of rGO (as a spacer layer between CuSCN and gold layers), examined at a maximum power point under continuous full-Sun illumination at 60°C in a nitrogen atmosphere. Reprinted with permission from Ref. [12], Copyright 2017, the American Association for the Advancement of Science.

inorganic contacts enables outstanding PCE (over 20%) and high thermal stability at 85°C in ambient condition in the dark, the CuSCN/Au based devices show poor photostability, losing >50% of their initial PCEs within 24 h due to an electrical potential-induced reaction of gold with the thiocyanate anions forming an undesired barrier. Graphene oxide (GO) has been firstly demonstrated by our group as an efficient hole extraction layer for PSCs [13]. The perovskite film deposited on GO exhibits high crystallization with preferred in-plane orientation of the (110) plane, which warrants its high PCE. Here, this unexpected poor operational stability is eliminated by incorporating reduced graphene oxide (rGO) as a spacer layer (Fig. 1c), simultaneously maintaining its excellent PCE (over 20%, Fig. 1b).

PSCs undoubtedly represent the most promising efficient and low-cost photovoltaic technique with bright future. Currently, each step of stability improvement will push it close to the real market. This study marks an

important breakthrough in the concept strategy of all-inorganic contacts enabling extremely stable device with shiny performance, and also highlights the significance of constructing robust contact interface with metal electrode. The impressive thermal and operational stabilities in this work will inspire future effort in achieving large-scale, cost-effective and stable photovoltaic application.

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