Carbon Dots on TiO₂ for Perovskite Photovoltaics, Methanol Oxidation and Water Splitting

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INTRODUCTION
Carbon dots (CDs) are a class of fluorescent nanoparticles including an extremely rich variety of structures and functional groups. Interestingly, not only the physicochemical properties are affected by the nature of the CD structure, but also their optical behavior. Fluorescence in CDs shows particular characteristics of strong intensity and wavelengths in the visible region. Consequently, an interesting issue arises on how structurally-different CDs modify the electron transport and photoactivity of semiconductor oxides, in particular TiO₂.

EXPERIMENTAL
Four CD samples were prepared in different solvents and bearing different chemical groups, including thiol (SH), o-phenylenediamine (o-PDA) and butyl chains (But). The CDs were deposited on layered substrates of mesoporous TiO₂ (m-TiO₂) and compact TiO₂ (c-TiO₂), which were in turn supported on conducting FTO/glass. The system was tested both in the counter electrode side of perovskite photovoltaic cells (glass/FTO/c-TiO₂/m-TiO₂ + CDs/perovskite/spiro/Au) and as the working electrode for the photo-electrochemical oxidation of methanol and water.

RESULTS
The perovskite cells demonstrated photo-conversion efficiencies (PCE) in the range of 17.2-18.3%. The presence of CDs in the TiO₂ layer did not cause substantial changes in the PCE. The o-PDA-CDs led to an increase of ~ 50 mV in the open circuit potential. In the photo-electrochemical cell, CDs on the TiO₂ electrode produced an increase in the photocurrent for both water and methanol oxidation, depending on the CD functionalization. In particular, the addition of But-CDs increased the water oxidation photocurrent by 126% over the blank electrode (Fig. 1) and by 116% over the electrode with the unmodified CDs. The photopotential in water did not substantially change upon the addition of CDs, and remained in the range of 485-511 mV. The photopotential in methanol increased from 758 mV up to 823 mV upon the addition of SH-CDs.

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Fig. 1 On-off galvanostatic experiment, 0.1M NaOH, E = -0.037 V vs. Hg/HgO, 150 W Xe arc lamp